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Characterization of microporous silica-based membranes by calorimetric analysis

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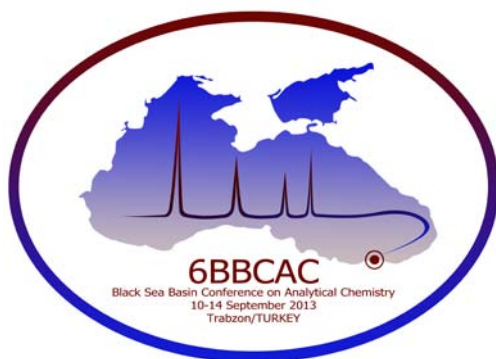
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6BBCAC
6th BLACK SEA BASIN CONFERENCE
ON ANALYTICAL CHEMISTRY

10-14 SEPTEMBER 2013
TRABZON/TURKEY



Book of Abstract

Hosted by
Karadeniz Technical University
Faculty of Science
Department of Chemistry

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Dear colleagues,

Great times are those shared with great people. Scientific meetings are the funfair of the scientists. Conferences feature panel discussion of studies in a professional way, publication of new results and create new ideas as well as meeting new people.

6BBCAC is the sixth conference of a biennial conference series of Black Sea Basin Conferences on Analytical Chemistry. Geographically centered around the Black Sea region being held in one of country located in this region. Since the first meeting in Odessa this event is the continuation of the previous successful conferences:

- 1st BBCAC, 11-15 September 2001 in Odessa/Ukraine
- 2nd BBCAC, 14-17 September 2003 in Şile-Istanbul/Turkey
- 3rd BBCAC, 12-14 September 2005 in Constanta/Romania
- 4rd BBCAC, 12-14 September 2007 in
- 5th BBCAC, 23-26 September 2009 in Fatsa/Turkey

Unfortunately conference was not organized in 2011 and after a four years period we are really pleased to organize this important meeting in Trabzon/Turkey. The main purpose of this meeting has been to establish a warm environment to share cutting-edge information on developments in all areas of Analytical Chemistry research. The conference aims to bring together the researchers from the entire spectrum of the multi-disciplinary fields of Chemistry and establish effective means of communication between them. Although it seems to be a regional conference participants from all over the world are keen to attend. Here in Trabzon this year we have colleagues from Romania, Bulgaria, Ukraine, Russia, Greece, England, France, Denmark, Spain, Croatia, Poland, Pakistan, India, Algeria, Tunisia, Egypt, Libya, Morocco, Palestine, Libya, Saudi Arabia, Iran, Iraq, Bangladesh and Canada. Since some economical problems many scientist from the Black Sea Region was not able to attend to the conference.

It was a hard work and we did our best to host you in this part of Turkey. On behalf of organizing committee members I like to thank you all coming all the way from your countries, spending your time and energy. As an integral and significant part of this conference, your attendance will add great value. I also like to thank many people who helped us in various ways in the organization. The first and most important one is friends, colleagues and university management. Governor of Trabzon, Governor of Rize, Trabzon Güç Birliği Holding, PROLAB, INFO KİMYA, SEM, TERRA, KRAL PESTİL, COCA-COLA, OFÇAY, DOĞADAN, REFRANS KİMYA has greatly supported us. Apart from these I especially thank to my family for their patient, our graduate students who have spent their energy for the success of this meeting.

I hope you have great time in Trabzon where is the center of natural heritage, tradition, culture and hospitality. Maçka is a distinguish town where have special music, dance and culture and our people are famous about their sense of humor, please enjoy it.

Best regards

Prof. Münevver SÖKMEN
Chair
September, 2013

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SPONSORS



INVITED SPEAKERS

- IS-1** Linking water chemistry to metal speciation and risk assessment analytical challenges
- IS-2** Multidimensional mass spectrometry methods for the analysis of synthetic polymers
- IS-3** Characterization of bioactive peptides in functional dairy foods with disease-preventing ingredients
- IS-4** Green extraction of natural products: Concept, principles and applications
- IS-5** Supramolecular solvents: Efficient and green nanostructured liquids for analytical extractions
- IS-6** FT-IR and Raman spectroscopy in phytochemical analysis of medicinal and aromatic plants
- IS-7** Versatile materialistic approaches toward separation science and sensor technology
- IS-8** NIR spectroscopy for pharmaceutical analysis

ORAL PRESENTATIONS

- OP-1** Preconcentration of arsenic and lead by willow leaves as biomass
- OP-2** Characterization of microporous silica-based membranes by calorimetric analysis
- OP-3** Highly selective enrichment of sialylated glycopeptides using titania sol-gels for mass spectrometry based glycoproteomics
- OP-4** Determination of fipronil and its metabolites residues in cauliflower by using GC/MS/MS triple quadrupole mass spectrometry
- OP-5** An aptamer mediated enrichment method for mass spectrometric detection of thrombin
- OP-6** Determination of clavulanic acid in human plasma by liquid-liquid chromatograph with mass detection
- OP-7** A tale of two papers
- OP-8** Determination of antioxidant capacities of individual and combined phenolics by CHROMAC method
- OP-9** Detection of some phenolic compounds in barley and rice shoot residues using derivative spectroscopy
- OP-10** Oxygen radical absorbance capacity and total phenolic content of oleaster
- OP-11** Surfactant effect on the separation and detection of biogenic amines and chiral amino acids by micellar electrokinetic chromatography coupled by laser induced fluorescence
- OP-12** Determination of mono- and di-nitrosopiperazine in the atmospheric particulates and their relationships between concentrations of nitrite, nitrate, piperazine and meteorological parameters
- OP-13** Microwave assisted extraction of green tea
- OP-14** SEM Laboratory Equipments
- OP-15** Preparation of solid phase micro extraction fibers by electropolymerization technique for the determination of endocrine disruptor pesticides
- OP-16** Application of novel polycaprolactone/polydimethylsiloxane fibers in membrane- solid phase microextraction technique for the isolation and preconcentration of organic pollutants in water samples
- OP-17** Solidified floating organic drop microextraction method for preconcentration and determination of some endocrine disruptor pesticides in well water samples
- OP-18** Developments in ultrasound-assisted microextraction techniques for isolation and preconcentration of organic analytes from aqueous samples
- OP-19** Green extraction techniques in analytical chemistry
- OP-20** Preconcentration of mercury(II)-crystal violet complex by solidified floating organic drop microextraction and analysis by flame atomic absorption spectrometry
- OP-21** Gas chromatographic analysis of fuel combustion products, anti-corrosive compounds, and de-icing compounds in airport runoff water samples
- OP-22** Spectrophotometric determination of fluoride in drinking water using polymeric aluminium complexes

- OP-23** Spectrophotometric detection of Fe(II) and kinetics inspection of the reactivity of its chelates
- OP-24** Simultaneous determination of selenium and lead in biological samples by multi-element electrothermal atomic absorption spectrometer
- OP-25** New design of flow injection unit using(malachite green-iodide) system for the determination of cerium(IV) by merging zone technique
- OP-26** An investigation of potential bio-accessible trace metal fractions in urban atmosphere of Karachi, Pakistan
- OP-27** A catalytic adsorptive stripping voltammetric procedure for chromium speciation in interstitial water samples isolated from sediments contaminated by tannery waste
- OP-28** Detection of prostate cancer biomarker in crude serum by SPR on microstructured Au film
- OP-29** Highly sensitive detection of amoxicillin based on gold nanoparticle modified ITO electrode
- OP-30** New electrochemical polymerization of 1-aminofluorenone
- OP-31** Study by FT-IR spectroscopy of adsorption onto activated carbon
- OP-32** Removal of nickel from aqueous solutions by activated carbon prepared from seawater algae
- OP-33** Solid-phase extraction and FAAS determination of trace amounts of cadmium and lead in natural water samples
- OP-34** The graphite “filter furnace” atomizer at the direct electrothermal atomic absorption analysis some of plant materials
- OP-35** Removal of reactive black 5 from aqueous solutions by TiO₂ immobilized onto activated carbon
- OP-36** Method development and validation for the simultaneous analysis of losartan, valsartan, atorvastatin, pravastatin and simvastatin using RP-HPLC and its application in pharmaceuticals
- OP-37** ¹⁸O-assisted ³¹P NMR and mass spectrometry for dynamic phosphometabolomic profiling
- OP-38** A novel spectrofluorometric method for determination of valsartan in spiked human plasma
- OP-39** Comparison of univariate and multivariate calibration techniques using ICP-OES
- OP-40** Molecularly imprinted solid-phase extraction of indapamide
- OP-41** The Photocatalytic properties of TiO₂ nanoparticles immobilized on waste polystyrene
- OP-42** Removal of Ni(II) from aqueous solution by adsorption onto drinking water treatment sludge
- OP-43** TUBITAK ARDEB Programs

POSTER PRESENTATIONS

- P-01** The Removal of Heavy Metals from Contaminated Sediments by Using Sequential Extraction and Soil Washing/Extraction
- P-02** Development a Proconcentration and Determination Method for Trace Amount of Uranyl Ions Based on Spectrophotometric Detection Flowing Cloud Point Extraction
- P-03** Use of Single Extractions for the Assessment of Metal Mobility in Mine Tailings
- P-04** Determination of Some Toxic and Nutritive Heavy Metal Contamination in Grape And molasses samples in Batman and Mardin Region by AAS and ICP-OES
- P-05** Determination of Chemical and Some Heavy Metal contamination in Some Spring and Thermal Waters in Eastern and Sout Eastern of Anatolian
- P-06** Determination of Some Toxic Traces Metal Contamination in Some Spring and Thermal Waters around Van by AAS and ICP-MS
- P-07** Characterization and Determination of Some Physicochemical Properties of an Anionic Surfactant
- P-08** Ultrasonically Assisted Extraction of Anthocyanins from Red Rose Petals and a New Spectrophotometric Method for Quantitative Determination of Total Anthocyanins

- P-09** Ecological Dyeing with Some Red Rose Petals on Woolen Fabric by Using Different Mordants
- P-10** Indirect Cloud Point Extraction and Spectrophotometric Determination of Trace Nitrite in Beverages with and Without Alcohol
- P-11** A Novel Preconcentration Procedure Using Cloud Point Extraction for Determination of Inorganic Dissolved Arsenic Species in Some Beverage Samples Using Spectrophotometry
- P-12** Simultaneous Preconcentration of Sb And B in Food and Beverage Samples and Determination by Atomic Absorption Spectrometry
- P-13** Kinetique of tanins extraction from Alep pine
- P-14** Development of a New Method on the Basis of "Co-Liquefaction with Organic Solvent" for the Extraction and Pre-Concentration of Trace Volatile Organic Compounds (VOCs) from Gaseous Samples
- P-15** Application of Solidified Floating Organic Drop Microextraction Method for Biomonitoring of Chlorpyrifos and its Oxon Metabolite in Urine Samples
- P-16** Comparison of Silica Monolith Fabrication and C₁₈ Phase Surface Modification Using Microwave and Conventional Heating Methods for Efficient Extraction of Small Organic Molecules
- P-17** Polyethylene Glycol as a Surfactant for Separation of Some Metal Ions from Aqueous Solutions by Cloud Point Extraction
- P-18** Selective Recognition of Copper (II) Ion by a New Phthalocyanine Compound With 2-(4,6-Diphenyl-1,3,5-Triazin-2-yl)-5-(Hexyloxy) Phenol Moiety oiety
- P-19** Selective Recognition of Silver (I) ion by a NS₃ Crown Ether Ligand Carrying Pyrene M
- P-20** Cancer Diagnosis by Mass Spectrometry
- P-21** Analytical Methods for Therapeutic Drug Monitoring
- P-22** Methodological Approach to Detailed Analysis of the Unknown Solid Samples
- P-23** An Extractive Spectrophotometric Method For Uranium(VI) Using Mwcnts and Arsenazo(III)
- P-24** Chromium Speciation in Environmental Samples by Using a New Chelating Resin and its Determination by FAAS
- P-25** Determination of gold and palladium by FAAS after dispersive liquid–liquid microextraction sampling
- P-26** Chromium Speciation in Environmental Samples by Solid Phase Extraction on Lewatit Sybron Lonac SR-7
- P-27** A New Dispersive Liquid-Liquid Microextraction Procedure for the Determination of Palladium
- P-28** Determination of gold by FAAS using DLLME sampling
- P-29** Preconcentration of Cu(II) and Ni(II) Ions with Solid Phase Extraction and Determination by Flame Atomic Absorption Spectrophotometry
- P-30** A New Application of the Recently Developed Ratio Difference Spectrophotometric Method for the Determination of Ternary Mixtures with Overlapping Spectral Data
- P-31** Spectroscopic Determination of Perlite Containing PVA,PVP,PAA Hydrogel Composites
- P-32** Characterization and Spectrophotometric Determination of Mn(II) in Aqueous Medium
- P-33** Chemical Fractionation of Copper in Malachite Ore (Elazig, Turkey)
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- P-35** The Fractionation of Copper with BCR Sequential Extraction Procedure
- P-36** Determination of Trace Elements in Human Hair by ICP-OES in Diyarbakir, Turkey
- P-37** Determination of Antimony in Gunshot Residue by GFAAS
- P-38** Application of Modified Tessier Sequential Extraction for Copper Fractionation in Dicle (Tigris) River Sediment Polluted by Historic Open-Cast Mining
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- P-43** Quantification of Synthetic Phenolic Antioxidants in Capsules and Chewing Gums by Derivative-Differential UV Spectrophotometry
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- P-128** The Effect of CaNa₂-EDTA On Zinc, Carbohydrate Metabolism and Glutamic Oxalic, Glutamic Pyruvic Aminotransferases (GOT, GPT) and Alkaline Phosphatase Activities in Experimental Diabetes
- P-129** Estimation of Lipid Components and Fatty Acid Composition of Human Serum in Fatty Liver Patients
- P-130** Design and Optimization of a New Kinetic Spectrophotometric Method for the Determination of Losartan Potassium in Pharmaceutical Products
- P-131** Indirect Spectrophotometric Determination of Ketoconazole in Pharmaceutical Products

- P-132** Comparison of Liquid Chromatographic, Capillary Electrophoretic and UV Spectrophotometric Methods for Determination of Leflunomide
- P-133** Electrochemical Aptasensor Design For Clinical Analysis
- P-134** Biochemical and Histological Studies on the Effect of the Patulin Mycotoxin on Male Rats' Liver and Treatment by Crude Venom Extracted from Jelly Fish
- P-135** Simultaneous Determination and Validation of a HPLC Method for Some Active Ingredients in Cough and Cold Pharmaceuticals
- P-136** Application of Derivative Spectrophotometric Method for the Analysis of a Ternary Mixture Containing Erythrosine, Quinoline Yellow and Indigotine in Tablets
- P-137** Simultaneous Spectrophotometric Determination of Three Food Colorants in Tablets by Using Derivative-Differential Spectrophotometry
- P-138** Application of Derivative-Differential Spectrophotometry for Determination of Synthetic Colorants in Tablets
- P-139** Validated Derivative Spectrophotometric Determination of Food Colorants in Pharmaceutical Products
- P-140** Resolution of Ternary Mixtures of Sunset Yellow, Ponceau 4r and Quinoline Yellow by the Derivative Double Divisor-Ratio Spectra and Derivative Ratio Spectra-Zero Crossing Methods in Pharmaceutical Tablets
- P-141** Simultaneous Determination of Synthetic Dyes in Tablets with the Use of Double Divisor-Ratio Spectra Derivative and Ratio Spectra-Zero Crossing Methods
- P-142** Spectrophotometric Determination of Clopidogrel in Bulk Drug and Pharmaceutical Preparation
- P-143** Spectrophotometric, Chromatographic and Electrophoretic Techniques to Quantify of Varenicline in Quality Control
- P-144** Determination of Zn Levels in Patients Who Have Undergone Coronary Artery Bypass Surgery
- P-145** Use of Ceric Ammonium Sulphate and Two Dyes, Methyl Orange and Indigo Carmine , in the Determination of Mefenamic Acid in Pharmaceuticals
- P-146** Method for A New Spectrophotometric the Determination of Promethazine Hydrochloride in Pharmaceutical Preparations
- P-147** Multi-Wavelength Spectrophotometric Determination of Acid Dissociation Constants of Fenopropfen and Indomethacin in Acetonitrile-Water Binary Mixtures
- P-148** In-Situ Evaluation of Idarubicin-DNA Interaction Using Spectroscopic Techniques
- P-149** Development and validation of UFLC-MS/MS method for determination of bosentan in rat plasma: Application to a rat real samples
- P-150** Spectrophotometric Assay of Some Nitrogen Containing Drugs in Pharmaceutical Formulations using p-Chloranilic Acid Reagent
- P-151** Validation of a Method for Determination of Phthalates in Common Use Objects (Toys and Child Care Articles) by Gas Chromatography Mass Spectrometry (Gcms)
- P-152** Application of Mesogenic Materials with Alkoxy Lateral Chains as Stationary Phases for the Separation of Derivatives Phenolic Compounds
- P-153** Application of Schiff Bases Liquid Crystals as Stationary Phases for the Separation of Positional Isomers Compounds
- P-154** Effect of Temperature on Terpenic Compounds Retention in Capillary Gas Chromatography
- P-155** Preparation Procedures and Chromatographic Determination of Organic Pollutants in Airport Runoff Waters
- P-156** Analysis of Xenobiotics in Runoff Waters Collected from Airport
- P-157** Experimental Design of Reversed-Phase High Performance Liquid Chromatographic Conditions for Simultane Determination of Ascorbic Acid, Potassium Sorbate and Sodium Benzoate
- P-158** Analysis of Organic Nitrogen Compounds in House Dust Samples using GCxGC-NCD
- P-159** Quantitative Determination of Ibuprofen and Famotidine in Their Combined Dosage Form by Thin Layer Chromatography- Densitometry and High Performance Liquid Chromatography

- P-160** Application of Novel Core-shell Type Polysaccharide-based Chiral Stationary Phases for Separation of Enantiomers in Nano Liquid Chromatography and Capillary Electrochromatography
- P-161** A New Spectrophotometric Method for Trace Mercury Determination
- P-162** Polymer/Clay Nanocomposites as a New Sorbent for Chromatographic Methods
- P-163** Ionic Liquid-Modified Clay Materials as a New Sorbent for the Gas Chromatographic Determination of Pesticides: Part 3. Application of 1-Methyl-3-Octadecyl-Imidazolium Bromide Modified Montmorillonite
- P-164** Development of a Sequentially Applied Spectrophotometric and Voltammetric Methods for the Determination of Iodide in Salt Samples
- P-165** Ionic Liquid-Modified Clay Materials as a New Sorbent for the Gas Chromatographic Determination of Pesticides: Part 2. Application of 1-Methyl-3-Undecyl-Imidazolium Bromide Modified Montmorillonite
- P-166** Ionic Liquid-Modified Clay Materials as a New Sorbent for the Gas Chromatographic Determination of Pesticides: Part 1. Application of 1-Methyl-3-Octyl-Imidazolium Bromide Modified Montmorillonite
- P-167** Chromatographic Analysis of α -tocopherol in Deodorizer Distillate by Cyano Column
- P-168** Selection of Optimum Condition For Simultaneous Determination of Three Carbapenem Drugs with Liquid Chromatography Method
- P-169** Application of Experimental Design to Optimisation and Validation of a RPLC Method for the Estimation of Tricyclic Antidepressants in Urine
- P-170** Determination of pKa Values of Methotrexate with Reversed Phase Liquid Chromatography Method in Different Acetonitrile-Water Binary Mixtures
- P-171** Application of Optimum Condition for Determination of Sulfasalazine in Human Urine by using Reversed Phase Liquid Chromatography Method
- P-172** Validation of RPLC Method for Assay of Azathioprine in Pharmaceutical Formulation
- P-173** Experimental Design Approach for Determination of Some Tricyclic or Tetracyclic Antidepressants with LC Method and Application of the Solid-Phase Extraction in Urine
- P-174** Effects of Chemical Substances on Pectin Lyase of Thermophilic *Aspergillus Niger* Isolated from Natural Sources
- P-175** Production and Purification of Pectin lyase enzyme from fruit residues in submerged culture
- P-176** Characterization of Pectin Lyase from Thermophilic *Aspergillus Niger* Isolated from Natural Sources
- P-177** Purification of Pectin Lyase with Chromatographic Techniques and Effects of Detergents on Enzyme Activity
- P-178** Central Composite Design for Investigating Chromatographic Behavior of Some Quinolones by Using Isocratic Reversed Phase Liquid Chromatographic Method
- P-179** Application of CCD to predict pKa values of Ofloxacin, Enrofloxacin, Danofloxacin
- P-180** Simultaneous Determination of Enalapril / Hydrochlorothiazide by HPLC Method
- P-181** Optimization and Validation of a HPLC Method for Simultaneous Determination of Chlortalidone and Atenolol Using an Experimental Design
- P-182** Application Of CCD To Optimisation Of RPLC Conditions For The Simultaneous Determination Of Amlodipine And Valsartan
- P-183** Separation of Ketoprofen Racemate by TLC Plate with Different Chiral Selectors
- P-184** Effect of polyherbs on some blood serum lipid compositions of diabetic patients -Type II isolated by capillary gas chromatography
- P-185** Fly Ashes from Bulgarian Power Plants as Potential Adsorbents for Cu(II) Removal
- P-186** Coal Fly Ash Characterization by the Combined Use of Analytical Techniques
- P-187** Argan and Almond Tree Walnuts Shells: Valuation and Application to the Adsorption of Methylene Blue
- P-188** Types of Adsorption In the Ion Exchange of Algerian Bentonite by Quaternary Ammonium Salts

- P-189** Comparison of Removal Lead (II) from Aqueous Solution on Novel Inorganic-organic Hybrid Materials
- P-190** Removal of Cationic Surfactant from Aqueous Solutions by Using Clay Mineral
- P-191** Removal Of Lead From Water Using Natural Zeolite And Granular Activated Carbon Adsorbents
- P-192** Equilibrium and Thermodynamic Data for Adsorption of Malachite Green, Sirius Blue and Congo Red onto Bentonite
- P-193** Analysis of Metal Contents in Spinach, Lettuce, and Parsley Marketed in Marmara Region
- P-194** Study by FT-IR Spectroscopy of Adsorption onto Activated Carbon
- P-195** Comparison of Aluminum Alginate and Aluminum Alginate – Montmorillonite Composite Beads on Defluoridation of Water
- P-196** Brilliant Yellow Adsorption onto Vinyl Imidazole Containing Microbeads
- P-197** Acid Blue 9 Adsorption on Amino Acid Containing Magnetic Microbeads
- P-198** Removal of 17 β -estradiol with Microparticle-Embedded Cryogel System
- P-199** Comparison of MLR And ANFIS Approaches For Biosorption Process
- P-200** Application of Response Surface Methodology For The Biosorption of Pb(II) Using Black Cumin
- P-201** Optimization of the Solid Phase Extraction Method by Using Box-Behnken Design
- P-202** Comparison of Orange and Mandarin Juices In Terms Of Water Soluble Vitamins
- P-203** Teawaste as an Adsorbent for Copper Removal from Aqueous Solutions
- P-204** Use of Carrot Peel to Remove Heavy Metals from Aqueous Solution
- P-205** Various Approaches for The Estimation of Thermodynamic Functions of Adsorption for a Number of Azo Dyes on Activated Carbon
- P-206** Adsorption of Cu(II) from Aqueous Solution using Drinking Water Treatment Sludge
- P-207** Using the Method of Experimental Design in the Determining Rate Biosorption of Cr(III)
- P-208** Determination of Some Heavy Metals in Four Medicinal Plants
- P-209** Investigation of Antioxidant Capacity of *Elaeagnus angustifolia* L. by Using CUPRAC and DPPH Methods
- P-210** Determination of Arsenic and Zinc Concentration in Some Brands of Tea Sold In Gharian-Libya
- P-211** Effect of Silane Treatment on the Structural, Thermal and Morphological Properties of Short Spartium Junceum Fibers Reinforced Polypropylene
- P-212** Properties of Poly(Vinyl Chloride)/Spartium Junceum Fibers Composites
- P-213** Determination of Cu, Fe, Mn and Zn Contents after Heat Treatment in Some Vegetables Grown in the Middle Black Sea
- P-214** Fluoride Content of Turkish Tea Samples
- P-215** Beneficial Effect of Popular Tea Samples Such as Black-Green-Rosemary-Sage in Terms of Their Antioxidant Profile
- P-216** Characterization of Fatty Acids, Essential Oils and In vivo Emitted Volatiles from Tunisian *Rosa canina* L. Leaves
- P-217** Determination of Catechin in Differently Brewed Tea
- P-218** Response Surface Optimized Ultrasonic Extraction of Antioxidant Compounds from *Pyracantha coccinea*
- P-219** Isolation of Phenolic Compounds from *Prunella* L. Extracts and Investigation of Their Anticarcinogenic Properties
- P-220** Isolation of Phenolic Compounds from Black Mulberry (*Morus nigra* L.) by Column Chromatography
- P-221** Antioxidant Effects of Resveratrol, Carvacrol and Ellagic Acid Against Fenton Reaction
- P-222** Pine and Tannins
- P-223** Determination of Essential Oils Constituents from *Caryopteris incana* by Retention Time Locking Gas Chromatography Flame Ionization Detector and Retention Time Locking Gas Chromatography Mass Spectrometry
- P-224** Antioxidative Responses to Lead Phytotoxicity on Germination and Seedlings Growth of Strong Wheat *Triticum durum* Desf

- P-225** Desorption of Copper from Lewatit Loaded with Copper Ions
- P-226** Copper Removal from Aqueous Solution by Lewatit
- P-227** Determination of Trace Elements of *Prunus avium* L. (Pulp, Bark, Stalk and Glue)
- P-228** The Utilization of Revised BCR Sequential Extraction Procedure for the Fractionation of Copper in Asphaltite Combustion Waste (Silopi, Turkey)
- P-229** Microwave Digestion Followed by ICP-OES for the Simultaneous Determination of Metals in Hazelnut (*Corylus avellana* L.)
- P-230** The Effects of Various Drying Conditions and Total Phenolic Content of Apple Slices
- P-231** Determination of Bioavailability and Bioaccessibility in soil and plant by in Vitro Digestion
- P-232** Antioxidant Activities of the Extracts from *Anemone albana* Stev by Different Extraction Techniques
- P-233** The effect of different extraction conditions on the antioxidant properties of Cranberry (*Cornus mas* L.)
- P-234** Antioxidant Properties of Different Extracts of Strawberry (*Fragaria vesca*)
- P-235** Comparison of Head-space GC MS and Head-Space Solid-Phase Microextraction Methods of Volatile Constituents and Antimicrobial Activity of Essential Oils of *Salvia staminea* Montbret & Aucherex Benth
- P-236** Chemical Composition of Essential Oil of *Hyssopus officinalis* Cultivated in Greece
- P-237** Chemical composition and antimicrobial activity of the essential oils from the flower, leaf, and stem of *Sempervivum brevifolium* Muirhead from Turkey
- P-238** Heavy Metal Determinations in Ruderal *Verbascum olympticum* Boiss. Growing Under Cadmium Stress by ICP-MS
- P-239** Total Antioxidant Capacities of Methanol and Water Extract of the Horse Tail (*Equisetum Arvense*) Species Wildly Growing in Kutahya and Trakya
- P-240** Fullerene C₆₀ Functionalized γ -Fe₂O₃ Magnetic Nanoparticle: Synthesis, Characterization, Analytical and Biomedical Applications
- P-241** γ -Fe₂O₃ magnetic nanoparticle functionalized with carboxylated multi walled carbon nanotube: synthesis, characterization, analytical and biomedical applications
- P-242** Catalytic Activity of Ag nanoparticles Modified Polymer Film Electrode for Dimethylamine Borane Oxidation
- P-243** Metal Oxide Synthesized Materials for a Textile Dye Removal
- P-244** Characterization of SiO₂ Materials Prepared by Using Sol-Gel Method
- P-245** Determination of Zeta Potential Surface of Nanoporous Polymer Membranes
- P-246** Synthesis and Antibacterial Activity of Thiosemicarbazide from Amino Acids Derives
- P-247** System Action of Copper Diacetate and Triphenylbismuth Diacetate on The Arylation of a Variety of Heteroaryl Amine
- P-248** Investigation of The Solvent Effect on The Fluorescence Properties of Some New Synthesized Schiff Bases
- P-249** Spectroscopic Investigations Aromatic of 2H-indazolo[2,1-b]phtalazine-triones
- P-250** Spectroscopic Investigation of Ethyl 4-(4-cyanophenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate
- P-251** Fluorescent Chemosensors For Iron (III) and Cu(II) Based on Symmetric Tetradentate Ligands Nanoparticles
- P-252** Separation of the Structural Isomers of Thiazolidin-4-one Synthesized from 1-(2,4-Dimethylphenyl)-3-(4-methylphenyl)thiourea by HPLC
- P-253** Synthesis of Substituted 6,7-Dihydrocyclopentapyrimidin-2-amine Compounds via One-Pot Method
- P-254** Synthesizing Different Size Emulsion Polymers and Characterization
- P-255** Synthesis Electrochemical, Spectroscopic and Biological Study of Benzidine's Ligand and its Complex Organometallic Cu (II) and Co (II)
- P-256** Effects of Interchange Reactions on the Dynamical and Thermal Properties of PC/PET Blends
- P-257** Thermoanalytical Investigation of New Phenyl Tetrazoles
- P-258** Synthesis and Characterization of Meloxicam Cu(II) Complex and Its Interaction with DNA

- P-259** Synthesis and Characterization of N, N'-bis (salicylidene)ethylenediamine. Study of Mining Properties vis-à-vis the Copper (II) in Sulphate Environment
- P-260** Synthesis of New Phthalocyanine Molecules and Characterization
- P-261** Oxidation Of Thymol with Potassium Peroxy monosulfate Catalyzed by Iron(III) PhthalocyanineTetrasulfonate
- P-262** The Photophysical and Photochemical Properties of New Unmetallated and Metallated Phthalocyanines Bearing Four 5-Chloroquinolin-8-Yloxy Substituents on Peripheral Sites
- P-263** Novel 4-(2-(Benzo[D]Thiazol-2-Yl)Phenoxy) Substituted Phthalocyanine Derivatives: Synthesis, Electrochemical and *in situ* Spectroelectrochemical Characterization
- P-264** Synthesis, Electrochemical, *in situ* Spectroelectrochemical and Electrocolorimetric Measurements of Novel Metal-Free and Metallophthalocyanines Bearing Oxadiazole Groups at The Peripheral Positions
- P-265** Development and Validation of RP-LC Method for The Determination of Mirtazapine
- P-266** Analysis and Identification of Chemical Components of Oil Dde Mastic (Fixed and Essential Oil)

SCIENTIFIC PROGRAMME

6 th BLACK SEA BASIN CONFERENCE ON ANALYTICAL CHEMISTRY Hotel Büyük Sümela 10-14 September 2013 Trabzon/TURKEY
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10 SEPTEMBER 2013 TUESDAY		
08:00-12:00	REGISTRATION	
12:00-13:00	LUNCH	
13:00-14:30	OPENING CERAMONY	
14:30-15:00	INVITED SPEAKER-I	Irina Karadjova Linking water chemistry to metal speciation and risk assessment analytical challenges
15:00-15:15	ORAL-1	Mehmet Yaman Preconcentration of arsenic and lead by willow leaves as biomass
15:15-15:30	ORAL-2	Vittorio Boffa Characterization of microporous silica-based membranes by calorimetric analysis
15:30-16:00	COFFEE BREAK	
16:00-16:30	INVITED SPEAKER-II	Chrys Wesdemiotis Multidimensional mass spectrometry methods for the analysis of synthetic polymers
16:30-16:45	ORAL-3	Hacı Mehmet Kayılı Highly selective enrichment of sialylated glycopeptides using titania sol-gels for mass spectrometry based glycoproteomics
16:45-17:00	ORAL-4	Anıl Duhan Determination of fipronil and its metabolites residues in cauliflower by using GC/MS/MS triple quadrupole mass spectrometry
17:00-17:15	ORAL-5	Ülkü Güler An aptamer mediated enrichment method for mass spectrometric detection of thrombin
17:15-17:30	ORAL-6	Hasan Ertaş Determination of clavulanic acid in human plasma by liquid-liquid chromatograph with mass detection
17:30-17:45	ORAL-7	Behice Yavuz Erdoğan A tale of two papers
19:30-24:00	OPENING COCTAIL-HOTEL BÜYÜK SÜMELA	

11 SEPTEMBER 2013 WEDNESDAY		
08:30-09:00	INVITED SPEAKER-III	Jose Barbosa Characterization of bioactive peptides in functional dairy foods with disease-preventing ingredients
09:00-09:15	ORAL-8	Cevdet Demir Determination of antioxidant capacities of individual and combined phenolics by CHROMAC method
09:15-09:30	ORAL-9	Nabil A. Fakhre Detection of some phenolic compounds in barley and rice shoot residues using derivative spectroscopy
09:30-09:45	ORAL-10	Görkem Yalçın Oxygen radical absorbance capacity and total phenolic content of oleaster
10:00-10:30	COFFEE BREAK	
10:30-11:00	INVITED SPEAKER-IV	Farid Chemat Green extraction of natural products: Concept, principles and applications
11:00-11:15	ORAL-11	F. Bedia Erim Berker Surfactant effect on the separation and detection of biogenic amines and chiral amino acids by micellar electrokinetic chromatography coupled by laser induced fluorescence
11:15-11:30	ORAL-12	Mehmet Akyüz Determination of mono- and di-nitrosopiperazine in the atmospheric particulates and their relationships between concentrations of nitrite, nitrate, piperazine and meteorological parameters
11:30-11:45	ORAL-13	Ezgi Demir Microwave assisted extraction of green tea
11:45-12:00	ORAL-14	SEM LABORATORY EQUIPMENTS
12:00-13:00	LUNCH	
13:00-15:30	CITY SIGHTSEEING TOUR	
16:00-19:00	POSTER SESSION- KTU OSMAN TURAN CONGRESS CENTER	

12 SEPTEMBER 2013 THURSDAY		
08:30-09:00	INVITED SPEAKER-V	Soledad Rubio Bravo Supramolecular solvents: Efficient and green nanostructured liquids for analytical extractions
09:00-09:15	ORAL-15	Levent Pelit Preparation of solid phase micro extraction fibers by electropolymerization technique for the determination of endocrine disruptor pesticides
09:15-09:30	ORAL-16	Agatha Spietelun Application of novel polycaprolactone/poly di methyl siloxane fibers in membrane- solid phase microextraction technique for the isolation and preconcentration of organic pollutants in water samples
09:30-09:45	ORAL-17	Füsün Okçu Pelit Solidified floating organic drop microextraction method for preconcentration and determination of some endocrine disruptor pesticides in well water samples
09:45-10:00	ORAL-18	Aleksandra Szreniawa-Sztajnert Developments in ultrasound-assisted micro extraction techniques for isolation and preconcentration of organic analytes from aqueous samples

10:00-10:30	COFFEE BREAK	
10:30-10:45	ORAL-19	Mustafa Özel Green extraction techniques in analytical chemistry
10:45-11:00	ORAL-20	İlknur Durukan Preconcentration of mercury(II)-crystal violet complex by solidified floating organic drop microextraction and analysis by flame atomic absorption spectrometry
11:00-11:15	ORAL-21	Anna Sulej Gas chromatographic analysis of fuel combustion products, anti-corrosive compounds, and de-icing compounds in airport runoff water samples
11:15-11:30	ORAL-22	Sameer Amereih Bsharat Spectrophotometric determination of fluoride in drinking water using polymeric aluminium complexes
11:30-11:45	ORAL-23	Lobna Abdel-Mohsen Ebaid Nassr Spectrophotometric detection of Fe(II) and kinetics inspection of the reactivity of its chelates
12:00-13:00	LUNCH	
13:30-14:00	INVITED SPEAKER-VI	Moschos G. Polissiou FT-IR and Raman spectroscopy in phytochemical analysis of medicinal and aromatic plants
14:00-14:15	ORAL-24	Khaled El Sherif Simultaneous determination of selenium and lead in biological samples by multi-element electrothermal atomic absorption spectrometer
14:15-14:30	ORAL-25	Dakhil Naser Taha New design of flow injection unit using(malachite green-iodide) system for the determination of cerium(IV) by merging zone technique
14:30-14:45	ORAL-26	Azam Mukhtar An investigation of potential bio-accessible trace metal fractions in urban atmosphere of Karachi, Pakistan
14:45-19:00	SUMELA MONASTRY TRIP	
19:00-23:00	DINNER IN SUMELA-GOVERNOR OF TRABZON	

13 SEPTEMBER 2013 FRIDAY		
08:30-09:00	INVITED SPEAKER-VII	Shahabuddin Memon Versatile materialistic approaches toward separation science and sensor technology
09:00-09:15	ORAL -27	Andrzej Bobrowski A catalytic adsorptive stripping voltammetric procedure for chromium speciation in interstitial water samples isolated from sediments contaminated by tannery waste
09:15-09:30	ORAL-28	Julien Breault-Turcot Detection of prostate cancer biomarker in crude serum by SPR on microstructured Au film
09:30-09:45	ORAL -29	Aftab Ali Shaikh Highly sensitive detection of amoxicillin based on gold nanoparticle modified ITO electrode
10:00-10:30	COFFEE BREAK	
10:30-10:45	ORAL-30	Fuad Asswadi New electrochemical polymerization of 1-aminofluorenone

10:45-11:00	ORAL-31	Mostefa Belhakem Study by FT-IR spectroscopy of adsorption onto activated carbon
11:00-11:15	ORAL-32	Fadila Nemchi Removal of nickel from aqueous solutions by activated carbon prepared from seawater algae
11:15-11:30	ORAL-33	Şengül Karadeniz Solid-phase extraction and FAAS determination of trace amounts of cadmium and lead in natural water samples
11:30-11:45	ORAL-34	Alexander Zacharia The graphite "filter furnace" atomizer at the direct electrothermal atomic absorption analysis some of plant materials
11:45-12:00	ORAL-35	Hanene Belayachi Removal of reactive black 5 from aqueous solutions by TiO ₂ immobilized onto activated carbon
12:00-13:30	LUNCH	
13:30-14:00	INVITED SPEAKER-VIII	Andrew J. O'neil NIR spectroscopy for pharmaceutical analysis
14:00-14:15	ORAL-36	Faiza Qureshi Method development and validation for the simultaneous analysis of losartan, valsartan, atorvastatin, pravastatin and simvastatin using RP-HPLC and its application in pharmaceuticals
14:15-14:30	ORAL-37	Emirhan Nemutlu ¹⁸ O-assisted 31P NMR and mass spectrometry for dynamic phosphometabolomic profiling
14:30-14:45	ORAL-38	Onur Şenol A novel spectrofluorometric method for determination of valsartan in spiked human plasma
14:45-15:00	ORAL-39	Özlem Bengü Daş Comparison of univariate and multivariate calibration techniques using ICP-OES
15:00-15:30	COFFEE BREAK	
15:30-15:45	ORAL-40	Hüma Yılmaz Molecularly imprinted solid-phase extraction of indapamide
15:45-16:00	ORAL-41	İlknur Altın Photocatalytic properties of TiO ₂ nanoparticles immobilized on waste polystyrene
16:00-16:15	ORAL-42	Nurcan Öztürk Removal of Ni(II) from aqueous solution by adsorption onto drinking water treatment sludge
16:15-16:30	ORAL-43	Nurettin Yaylı TUBITAK ARDEB Programs
16:30-17:30	DISCUSSION-CLOSING CEREMONY	
19:30-24:00	GALA DINNER-PROLAB	

ABSTRACTS

INVITED SPEAKERS

Linking water chemistry to metal speciation and risk assessment – analytical challenges

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Considerable effort is being expended to incorporate bioavailability concepts into regulatory frameworks for metals. Nowadays it is widely accepted that the degree to which metals are available to aquatic environment and organisms varies depending on the site-specific geochemical conditions, controlling metal speciation. In general, from the perspective of a risk assessment it is crucial to understand which geochemical characteristics influence the speciation and thus toxicity of metals and to incorporate results into regulatory framework. In order to increase the ecological relevance of the assessment both effects and/or exposure data should be normalized to the bioavailable metal fraction. Different experimental approaches have been suggested in the last few decades to determine metal species in surface waters. The methods are mainly focused on the determination of free ion concentrations, labile inorganic and organic metal complexes and metal complexes with high molecular organic matter. Direct methods based on electrochemical procedures such as anodic stripping voltammetry, competing ligand exchange with adsorption cathodic stripping voltammetry as well as stripping chronopotentiometry seem to be promising to evaluate the free metal concentration at the low levels in surface waters. Separation techniques based on ion exchange, complexing resins, micro separation methods as the Donnan membrane technique, diffusive gradients in thin-film gels and the permeation liquid membrane, are another analytical approach to perform this difficult analytical task.

The present study focuses on:

- Quantification of metal speciation and role of dissolved organic matter (DOM);
- Bioavailability characterization by measurements of adsorbed and internalized metal content in algae;
- Determination of toxicity of Cd, Cu, Ni and Pb toward unicellular estuarine alga *Chlorella salina* (Chlorophyta) in artificial and natural Black sea water.

Free metal ion concentrations in Black sea water spiked with environmentally relevant metal concentrations were measured by permeation liquid membranes and diffusive gradients in thin-film gels. In addition excitation emission matrix fluorescence spectroscopy and asymmetrical flow-field flow fractionation coupled with UV detection were used for the characterization of specific Black sea dissolved organic matter and organic matter released from algal cells exposed to micromolar concentrations of Cd, Cu, Ni and Pb. Bioassays revealed that both intracellular and adsorbed metal content increased linearly (1:1) with increasing metal concentration after a 72-h exposure by using metal concentrations measured by permeation liquid membranes. No significant difference (t-test, $p < 0.05$) in the uptake was found between algae exposed to spiked artificial and natural Black Sea water, when the results were expressed as a function of the free metal ion concentrations. Cell distribution for all four metals is dominated by the insoluble metal fraction, representing 67-71% from the total cellular metal, while the soluble was in the range from 20 to 23% and adsorbed fraction from 7.7 to 9.8%. Additionally the variations of nutrient conditions as well as dissolved organic matter content in natural Black sea water on the specific ecotoxicity characteristics such as EC₅₀, LOEC and NOEC were defined.

The obtained values were compared with dissolved and free metal ion concentrations measured in different sampling locations of Bulgarian Black sea coast. Conclusions on chemical and ecological status of Black sea water (Bulgarian coast) were presented.

KEYWORDS: metal speciation, bioavailability, Black sea, permeation liquid membrane, diffusive gradients in thin-film gels.

Acknowledgments: The authors gratefully acknowledge the financial support provided by Swiss National Science Foundation SCOPES program, Projects IB7320-110933/1 “Black Sea ecotoxicity assessment” and project DNTC-01/11 of Bulgarian National Scientific Fund.

Multidimensional Mass Spectrometry Methods for the Analysis of Synthetic Polymers

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Matrix-assisted laser desorption ionization and electrospray ionization have enabled mass spectrometry (MS) analyses for a wide variety of synthetic polymers, but considerable challenges still exist. Polymerizations often create complex mixtures that are impossible to characterize by single-stage MS because of superimposed compositions or discrimination effects. These problems can partly be resolved by tandem mass spectrometry (MS²). Depending on the polymer, MS² via either collisionally activated dissociation (CAD) or electron transfer dissociation (ETD) may lead to fragmentation patterns that permit unequivocal identification of the corresponding architecture, functionality location, and comonomer sequence. For the characterization of more complex systems, MS must be combined with separation methods, such as liquid chromatography (LC) or ion mobility (IM) spectrometry. Particularly powerful for such studies are approaches that couple ultrahigh performance LC (UPLC), which significantly reduces elution times, with the ion mobility dimension, which enhances separation and spectral decongestion. Different combinations of LC, IM, and MS² may be used to address questions about polymer composition, structure, and architecture. Analyses involving top-down methods (the entire analysis is performed in the mass spectrometer) as well as methods including prior LC separation or mild thermal desorption/degradation with the ASAP (analysis of solids at atmospheric pressure) probe will be demonstrated with a variety of synthetic polymers designed and engineered in Northeast Ohio's "polymer valley."

Characterization of Bioactive Peptides in Functional Dairy Foods with Disease-Preventing Ingredients

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Milk proteins are precursors of many different bioactive peptides that may remain latent until being released by enzymatic proteolysis during gastrointestinal digestion or food processing. These bioactive peptides have been described as showing, among others, immunostimulating, antimicrobial, opioid, angiotensin converting enzyme inhibition, mineral binding, antithrombotic or allergenic bioactivities [1]. However, identification and quantification of bioactive peptides in milk protein hydrolysates, fermented dairy products or, in general, in functional dairy foods with health-promoting or disease-preventing peptides ingredients is a challenging task because these highly complex samples may contain up to hundreds of different peptides at different levels of concentration. This is the case of functional yoghurt with bioactive peptides. In our work, we have used capillary electrophoresis coupled to mass spectrometry (CE-MS) and microliquid chromatography coupled to mass spectrometry (microLC-MS) for the identification of bioactive peptides in dairy products. A sample clean-up pretreatment with a citrate buffer containing dithiothreitol and urea followed by solid-phase extraction (SPE) was applied. The use of different commercial sorbents was investigated to achieve optimum detection sensitivity in CE-MS and microLC-MS. Hundreds of low molecular mass compounds were detected. Experimental mass of the detected compounds is search in a lab-made database, obtained from about 300 bioactive peptides, containing accurate monoisotopic molecular mass (Mteo) values, the location in the sequence of the protein precursor and the type of biological activity. The presence of some of proposed bioactive peptides was later confirmed using the accurate molecular mass data obtained by TOF-MS [2]. Other dairy functional product, such as a yoghurt with bioactive peptides, have been analyzed by microLC-TOF-MS [3]. The pretreatment of the sample was applied and more than 1000 low molecular mass compounds were identified. Taking into account the lab-made database and a final revision of raw extracted ion chromatograms (EIC), the presence of 52 bioactive peptides were identified. In order to improve identification, Normalized Elution Times (NET) models for peptides were used. Finally, 36 bioactive peptides were identified in the studied commercial yoghurt, 28 were ACE inhibitors, 1 antimicrobial, 1 citomodulatory, 1 opioid, 1 mineral binding and 9 antihypertensive peptides.

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Green Extraction of Natural Products: Concept, Principles and Applications

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The design of green and sustainable extraction methods of natural products is currently a hot research topic in the multidisciplinary area of applied chemistry, biology and technology. Herein we aimed to introduce the six principles of green-extraction, describing a multifaceted strategy to apply this concept at research and industrial level. The mainstay of this working protocol are new and innovative technologies, process intensification, agro-solvents and energy saving. The concept, principles and examples of green extraction here discussed, offer an updated glimpse of the huge technological effort that is being made and the diverse applications that are being developed.

The listing of the six principles of Green Extraction of Natural Products should be viewed for industry and scientists as a direction to establish an innovative and green label, charter and standard, and as a reflection to innovate not only in process but in all aspects of solid-liquid extraction:

Principle 1: Innovation by selection of varieties and use of renewable plant resources.

Principle 2: Use of alternative solvents and principally water or agro-solvents.

Principle 3: Reduce energy consumption by energy recovery and using innovative technologies.

Principle 4: Production of co-products instead of waste to include the bio- and agro-refining industry.

Principle 5: Reduce unit operations and favour safe, robust and controlled processes.

Principle 6: Aim for a non denatured and biodegradable extract without contaminants.

Supramolecular Solvents: Efficient and Green Nanostructured Liquids for Analytical Extractions

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The increasing pressure to decrease organic solvent usage in laboratories is fostering the search for alternative solvents. Supramolecular solvents are nanostructured liquids generated from aqueous or hydro-organic solutions of amphiphiles through self-assembly processes. Self-assembly based synthetic procedures are within everyone's reach and provide unique opportunities to obtain tailored solvents with advanced functional features.

This talk will focus on the most significant developments concerning both theoretical and practical aspects related to the use of supramolecular solvents in analytical extractions. Theoretical aspects will include those advances allowing a better understanding of the mechanisms of solvent production and solvent structure and composition. A comprehensive understanding of these fluids is no doubt essential with a view to their rational exploitation in a number of fields. Practical aspects will include the consequences of the unique array of physico-chemical properties of supramolecular solvents on extraction efficiency, suitability for extracting solutes spanning a wide polarity range and potential for developing generic sample treatments and multiresidue analysis. In this context, recent developments in formats and strategies making supramolecular solvents compatible with separation and detection techniques and the most outstanding applications reported so far will be discussed. Trends and topics deserving development in this area will be finally outlined.

FT-IR and Raman Spectroscopy in Phytochemical Analysis of Medicinal and Aromatic Plants

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Public interest in high-quality food products with clear geographical origin has increased significantly in recent decades [1]. Demand for high levels of quality and safety in medicinal and aromatic plants requires high standards in quality assurance and thus, appropriate analytical tools. Desirable properties of such tools include rapidity, ease-of-use, minimal or no sample pre-treatment and the avoidance of sample destruction. In this context, among the advanced spectroscopic vibrational methods possessing these features, Fourier transform infrared (FT-IR) and Raman spectroscopy could represent effective analytical techniques for the analysis of valuable natural substances, the simultaneous analysis of multiple compounds or adulterants and for identifying the geographical origin of raw materials in a single instrumental measurement [2].

The use of FT-IR spectroscopy has allowed many applications such as pollen identification, differentiation of saffron (*Crocus sativus*) from four different countries and quantitative determination of pulegone in pennyroyal oil [1, 3-5]. The interaction of numerous secondary metabolites derived from medicinal and aromatic plants with biomacromolecules such as DNA, tRNA and HSA (human serum albumin) has also been investigated by FT-IR [6-7].

The application of Raman spectroscopy to phytochemical analysis has successfully resulted in the characterization of *cis*- and *trans*-crocin isomers of saffron, the characterization of essential oils from Lamiaceae species and the quantification of crocetin esters in saffron [8-12].

FT-IR and Raman spectroscopy, usually combined with multivariate data analysis, provide high-throughput and cost-effective methods for determining quality, authenticity and biological activity of medicinal and aromatic plants and related products.

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Versatile Materialistic Approaches toward Separation Science and Sensor Technology

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The functional materials with high selectivity for ions/molecules are of interest for analytical purposes and for the recycling of resources as well as for waste water treatment; for example, the sensing removal of toxic substances. In this respect, different approaches have been launched to search for molecular structures that can serve as building blocks for the production of sophisticated functional materials by anchoring various groups oriented in such a way that they delineate a suitable binding site. Among other polymeric functional materials, calixarenes [1-2] are a class of supramolecular building blocks that are readily amenable to chemical modification at the phenolic hydroxy groups, thereby leading to nanoporous molecules with selective host-guest properties [8]. The interest that calixarenes have aroused in the last twenty years is facilitated by their ready availability. Multigram amounts can be obtained on a laboratory scale in a relatively simple manner, starting from cheap starting materials. In this way, calixarenes differ from many other synthetic macrocycles. Moreover, their application in diverse areas of separation science and technology in particular makes them a better choice for extraction, membrane technology and chromatography etc. Herein, different aspects of the synthesis and applications of different functional materials in separation and sensing of ionic and or neutral molecules will be discussed.

KEY WORDS: Calixarene, Complexation, Sensor technology, Separation science, Supramolecular chemistry.

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NIR spectroscopy for pharmaceutical analysis

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Near infrared spectroscopy (NIR) is becoming an increasingly important analytical tool in pharmaceutical development and manufacture. This is due to several factors: the lower molar absorptivity of the NIR region compared with that of the mid-infrared permits direct analysis of pharmaceutical matrices (solids and liquids) with minimal or no sample preparation and radiation penetrates further into solid materials, providing transmission and diffuse reflection measurements that are representative of the bulk material analysed. Spectra of materials may be rapidly acquired and contain both physical (in the case of solids) and chemical information, enabling the qualification and quantification of materials, including: excipients, active pharmaceutical ingredient, moisture, particle size and distribution, amorphous and crystalline form, etc. In keeping with the process analytical technology (PAT) initiative of the US Food and Drug Administration, this therefore affords the possibility for the replacement of many traditional pharmaceutical analytical tests with a single NIR measurement, and the analysis and control of pharmaceutical processes and products:

"...through timely measurements of critical quality and performance attributes of raw and in-process materials and processes with the goal of ensuring final product quality".[1]

This presentation will illustrate the potential of NIR spectroscopy and multivariate analysis for replacement of many traditional, pharmacopoeial tests and implementation of PAT. Several case studies will be presented, including the qualification of raw materials (such as identity, particle size, moisture content, polymorphic form), the control of pharmaceutical processes (such as powder blending and tableting) and extension of the analytical technique for the authentication of medicines and detection of counterfeit medicines.

KEYWORDS: NIR, near infrared spectroscopy, multivariate analysis, pharmaceutical analysis, process analytical technology, PAT, authentication, counterfeit medicine.

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ORAL PRESENTATIONS

Preconcentration of Arsenic and Lead by Willow Leaves as Biomass

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Heavy metal contamination has been a serious issue because of the adverse effects of heavy metals on human and environmental health. So, it is necessary the development of rapid and sensitive methods for accurate determination of heavy metals. For this purpose, ICP-AES and AAS are widely recognized. However, direct determinations in environmental, food and biological samples at trace levels are difficult due to insufficient detection limits of those techniques. This limitation can be overcome by the using enrichment methods in that metals ions of interest from solution are selectively separated and concentrated into smaller volumes to achieve better detection by the techniques [1]. This task can be achieved by using various methods, such as ion exchange, cloud point extraction, electro-deposition, coprecipitation, membrane filtration, dispersive liquid-liquid micro extraction, flotation, and solid-phase extraction (SPE). Among these methods, SPE is the most frequently employed as it offer the highest attainable enrichment factors with relatively rapid separation and low cost [2].

In this work, biomass, willow leaves as a new sorption material, was used for determination of arsenic and lead in water samples. The method is based on the sorption of As and Pb ions on the ground willow leaves. The optimization of procedure was performed using parameters including pH, amount of biomass, contact time, first volume of sample and eluent. Using the experimental conditions defined in the optimization, the method was applied to preconcentration of As and Pb at ppb level in model solutions. Inductively coupled plasma atomic emission spectrometry (ICP-AES) was used for element determinations. The optimum pH was found to be 4.0

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Characterization of microporous silica-based membranes by calorimetric analysis

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Microporous sol-gel derived silica membranes are attractive device for efficient molecular separation systems, as hydrogen purification, carbon dioxide capture, and alcohol dehydration. However, the poor steam-stability of these devices still hampers their practical application. Indeed, porous silica membranes have been reported to undergo densification when exposed to steam at temperatures as low as 60 °C. The intrinsic hydrothermal instability of sol-gel derived porous silica membranes can be understood by considering their high free-energy content, which is due to their large specific surface area, high silanol content, low cross-links density, and high free volume. Therefore, calorimetric analysis is an ideal tool for investigating structure and stability of these membranes. Glass transition temperature (T_g) was determined by calorimetric analysis for silica-based membrane with different composition and thermal history. In general, the higher was the T_g , the lower was the specific surface area loss after hydrothermal exposure. These results support the hypothesis that some of the transition metal ions can as network formers in silica-based membranes, stabilizing their porous structure by enhancing their network connectivity.

KEYWORDS: silica, membranes, DSC analysis, stability, sol-gel.

OP-03

Highly Selective Enrichment of Sialylated Glycopeptides Using Titania Sol-Gels For Mass Spectrometry Based Glycoproteomics

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Glycosylation is one of the most important post-translational modifications of proteins that are played an important role in many cellular processes, such as receptor–ligand interactions, cell adhesion, signal transduction, and immune response[1]. Protein glycosylation can drastically change protein conformation and activity. Protein glycosylation modifications have been related to different diseases such as cancer, neurodegenerative diseases and rheumatoid arthritis[2]. Therefore, characterization of glycoprotein structures is important for fully understanding these cellular processes. Particularly, glycosylation site occupancy and glycan heterogeneity at each glycosite site is needed to characterize for investigating the systems by glycans in healthy and disease situations. Mass spectrometry (MS) has become an important tool for peptide and protein structure analysis because of high accuracy, resolving power and sensitivity[3]. Electrospray ionization (ESI) and matrix assisted laser desorption/ionization (MALDI) have been widely used for several years for peptide sequencing. Although developments in mass spectrometric techniques, glycosylation analysis in complex biological samples contains quite challenging steps. When proteins are digested into peptides, amount of glycopeptides are very lower than ordinary peptides. Moreover, heterogeneity of glycans present on glycoproteins is made difficult extensive analysis of glycosylation[4]. Also, the ionization efficiency of glycopeptides is moderately poorer than that of non-glycosylated peptides. Therefore, it is crucial to selective and effective enrichment of glycopeptides prior to MS analysis. Recent years, several methods have been developed for the enrichment of glycopeptides, that is, lectin affinity chromatography, hydrazide and boronic-acid chemistry and hydrophilic interaction chromatography. Lectin affinity chromatography is widely utilized tool by lectins binding with glycans such as mannose (Man), N-acetylglucosamine (GlcNAc), N-acetylgalactosamine (GalNAc), sialic acid (Sia), and fucose (Fuc). However, same lectins are showed low specificity to constant glycan residues. Hydrazide chemistry, which has low glycosylation heterogeneity coverage, particularly isolates glycopeptides from complex mixtures. Hydrophilic interaction chromatography in solid-phase extraction (SPE) mode is increasingly occupied to enrich glycopeptides. In this study, highly selective enrichment method was successfully carried out using titania sol-gel for the sensitive detection and identification of the glycopeptides by mass spectrometry. Titania sol-gel was synthesized by easy and cheap pathway and an enrichment method was developed on the basis of specific interactions between the titania sol-gel and sialylated glycans. Human transferrin, which has highly sialylated glycans and mainly two-glycosylation site on Asn⁴³² and Asn⁶³⁰ amino acids, was selected as a standard glycoprotein. The site-specific enrichment method was developed on the basis of interaction between Lewis acid and base pairs such as the titanium centers on the sol-gel and sialic acids on glycans. MALDI-MS data indicated that the sialylated glycopeptides in a complex peptide mixture of human transferrin proteolytic products were selectively captured by the titania sol-gels. The interaction between titania sol-gels and sialylated glycopeptides are achieved specific loading conditions that contain 1 M glycolic acid in acetonitrile (ACN):water:trifluoroacetic acid (TFA) mixture (8.5:1:0.5, v/v). To substantially remove the non-glycopeptides, titania sol-gels were washed with the buffer solutions increasing polarity and pH of the medium. The addition of 1.0 M glycolic acid into the loading buffer dramatically improved the selectivity of titania sol-gels for the glycopeptides. And, sialylated glycopeptides were successfully eluted using the buffer solution at alkaline (pH 9–10) conditions. After the enrichment of sialylated glycopeptides, PNGaseF treatment was carried out for determination of glycosite site and glycan portion of glycopeptides. The specific losses such as 162 Da Hexose (Hex), 203 Da N-Acetyl Hexose (HexNAc) and 291 Da N-Acetylneuraminic Acid (NeuNAc) were observed by MALDI mass spectra using 2,5-dihydroxybenzoic acid matrix due to prompt fragmentation of the glycans originated from sialylated glycopeptides of human transferrin. Consequently, a novel titania sol-gel was developed for highly selective enrichment of the sialylated glycopeptides in mass spectrometry based glycoproteomics applications.

KEYWORDS: Glycosylation, Glycopeptide Enrichment, Mass Spectrometry, Post Translational Modifications

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Determination of Fipronil and its Metabolites Residues in Cauliflower by Using GCMS/MS Triple Quadrupole Mass Spectrometry

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Fipronil [\pm 5 amino-1-(2, 6-dichloro - α , α - trichloro -p- tolyl) -4- trifluoromethylsulfinyl pyrazole -3- carbonitrile] insecticide has biological activity against many insect pests. Persistence of fipronil and its metabolites may have adverse effects on human health. A supervised trial was conducted at CCS Haryana Agricultural University Hisar, India to access the residues status of parent fipronil compounds and its three metabolites i.e. fipronil sulfone, sulfide and desulfinyl using GCMS/MS Triple Quadrupole Mass Spectrometry in cauliflower at recommended dose of 56 g a.i. ha⁻¹. Periodic sampling of cauliflower was done on 0 (2hrs after spray), 1, 3, 7, 10, 15 and 30 days. Effect of different culinary household processes like washing and washing followed by cooking and residues status in washed water was also studied. Fipronil was extracted from cauliflower by acetone and processed by QuEChERS method using MgSO₄ and PSA. The final solution was reconstituted in n-hexane and quantified by using GCMS/MS. Limit of detection (LOD) and limit of quantification (LOQ) were 0.01 and 0.001 mg kg⁻¹, respectively. Recovery experiment was performed by fortifying the cauliflower at the rate 0.25, 0.50 and 1.0 ppm levels. The average recoveries ranged from 85.40 to 98.10 percent. Residues of parent fipronil and its various metabolites were found below detectable level with 100% dissipation after 30 days with half life of 3.66 days. Washing and washing followed by cooking was found very effective in removing parent fipronil and its metabolites upto 75 to 80 percent in third day's samples. In water left after washing of cauliflower, it was observed that near half of the residues of fipronil along with its various metabolites goes in water.

Table 1: Residues (mg kg⁻¹)* of fipronil and various metabolites in cauliflower.

Sampling interval (days)	Residues (mg kg ⁻¹)				Total	Reduction (%)
	Parent fipronil	Fipronil sulfone	Fipronil sulfide	Fipronil desulfinyl		
0	0.959	0.166	0.067	0.422	1.614	–
1	0.768	0.075	0.045	0.195	1.083	32.89
3	0.597	0.039	0.035	0.155	0.826	48.82
7	0.307	0.021	0.030	0.083	0.441	72.67
10	0.165	0.010	0.023	0.045	0.243	84.94
15	0.060	0.001	0.006	0.004	0.083	94.98
30	BDL	BDL	BDL	BDL	BDL	100
Correlation Coefficient $r = -0.9961$						
Regression Equation $y = 3.1761 - 0.0821x$						
$t_{1/2} = 3.66$ days						

*Average of three replicates; BDL: 0.01 mg kg⁻¹

KEYWORDS: fipronil, residues, half-life, GCMS/MS triple quadrupole mass spectrometry analysis.

An Aptamer Mediated Enrichment Method for Mass Spectrometric Detection of Thrombin

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Aptamers are single-stranded oligonucleotides (DNA or RNA) selected by a molecular selection process called Systematic Evolution of Ligands by Exponential Enrichment (SELEX). Numerous high-affinity and highly specific aptamers have been selected against a wide variety of target molecules including small organics, peptides, proteins, and even supramolecular complexes such as viruses or cells. Aptamers are alternative candidates to antibodies in respect to their sensitivities and affinities. Protein - antiprotein interactions are weaker than the interactions between protein and aptamer. The binding affinities of aptamers are highly target dependent and range from the picomolar scale (1×10^{-12} M) to the high-nanomolar scale (1×10^{-7} M) for various protein targets. Due to the convenient properties of the aptamers mentioned above, the aim of the study is to enrich the thrombin on its selective aptamer attached on the polymeric surfaces. Thrombin is a multifunctional serine protease that plays major roles in the coagulation cascade. Also, the amount of thrombin is used as a clinical index for the number of pathological processes, such as metastasis, cardiovascular diseases, angiogenesis, inflammation, and has been considered as a biomarker for tumor diagnosis¹⁻⁴. Various methods such as electrochemical, fluorescence, quartz crystal microbalance, ICP-MS have been used to detect thrombin using aptamer. However, with these methods it is not possible to obtain high sensitive detection of thrombin⁵. In the scope of this study, therefore, highly sensitive and selective thrombin enrichment was carried out using a novel aptamer attached surface and bioanalytical method prior to MALDI-MS (Matrix-Assisted Laser Desorption/Ionization-Mass Spectrometry) analysis. Mass Spectrometry is one of the most powerful tools for the detection of biomolecules with very high sensitivity and selectivity even at very low concentrations. For the enrichment of thrombin, its specific aptamer which has SH- functional group at 5' end was attached to the amine functionalized PS-DVB microbeads covalently using Sulfo-succinimidyl-4-(*N*-maleimidomethyl)cyclohexane-1-carboxylate (Sulfo-SMCC) cross-linker. The aptamer attached polymeric microbeads were incubated with thrombin solution and then tryptic digestion procedure was applied. When the digest solution was analyzed using MALDI-MS following the enrichment, it was noticed that 0.0007 pmol/ μ L thrombin could be detected in the case of conventional detection level about 1 pmol/ μ L. The same procedure was also applied for the enrichment of thrombin from complex biological sample which contains different type of proteins at high concentrations. The results obtained from MALDI-MS showed that thrombin could be enriched from the complex solution with high selectivity. Finally, the enrichment of the thrombin from human plasma as a real complex sample was studied and it was observed that thrombin could be selectively enriched from real complex samples using the new material and successfully detected by MALDI-MS.

KEYWORDS: Oligonucleotide, Aptamer, Antibody, Sulfo-SMCC, Thrombin, Mass Spectrometry, Protein enrichment.

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Determination of Clavulanic Acid in Human Plasma By Liquid-Liquid Chromatograph with Mass Detection

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The clavulanic acid (CA) is a beta-lactam antibiotic, produced by *Streptomyces clavuliger*, with a strong inhibitory activity against beta-lactamase from a variety of Gram-positive and gram-negative bacteria. This antibiotic is highly unstable at a pH < 5.0 and > 7.0 and degradation rate increases remarkably with temperature. [1,2]

Due to its very strong polarity, it was not retained on Reversed-Phase column, given poor peak shape and relatively low response. Then, a simple and fast high-performance liquid chromatograph – mass spectrometric method has been developed for determination of clavulanic acid in human plasma. After precipitation of the plasma proteins with acetonitrile, the analytes were separated on a Hilic Silica 3 μ m 2.1 x 150 mm column with 10 mM ammonium formate in water - 10 mM ammonium formate in water-acetonitrile (1:9) (20:80, v/v).

The limit of detection and limit of quantitation are 0.7 ng/mL and 2.0 ng/mL, respectively. Linear range of calibration curve of clavulanic acid was ranged from 10.0 to 2500.0 ng/mL. The average absolute extraction recovery of clavulanic acid for, low (75.0 ng/mL), middle (250.0 ng/mL) and high (1000.0 ng/mL) concentration levels were obtained as % 53.6, % 52.5, and % 64.0 respectively by using Liquid-Liquid Extraction (LLE) technique.

The stability of stock solution of clavulanic acid was assessed during 24 hours and 4 days separately. It was found that no significant change was observed within the concentration of clavulanic acid for imposed time intervals. It also presents a good stability at the end of the three cycle of freeze-thaw stability study.

KEYWORDS: clavulanic acid, liquid chromatography mass spectrometry, Liquid-Liquid Extraction

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A Tale of Two Papers

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In scientific meetings we occasionally watch presentations about “how to write a scientific paper”. We also sometimes follow lectures explaining the plagiarism with its ethic basis. This talk will not be one of them.

We would like to share our experience about publishing a manuscript with our colleagues, because this seems to be an ongoing story for us and may happen to everyone.

We intended to publish our manuscript, which was prepared after conducting the laboratory hard working, in a respected journal. However we ended up with two published papers with the same name and similar content in two different journals.

KEYWORDS: duplication, scientific paper, publishing a manuscript.

Determination of Antioxidant Capacities of Individual and Combined Phenolics by CHROMAC Method

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Fruits and plants contain a wide range of antioxidant components in plant tissues which are responsible for their antioxidant capacity. These antioxidants include vitamins, carotenoids, phenolic acids and flavonoids which could play an important antioxidant role since they behave as free radical scavengers, singlet and triplet oxygen quenchers, enzyme inhibitors and metal-chelators [1]. Phenolics are reported to inhibit low density lipoprotein (LDL) oxidation and have antioxidant, anticancer, and antiinflammatory activity [2]. Therefore, plants have shown a remarkably high scavenging activity towards generated radicals.

Several methods have been reported for determination of antioxidant capacity in plants and foods. Antioxidant capacity methods differ in terms of their assay principle and experimental conditions. Because of multiple reaction characteristics and mechanisms, a single assay will not accurately reflect all antioxidants in a mixed or complex system [3]. The CHROMAC is a novel assay as a spectrophotometric total antioxidant capacity assay based on the reaction of excessive Cr (VI) with phenolic compounds and formation of coloured complex with remaining Cr(VI) and diphenylcarbazide. CHROMAC assay is simple, inexpensive, sensitive and selective indirect spectrophotometric assay for the determination of total antioxidant capacity of different types of food antioxidants. The CHROMAC assay has some advantages over the other commonly used antioxidant capacity measurement assays with regard to interference effects of protein, citric acid and glucose, and time required for measurement [4].

Antioxidant capacities of 20 individual, two and three combined phenolic compounds in different classes were determined by developed CHROMAC assay. Additivity of different classes of phenolics was above 93% which implies that CHROMAC assay is not influenced by other phenolics and interfering compounds. Position and number of OH group in the structure has important effect on the antioxidant capacity. The TEAC values of flavones, flavonols, flavanones, flavonoids and hydroxybenzoic acids are high with respect to the number of OH groups. On the other hand, methoxyl group has adverse effect on the antioxidant capacity.

KEYWORDS: CHROMAC assay, phenolic acids, flavonoids, HPLC

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Detection of Some Phenolic Compounds in Barley and Rice Shoot Residues Using Derivative Spectroscopy

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The cereals are the most important sources of plant food for man and animals. This is not only true today, but it is being established since the earliest time. The true cereals are classified to be wheat, barley, rice, maize, oats and rye. Rice, barely, and wheat are the most important food cereals worldwide creating the daily source of nutrient for billions of people (Olofsdotter et al., 1997). On the other hand the importance of allelopathy in nature and agroecosystems has attracted researcher's attention with the main goal of using this phenomenon in biological control of weeds (Jones et al., 1999). Wheat, barley, and rice are the most important cereals in Iraq, where they are used for human food and livestock forage. Barley and wheat are cultivated in rainfed regions of the northern part of Iraq, while irrigated in the middle and the southern parts, thus, weeds cause great loss of yield that may reach 30-50% of total yield yearly.

This study was aimed to investigate the allelopathic potential which might be found in local rice and barley cultivars. Most of the experiments were achieved in laboratory after optimizing all environmental factors to be suitable for growing crop plants and weeds. Second, soil type and texture were taken into consideration whether there may be any effect of soil porosity and particle size on allelochemical movement and action. Third to find out and evaluate the allelopathical magnitude of rice and barley residues as autotoxicity or as biocontrol for growing weeds through their decays. Time was insured for such decays to release various biochemics where two months were allowed before harvesting to plants in such soil amended with plant debris.

The normal spectra of a mixture of various phenolic acids (vanillic, syringic, m-coumaric, p-coumaric, and p-hydroxybenzoic acids) and the aqueous extracts of shoots of Black barley, White barley, Aqra rice and Kasnadita rice. The comparison of the above curves showed that there were no characteristic peaks attributed to the presence of phenolic acids in the plant residue extracts. Therefore, the derivative spectra of the mentioned samples have been recorded. Derivative spectra have been used to identify the various phenolic acids present in the natural sample.

KEYWORDS: detection, phenolic compounds, barley and rice shoot residues, derivative spectroscopy.

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Oxygen Radical Absorbance Capacity and Total Phenolic Content of Oleaster

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Dietary antioxidants can reduce the harmful effects of free radicals on a number of biological and pathological processes. With increasing interest in the function and diversity of antioxidants in foods, a wide range of spectrophotometric assays have been adopted to measure antioxidant capacity of fruits and vegetables [1]. Among them, the oxygen radical absorbance capacity (ORAC) assay has gained much attention so that it deals with peroxy radicals, which are the most abundant radicals in biological systems [2].

Elaeagnus angustifolia L. (oleaster) is one of the widely consumed medicinal plant in Turkey. Fruits, leaves and flowers of oleaster are used in the treatment of nausea, vomiting, jaundice and as the main folk medicine [3]. In this study, antioxidant capacities of different oleaster parts extracts obtained with ethanol/acetone (7:3,v/v) and methanol (100%) extraction solvents were evaluated by using ORAC method. The amounts of phenols in the extracts were investigated by Folin-Ciocalteu assay. Ethanol/acetone extract of seed (3.65 mg gallic acid equivalent/g) and methanol extract of leaf (5.13 mg gallic acid equivalent/g) showed higher total phenolic content than the other parts extracts in same extraction solvent. Leaf extracts of both extraction solvents (328.00 and 428.00 μmol trolox equivalent/g for ethanol/acetone and methanol, respectively) exhibited higher antioxidant capacity values than the other parts extracts.

KEYWORDS: ORAC, total phenolic content, oleaster

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Surfactant Effect on the Separation and Detection of Biogenic Amines and Chiral Amino Acids by Micellar Electrokinetic Chromatography Coupled by Laser Induced Fluorescence

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The effects of surfactants on the separation and detection of biogenic amines and chiral amino acids by the micellar electrokinetic chromatography method coupled to laser-induced fluorescence detection (MEKC-LIF) were investigated. Sodium dodecyl sulfate (SDS) is the dominantly used surfactant in the capillary electrophoretic separations of biogenic amines. Here, a non-ionic surfactant, Brij 35, was used in the separation electrolyte. Besides a considerable decrease in separation times, the fluorescence intensities of biogenic amines derivatized with fluorescein isothiocyanate (FITC) increased to between about 4 and 21 times when Brij 35 was substituted for SDS in the same buffer (1). The detection limits of the method for biogenic amines were found to be between 0.416 and 1.26 nM. The method is simple and rapid, and widely applicable for the determination of biogenic amines in food samples. We applied our developed method to the analysis of biogenic amines in salted fish samples, in wines, and in pomegranate molasses.

A new chiral MEKC-LIF method was developed using sodium dodecylbenzene sulfonate (SDBS) as surfactant for the determination of chiral amino acids. The use of SDBS as the micellar medium enhanced the fluorescence intensities of amino acids derivatized with FITC. LOD values changed between 0.848-3.99 nM. This new method was used to produce the amino acid profile of pomegranate juice.

KEYWORDS: Capillary Electrophoresis, Micellar Electrokinetic Chromatography, Biogenic Amines, Amino Acids, Chiral Separation

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Determination of Mono- and Di-nitrosopiperazine in The Atmospheric Particulates and Their Relationships between Concentrations of Nitrite, Nitrate, Piperazine and Meteorological Parameters

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The chemical composition of airborne particulate matters (PMs) in polluted atmospheres has become a topic of considerable importance over recent years in relation to public health because epidemiological studies have shown that exposure to particulates with aerodynamic diameters $< 10 \mu\text{m}$ (PM_{10}) and especially $< 2.5 \mu\text{m}$ ($\text{PM}_{2.5}$) induces an increase of lung cancer, morbidity and cardiopulmonary mortality. *N*-Nitrosamines can be found in ambient air [1], especially in atmospheric particulates as a result of direct emissions from polymer industry, combustion of rubber and plastic materials and their formations from secondary amines [2]. *N*-Nitrosamines, which can be formed easily by the reaction between primarily secondary amines and nitrogen oxides, are known to be toxic and/or carcinogenic compounds for human based on sufficient evidence of carcinogenicity in experimental animals [3]. Mono-nitrosopiperazine (MNPIZ) and di-nitrosopiperazine (DNPIZ) are thought to be definitely tumorigenic, although it showed no selectivity of site for tumour induction and induced tumours in a wide range of organs and tissues of rats [4]. MNPIZ and DNPIZ are carcinogenic in rats and DNPZ has also been shown to induce tumours in mice [5,6]. Therefore, the monitoring of the seasonal levels of *MNPIZ* and *DNPIZ* in airborne particulate matter and determination of the effects of nitrite, nitrate, piperazine and meteorological parameters on concentrations of these pollutants are important to control the factors which produce or disperse these pollutants to protect human health and the environment because of human exposure to these toxic compounds through inhalation. The aims of the study were the determination of total PM-associated nitrite, nitrate, piperazine, *MNPIZ* and *DNPIZ* and investigation of their correlations with meteorological parameters. The method of and mono and di-nitrosopiperazine analysis includes collection of the particulate matter ($\text{PM}_{2.5}$ and PM_{10}) using dichotomous Partisol 2025 sampler, extraction of the compounds from aqueous solution with dichloromethane/2-propanol after sonication with slightly basic water solution prior to their GC-MS analysis in EI mode. The method of piperazine analysis includes ion-pair extraction of amines with bis-2-ethylhexylphosphate (BEHPA) from airborne particulate matter and derivatisation with isobutyl chloroformate (IBCF) prior to their GC-MS analysis. The methods of nitrite and nitrate analysis includes derivatization of aqueous nitrite with 2,3-diaminonaphthalene (DAN), enzymatic reduction of nitrate to nitrite, extraction with toluene and chromatographic analyses of highly fluorescent 2,3-naphthotriazole (NAT) derivative of nitrite by using liquid chromatography-fluorescence (LC-FL). The seasonal variations of nitrite, nitrate, piperazine, MNPIZ and DNPIZ concentrations in atmospheric particulates were investigated together with their relationships with meteorological parameters. The concentration levels of MNPIZ and DNPIZ fluctuated significantly within a year with higher means and peak concentrations in the winter compared to that of summer times. There were significant negative correlations between MNPIZ and DNPIZ concentrations and piperazine, daily sunlight time, relative humidity, temperature in $\text{PM}_{2.5}$ and $\text{PM}_{2.5-10}$ samples in winter and summer. MNPIZ and DNPIZ concentrations were positively correlated with nitrite and nitrate in $\text{PM}_{2.5}$ and $\text{PM}_{2.5-10}$ samples in winter. In addition, discriminant analysis was used to classify the particle samples by particle size according to seasons and the classification results of the particle samples in different seasons were very satisfactory.

KEYWORDS: Nitrosamines, GC-MS, atmospheric particulates, Mono-nitrosopiperazine, di-nitrosopiperazine.

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Microwave Assisted Extraction of Green Tea

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In this study, microwave assisted extraction method was used to extract catechins, caffeine and other ingredients from green tea collected different periods in East Black Sea Area. For this, 5 g of green tea sample was used to prepare three different mixture. In the first mixture 100 mL 1:1 ethyl alcohol + distilled water, in the second only the difference 90 minutes preliminary shake and in the third only 100 mL distile water was used. All mixtures was extracted 80⁰ C, 10 minutes, 600 W with microwave [1]. Then it was filtered and extracted with water/chloroform(1:1 v/v) to separate caffeine and other impurities. The water phase was collected and extracted with water/ethyl acetate (1:1 v/v) to get catechin mixture. MgSO₄ was added to remove residual water for one night then organic phase was evaporated [2]. The highest yield was obtained from the second mixture which 90 minutes preliminary shake applied before extraction. HPLC analyses were performed with Waters HPLC set-up Pump Controller 600, Delta 600 Injection System, Autosampler 2707 ve PDA 2996 detector, C18 (4,6 x 150mm) 5µm column, 1mL/min flow rate, 20µL injection volume. HPLC analyses were carried out for identification of each individual catechin and caffeine quantification. The quantifications which were calculated after extractions are given in Table 1. The chromatogram of one of green tea sample is given in Figure 1.

Table1.

	Caffeine	Catechin
80 °C water, 10 min. 600 W microwave	0,0482 g	0,0135 g
80 °C Ethyl alcohol + water, 10 min. 600 W microwave	0,0975 g	0,0472 g
80 °C Ethyl alcohol + water , 90 min. shake and 10 min. 600 W	0,1638 g	0,1434 g

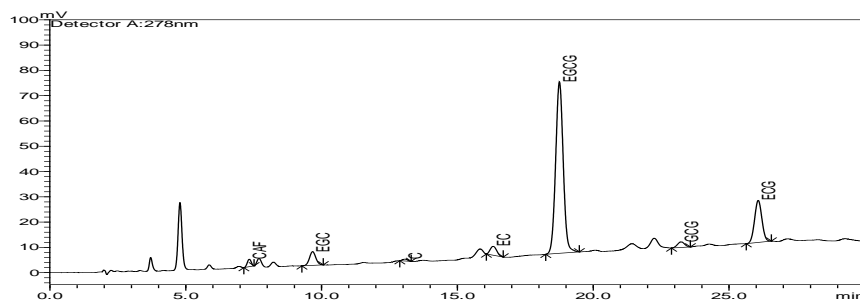


Figure 1. Chromatogram of green tea sample

KEYWORDS : microwave, extraction, green tea, HPLC

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Preparation of Solid Phase Micro Extraction Fibers by Electropolymerization Technique for the Determination of Endocrine Distruptor Pesticides

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One of the major challenges in analytical chemistry is to develop faster, easier and reliable methods for the quantification of the analyte within acceptable accuracy. Growing demand for greener and faster preconcentration techniques has resulted in intensive research on alternative extraction methods. Solid phase micro extraction (SPME) is a simple, solvent free, fast and inexpensive, technique for attaining very low limit of detection for trace organic compounds [1] and also it produces cleaner extracts than (LLE) or (SPE) extraction techniques and analysts do not always need sophisticated or expensive instrumentation [2]. In SPME method, analytes are concentrated on the thin polymer film coated SPME fiber and then are rapidly delivered to a capillary GC column. The coatings used in SPME are selected to have strong affinities for the organic compounds those are intended to extract. Several kinds of commercially available SPME fibers which are often prepared on deep or spin coating way [3] were used to determine pesticide residues in water samples including polydimethylsiloxane (PDMS) [4] carboxen-polydimethylsiloxane (CAR-PDMS) [5] polydimethylsiloxane-divinylbenzene (PDMS-DVB) [6], polyacrylate (PA) [7], divinylbenzene-carboxen-polydimethylsiloxane (DVB-CAR-PDMS) [8]. In recent years, studies have been focused on fabricating low cost, simple, robust and long-life fiber for the target analyte [9]. A variety of methods for the production of fibers have been developed such as sol-gel [10], and physical and electrochemical polymerization [11]. Among these, electrochemical polymerization is the method of choice as the film thickness can be controlled easily and polymers with different functional groups can be formed under controlled electrochemical conditions [23]. In this study, Polypyrrole (PPy), Polythiophene (PTh) and Polyaniline (PANI) coatings were prepared by using electropolymerization technique at laboratory conditions on a stainless steel for SPME applications to provide higher extraction efficiency. The surface of the fibers were characterized by using scanning electron microscopy (SEM) and thermo gravimetric analysis (TGA) technique was also applied for evaluating thermal stability of the fibers. The fabricated fibers efficiencies were tested for the determination of endocrine disruptor pesticides namely; Chlorpyrifos, Penconazole, Procymidone, Bromopropylate and Lambda-Cyhalothrin by headspace application. Operational parameters effecting the extraction, mainly, pH, sample volume, adsorption temperature and time, desorption temperature, stirring rate and salt amount were optimized for all three fibers. Pth fiber has given very satisfactory results when compared with PPy, PANI and commercially available fibers. The separation power of the gas chromatography was coupled with the excellent sensitivity of the developed fiber enabling us to determine the pesticide mixtures simultaneously in ppt range with satisfactory RSD values after 400 injection usage. Limit of detection was estimated in the range of 0.02-0.64 ng mL⁻¹ for the pesticides studied. The developed method was applied in water samples of vineyards with acceptable recovery values (92-110 %).

KEYWORDS: SPME, Electropolymerization, Endocrine Distruptor Pesticides, Gas Chromatography

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Application of Novel Polycaprolactone/Polydimethylsiloxane Fibers in Membrane- Solid Phase Microextraction Technique for the Isolation and Preconcentration of Organic Pollutants in Water Samples

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The admissible concentration of organic compounds having adverse effect on human health in drinking water is very low, therefore in order to secure the proper water quality, monitoring the pollution requires application of additional isolation and/or preconcentration step prior to the final determination of the critical compounds. In addition, analytical procedure and analytical tools applied should meet requirements of sustainable development and green chemistry. Solid Phase Microextraction (SPME) is one of the most popular solvent-free techniques of sample preparation, widely applied in analytical practice because of its undoubted advantages: simplicity of procedure, short extraction time, low analytical costs per sample, the possibility of automation and easy coupling with measuring instruments. However, SPME has significant limitations: due to small volume of the extraction phase only limited quantities of isolated analytes are obtained; affinity for polar compounds is also low. The latter is particularly important in case of isolation of polar analytes from samples with a polar matrix (like water).

One of the concepts for overcoming these problems is to separate polar retention medium from the sample by means of a impermeable membrane (made of polydimethylsiloxane, PDMS) to avoid mixing of extraction and sample phases. In our studies this system has been implemented in SPME technique as Membrane-Solid Phase Microextraction (M-SPME) and used for the isolation and preconcentration of organic pollutants from aqueous medium. The practical aspects of M-SPME approach create new opportunities in SPME, such as the use of new classes of polymers, which have so far been rejected from these applications due to their solubility in water.

The idea of this technique along with the first results have been published in 2009 [1]. Results presented so far concern application of double layer sorbent system with polyethylene glycol (PEG) used as extraction medium, applied to extraction of fenols [2] and volatile organic compounds [3]. Latest results concern application of new extraction phase made of polycaprolactone (PCL) in the concept of M-SPME. This new variant of SPME has provided interesting and valuable results during studies on the extraction of organic pollutants from different media, indicating that Membrane-SPME may become a powerful tool that can be used for the step of sample preparation in monitoring of environmental pollution.

KEYWORDS: solid-phase microextraction, SPME, organic pollutants, sample preparation, green analytical chemistry

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Solidified Floating Organic Drop Microextraction Method for Preconcentration and Determination of some Endocrine Disruptor Pesticides in Well Water Samples

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As a consequence of the widespread use of pesticides, the presence of their residues in the environment has become an important issue in analytical science. Legislation upon drinking water in EU set the limits at sub ppb level for total pesticide residue [1]. These levels require very sensitive methods for pesticide determination in water samples. Chromatographic techniques are widely employed since they are powerful separation techniques but, the sensitivity and selectivity of the method usually depend on the sample preparation method used prior to the analysis. In recent years, simplification and increasing automation of sample preparation steps are one of the modern trends in analytical chemistry. Classical extraction methods (e.g. liquid-liquid extraction, solid phase extraction) were used for the sample preparation steps generally. However, they display some drawbacks such as large consumption of reagent, low enrichment factor, multistage operation [2]. To overcome the drawbacks of the classical extraction methods microextraction methods such as single drop microextraction (SDME) [3], solid phase microextraction (SPME) [4], dispersive liquid liquid microextraction (DLLME) [5] techniques have been developed for the determination of pesticides in water samples. Also as an alternative to liquid microextraction techniques a novel liquid phase microextraction method based on solidification of floating organic drop (SFODME) has been introduced by Zanjani et al. [7]. A rapid, simple and cost effective method for the preconcentration and determination of endocrine disruptor pesticides namely, Aldrin (ALD), Chlorpyrifos (CP), Penconazole (PNC), Procymidone (PRO), Iprodione (IP), Bromopropylate (BRP) and Lambda-Cyhalothrin (LMD) has been developed by using solidified floating organic drop microextraction. In this technique a free microdrop of 2-dodecanol which has a melting point near to room temperature was used as an extracting solvent. Considering the number of parameters those are likely can affect the signal, extraction solvent type, extraction solvent volume, extraction time and temperature, sample volume and salt effect on pesticides extraction were optimized. The analytes were extracted from the 10.0 mL of water samples by using 10 μ L of 2-dodecanol for 20 min at 70°C in the presence of 0.5 g NaCl. The separation power of the GC was coupled with the excellent sensitivity of microextraction technique enabling us to determine the pesticide mixtures simultaneously in ppt range with satisfactory RSD values. The method was validated for the determination of endocrine disruptor pesticides in well water samples. The regression coefficients relating to linearity were at least 0.99. Recoveries from spiked well water sample range from 81 to 108% and relative standard deviations were no higher than 9.5% in the most unfavorable case. Individual detection limits were in the range of 0.005-0.043 ng/mL. The concentration levels found for endocrine disruptor pesticide residues in well water samples were above the levels (0.01 μ g L⁻¹ for drinking water) established by the IUPAC Technical Report [8] thus, causes problems in terms of pollution for ALD, CP, PNC, PRO, IP, BRP and LMD pesticide in well waters. This method can easily be adopted by environmental laboratories that do not have expensive equipment. In order to reduce effort and cost in environmental monitoring programs, the sample preparation method used in this work will save time and money over other routine extraction techniques.

KEYWORDS: Solidified floating organic drop microextraction, Pesticide, Gas Chromatography, Well water, Endocrine disruptor

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Developments in Ultrasound-Assisted Microextraction Techniques for Isolation and Preconcentration of Organic Analytes from Aqueous Samples

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A great potential of ultrasonic assistance in sample preparation especially including extraction is being recognized. Due to its main advantages, such as environmental friendliness, high performance of extraction, low cost laboratory equipment, ease of operation, and lowering the temperature of the extraction process, ultrasounds have attracted extensive attention and gained popularity in many areas of analytical chemistry including modern sample preparation techniques. There are two available sources of ultrasonic radiation in analytical laboratories, the most common - ultrasonic baths and less applied - ultrasonic probes. Although US baths are more widely used, they have two main disadvantages that substantially decrease experimental repeatability and reproducibility a lack of uniformity in the distribution of US energy (only a small fraction of the total liquid volume in the immediate vicinity of the US source experiences cavitations); and a decline in power with time. US baths are perfectly known and available laboratory devices, therefore detailed description of an US bath construction and operation is not needed. Otherwise the matter is in the case of the ultrasonic probe. US probes was predominantly applied in solid-liquid and biological sample extraction, but can also be used effectively in liquid-liquid extraction. In 2011, for the first time an US probe was applied to perform ultrasound-assisted dispersive liquid-liquid microextraction of nitroaromatic explosives from waste water and reservoir water. This paper is the only scientific publication until present, where applying an US probe in analyte extraction from liquid samples is described. From above information it follows that US probes application is commonly used on an industrial scale however trials are being carried out on a laboratory scale. In the present work, simple and rapid methodology based on ultrasound-assisted emulsification-microextraction (USAEME) using ultrasonic probe (direct sonification mode) followed by gas chromatography with mass spectrometry (GC-MS) has been developed for the determination of constituents of personal care products residues in water samples. The recent applications on this topic as well as data obtained and a summary of the research are planned to be presented.

KEYWORDS: ultrasonic probe, ultrasound-assisted emulsification-microextraction, isolation and preconcentration procedure, organic analytes, environmental analysis, water samples

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Green Extraction Techniques in Analytical Chemistry

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Natural and bio-derived solvents can provide environmentally sustainable and economically attractive alternatives to conventional solvents in Analytical Chemistry. The European Union directive on natural ingredients only permits the use of the 'natural' label for materials extracted using water, ethanol or carbon dioxide (CO₂). CO₂ is non-polar, water is very polar and ethanol is a polar alternative to toxic organic solvents. Polarity differences of green solvents are shown in Figure 1. Subcritical or superheated water extraction (SWE) has been used to extract flavour and fragrance components from various plants (*Thymbra spicata*, *Rosa canina*) [1,2]. Optimum conditions were found to be 150 °C, 2 ml min⁻¹ and 60 bar for 30 minutes. SWE is a notably faster extraction method when compared to conventional essential oil production techniques, in addition to being low cost and environmentally friendly. Selective and complete extraction of wheat-straw waxes can be achieved using environmentally benign supercritical CO₂. Wheat straw, like many other plants, is known to contain a significant quantity of wax (ca. 1% by weight) [3]. CO₂ adds value to the process by extracting secondary metabolites including fatty acids, wax esters and fatty alcohols. Microwave-assisted processing is promising methods for rapid extraction and pyrolysis. Microwave pyrolysis has found to efficiently deliver comparable evolution of bio-gases in the system as compared with conventional pyrolysis at significantly reduced temperatures (120-180 °C vs 250-400 °C) [4]. Bio-derived solvents (ethanol, limonene, ethyl acetate, 2-methyltetrahydrofuran, glycerol), supercritical CO₂, superheated water and microwave-assisted processing can extract and fractionate aroma, flavour, fragrance, cosmetic compounds, essential oils and waxes from plant materials effectively.

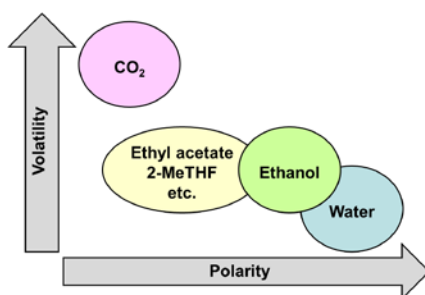


Figure 1. Green solvents selection

KEYWORDS: Green extraction, bio-derived solvents, superheated water, supercritical CO₂, microwave-assisted processing

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Preconcentration of Mercury(II)-Crystal Violet Complex by Solidified Floating Organic Drop Microextraction and Analysis by Flame Atomic Absorption Spectrometry

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Mercury in any form is poisonous and toxicity of mercury most commonly affects the neurologic, gastrointestinal and renal organ systems. Poisoning can result from mercury vapor inhalation, mercury ingestion, mercury injection, and absorption of mercury through the skin. In environmental hazard researches, the analysis of trace level of mercury ions has a crucial role due to its toxicity. A rapid, simple and cost effective solidified floating organic drop microextraction (SFODME) and flame atomic absorption spectrometric determination (FAAS) method for mercury was developed. In this method [1], a free microdrop of dodecanol containing Crystal Violet (CV) as the complexing agent in the presence of potassium iodide (KI) was transferred to the surface of an aqueous sample containing Hg(II) ions, while being agitated by a stirring bar in the bulk of the solution. Under the proper stirring conditions, the suspended microdrop can remain at the top-center position of the aqueous sample. After the completion of the extraction, the sample vial was cooled by placing it in a refrigerator for 10 min. The solidified microdrop was then transferred into a conical vial, where it melted immediately and diluted to 500 µL with ethanol. Finally, mercury ions in diluted solution were determined by FAAS. Several factors affecting the microextraction efficiency, such as type of extraction solvent, pH, complexing agent concentration, extraction time, stirring rate, sample volume and temperature were investigated and optimized. Under optimized conditions, the preconcentration factor and the enrichment factor were obtained. The values for limit of detection (3s), the limit of quantification (10s) and the relative standard deviation (RSD) for 10 replicate measurements were calculated. The proposed method was successfully applied to the determination of mercury in certified reference material and different water samples.

KEYWORDS: SFODME, flame atomic absorption spectrometry (FAAS), mercury, Crystal Violet (CV), microextraction.

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Gas Chromatographic Analysis of Fuel Combustion Products, Anti-Corrosive Compounds, and De-Icing Compounds in Airport Runoff Water Samples

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Increases in aviation developments have serious consequences on the environment [1]. One of the more important problems in this respect are the runoff waters that form when precipitation or atmospheric deposits flush the airport surface during daily airport operation, aircraft and round vehicle washing, cleaning, fuelling operations, fuel combustion and de/anti-icing operations. Runoff waters often contain high concentrations of various toxic pollutants, in particular polycyclic aromatic hydrocarbons (PAHs), benzotriazoles and glycols. Airports runoff gets into the soil, surface waters and even into ground water sources of drinking water. It is essential to monitor levels of these pollutants emitted into the environment [2,3,4].

This paper presents research regarding the possible influence of airport runoff water on the composition and concentration of pollutants present in runoff water samples collected from four international airports. The samples of runoff were collected in four seasons—winter, spring, autumn and summer—from 2008 to 2012. This work presents the investigation and optimization of the conditions under which the target analytes – PAHs glycols and benzotriazoles can be isolated using different various of solid-phase extraction (SPE) and solid phase microextraction (SPME) and finally determination by gas chromatography with mass spectrometry (GC-MS) and two-dimensional gas chromatography coupled to time-of-flight mass spectrometry (GCxGC-TOF-MS). Target analytes concentrations in stormwater samples are discussed in terms of sampling location, seasonal variation and origin. Analyses such as these will provide a sound basis for developing airport infrastructure management methods, inter alia, procedures for reducing the emission of contaminants, the recirculation of wastes, technologies for the remediation of polluted waters.

Spectrophotometric Determination of Fluoride in Drinking Water Using Polymeric Aluminium Complexes

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Polymeric aluminium complexes of 5-(2-carboxyphenylazo)-8-hydroxyquinoline (LH2), triphenylmethane dyes and Flavonoid Chrysin have been prepared as new specific reagents for fluoride determination in water samples. Job's method of continuous variation was adopted for the determination of the composition of the coloured complexes, which were characterized by UV-VIS spectroscopic studies. The molar absorptivities of the complexes formation were determined. Furthermore the coloured complex of polymeric aluminium complex of 5-(2-carboxyphenylazo)-8-hydroxyquinoline (LH2) was fixed on an impregnated paper where its colour changes are dependent on the concentration of fluoride in water samples. The change in the colour was measured using the Arsenator, which is a commercially available instrument used successfully for reliable determination of arsenic. In the proposed method the functionality of the Arsenator, which is based on a photometric measurement of a spot on a reagent paper is expanded to analyse fluoride. The method allows a reliable determination of fluoride in the range 0.3 to 2.0 mg L⁻¹. The determination is based on the reaction of aluminium complex with fluoride in the examined samples. Beer's law is obeyed in the range 0.3 to 2.0 mg L⁻¹ of fluoride at 495 nm. Sensitivity, detection limit and quantitation limit of the method were found to be 0.25 ± 0.007 mg⁻¹ mL, 0.1 mg L⁻¹ and 0.3 mgL⁻¹, respectively. The optimum reaction conditions and other analytical conditions were evaluated. The effect of interfering ions on the determination is described. There is no interference by nitrate or chloride. Sulphate interfered only at high concentrations which are not expected in drinking water.

KEYWORDS: fluoride analysis; drinking water; field method; impregnated paper; aluminium-azo dye complex; Arsenator

Spectrophotometric Detection of Fe(II) and Kinetics Inspection of the Reactivity of its Chelates

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Fe(II) was detected spectrophotometrically via complex formation by the reaction with Schiff base amino acid ligands. The obtained complexes were prepared and characterized by elemental, electronic and IR spectral analyses, conductance and magnetic moment measurements and spectrophotometric determination of the stoichiometry. The stability and solubility of the prepared complexes were determined. The reactivity of the resulted chelates against the base hydrolysis, acid aquation and the oxidation by hydrogen peroxide was screened spectrophotometrically in aqueous media, organic co-solvents mixtures, and in the presence of different concentrations of hydrophilic and hydrophobic salts. The rate laws and relevant mechanisms were assumed. Moreover, the activation parameters were calculated and discussed for structures and other physical properties.

KEYWORDS: Fe(II) – uv-vis spectrophotometry – kinetics – complexes – hydrolysis – aquation - oxidation

Simultaneous Determination of Selenium and Lead in Biological Samples by Multi-Element Electrothermal Atomic Absorption Spectrometry

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Direct and simultaneous determinations of Pb and Se in different biological samples using a multi-element electrothermal atomic absorption spectrometer (Perkin-Elmer SIMAA 6000) are described. Two kinds of modifiers; Pd(NO₃)₂ + Mg(NO₃)₂ mixture modifier and Ir-permanent modifier were tested. The electrothermal behaviour of the elements in single-element and multi-element mode (with and without modifiers) was studied. The pyrolysis and atomization temperatures for the simultaneous determination using the mixture modifier were 1000 and 1900°C and using permanent modifier they were 800 and 2000°C. The detection limits were 0.40 - 0.75 µg.l⁻¹ for Pb and 0.80 – 1.1 µg.l⁻¹ for Se. The characteristic masses were 44.0 - 73.3 pg for Pb and 58.7 - 146.7 pg for Se. A standard reference material (Seronom Trace Elements Urine) was used to find the optimal temperature program. The reliability of the entire procedure was confirmed by analysis of certified reference materials as Trace Elements Urine Sample (from Seronom 05115459), Lyphocheck Urine Metals Control- Level 1 from BIO-RAD, Pork Liver from National Research Centre for Certified Reference Materials, and Tea sample from National Research Centre for Certified Reference Materials. A Standard additions method was used to determine Pb and Se in the samples simultaneously. Results of analysis of standard reference materials were in agreement with the certified values.

Keywords: Simultaneous multi-element, Graphite Furnace AAS, Lead, Selenium

New Design of Flow Injection Unit Using(malachite green-iodide) System for the Determination of Cerium(IV) by Merging Zone Technique .

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The aim of this work was to design a new flow injection analysis unit for the determination of cerium(IV) by the reaction of potassium iodide with Ce^{4+} in an acidic medium to released I_2 which have yellow color, which reacts with the malachite green dye to give a complex which have λ_{max} at 684 nm. The method involves manufacturing a new valve from cheap material can be used in reactions containing five materials and then study the optimum condition for unit which include acid concentration, flow rate, potassium iodide concentration, malachite green concentration, acid volume, sample volume, malachite green volume, reaction coil length. Beer's law is obeyed over concentration rang (1- 40 mg/l), correlation coefficient(R^2) was 0.998, and the dispersion coefficient equal to 1.160, 1.147 for the concentrations of 10 and 30 mg / L respectively, and interference effects were studied.

KEYWORDS: Flow injection, Merging Zone, Cerium(IV), malachite green.

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An Investigation of Potential Bio-Accessible Trace Metal Fractions in Urban Atmosphere of Karachi, Pakistan

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The present study reports a profile of potential bio-accessible trace metal fractions in urban atmosphere of Karachi. For this purpose, an in-vitro physiologically based extraction test has been applied for extraction of bio-accessible trace metal fractions in airborne particulate matter (APM) samples collected from different urban sites in Karachi using most widely applied leaching agents in literature for risk assessment studies (H₂O, sodium chloride, ammonium acetate, ammonium citrate, synthetic gastric juice and artificial lung fluids). Obtained extracts were then measured using an ETV-ICP-OES procedure which allowed highly sensitive measurement of dissolved analytes even in the presence of leaching agents as well as complex sample matrix. Derived results indicated that the urban atmosphere of Karachi was highly contaminated with potential bio-accessible trace metal fractions. The concentrations of bio-accessible metal fractions varied from 0.5 ng m⁻³ (Cd) to 753 ng m⁻³ (Zn) for PM₁₀ samples collected from Karachi (Pakistan).

Furthermore, it was found that investigated leaching agents extract different amounts of potential bio-accessible trace metals. In general, leaching agents with organic nature yielded comparatively greater extractable and thus bio-accessible trace metal fractions to that of simple solvents like H₂O or aqueous NaCl solution. With water, only 25.4±3.8% of Cd was found to be bio-accessible whereas 87.4±22.6% of Cd was obtained as bio-accessible fraction with the use of synthetic gastric juice. Further outcome of present study was that the leaching agents which mimic conditions of body fluid give more realistic data about potential bio-accessible trace metals.

KEYWORDS: bio-accessible trace metal fractions, airborne particulate matter, ETV-ICP-OES, karachi

A Catalytic Adsorptive Stripping Voltammetric Procedure For Chromium Speciation in Interstitial Water Samples Isolated from Sediments Contaminated by Tannery Waste

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Tannery effluents are major sources of Cr in surface waters. They discharge chromium mostly in the form of Cr(III) along with considerable inputs of organic matter. Because of the low mobility of Cr(III), large quantities of Cr discharged from tanneries tend to accumulate in bed sediments, where a series of redox processes may trigger the oxidation of Cr(III) to Cr(VI) and, consequently, the remobilization of Cr to the water column. Knowing whether and to what extent Cr(III) contained in sediments is converted to Cr(VI) is therefore important in the environmental assessment of rivers contaminated by tannery effluents. To answer these questions it is necessary to quantify trace concentrations of Cr(VI) in sediment pore waters, i.e., in the presence of large excesses of Cr(III) and high concentrations of organic matter. Catalytic Adsorptive Stripping Voltammetry (CAAdSV) has proved to be useful in the determination of Cr(VI), with a very low detection limit in different water samples including rain, sea, river, lake water and landfill leachate. The method is based on the accumulation of the Cr(III)-DTPA complex formed instantaneously from the very active Cr(III) ions generated by the reduction of Cr(VI) at the electrode surface, and the utilization of the catalytic reaction in the presence of nitrate ions [1-3]. One of the main reasons why the application of electrochemical methods in the analysis of real samples has not always been successful is the inevitable presence of surface active substances (SAS). Depending on their concentration and type, SAS can partially or completely suppress the observed chromium voltammetric signal. In particular, overlying and pore water samples from natural aquatic systems often contain high concentrations of organic matter (up to 160 mgL⁻¹) coupled with low concentrations of chromium (less than 1 µgL⁻¹ Cr(VI)); Cr(VI) determination may thus be exceptionally difficult.

In this work, well-known voltammetric procedures for the determination of chromium with DTPA and nitrate [1-3] have been adopted for Cr(VI) quantification in the presence of a great excess of SAS and Cr(III). This task was achieved by means of selective separation of organic matter on the Amberlite XAD-7 resin. The SAS were separated directly in the voltammetric cell by adding Amberlite XAD-7 and stirring the solution for 5 min before determination. The difference in CAAdSV curves with and without or after separation on Amberlite XAD-7 resin is illustrated in Fig. 1. The CAAdSV method combined with the adsorption of surface-active substances on the XAD-7 Amberlite resin was successfully applied for the determination of Cr(VI) in the vertical ~~file~~ ^{pile} in sediments from Dunajec River (Poland), which are severely polluted with chromium from tannery wastes. The results obtained using the elaborated method were verified by those achieved with the CAAdSV procedure based on the matrix exchange in flow systems [4].

KEYWORDS: catalytic adsorptive stripping voltammetry, chromium(VI), sediments, speciation, surface active substances

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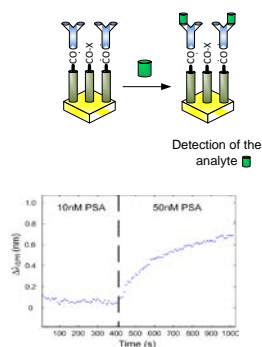
Detection of Prostate Cancer Biomarker in Crude Serum by SPR on Microstructured Au Film

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Biofouling of proteins contained in complex biological fluid can generate an important nonspecific signal for label-free analytical technique such as surface plasmon resonance (SPR) sensors. Nonspecific adsorption can be reduced in SPR by using an appropriate self-assembled monolayer (SAM) that covers and protects the metallic surface. Peptide SAMs were previously shown to decrease the nonspecific adsorption of proteins to approximately 10 ng/cm² [1]. In addition, using a peptide monolayer to build a biosensor seems to ensure a better preservation of the molecular receptor activity. The peptide monolayer use in the current research is 3-MPA-HHHDD-OH, which structure provides on one extremity a thiol that can be linked to the gold surface and several COOH at the other extremity of the molecule, which was suited to immobilize a molecular receptor on the surface. This SAM provides an excellent platform for biosensing directly in crude biological fluids. Another innovation involves the use of a micropatterned Au film instead of the continuous Au film generally used in SPR. A microhole array with a periodicity of 3.2 μm and a diameter of 1.6 μm has showed increased sensitivity to bulk refractive index and binding event occurring at the SPR sensor [2]. This new combination of surface chemistry/plasmonic material has been extensively investigated with IgG detection and compared to smooth Au film with conventional SAM. Detection of IgG at pM level in crude bovine serum has also been performed. Prostate specific antigen (PSA), a biomarker used for the diagnosis of prostate cancer, was then studied by using this new combination of plasmonic material and surface chemistry. Since PSA is a smaller protein than IgG, a secondary antibody was use in order to obtain a detection limit sufficiently low for analysis of sample that contain that protein at the pM level.



KEYWORDS: biosensor, SPR, biomarker, protein, cancer

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Highly Sensitive Detection of Amoxicillin Based on Gold Nanoparticle Modified ITO Electrode

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Based on a gold nanoparticle (GNP) modified indium tin oxide (ITO) electrode, a highly sensitive electrochemical method has been developed for the ultra-trace level determination of amoxicillin (AMX). GNPs were electrochemically deposited onto ITO electrode from 0.1 mM HAuCl₄. AMX was adsorbed onto ITO/GNP through the strong interaction between GNP and -NH₂ functional group of AMX. The ITO/GNP/AMX electrode was further modified with Cu(II) by simple dropping of Cu(II) solution, which led to the chemical deposition through the complexation with Cu(II) ions. The resulting modified electrode surface was characterized with scanning electron microscopy and electrochemical methods. AMX was determined by the square wave voltammetric response of Cu(II). It was found that the peak currents increased with the increasing concentration of AMX. A linear concentration range from 10 to 1000 nM with a detection limit of 0.5 nM for AMX was found. The reproducibility expressed in terms of relative standard deviation (RSD) of the identical electrode in 10 successive measurements was 0.44% for AMX (0.5 μM), indicating that the proposed method is highly reproducible. The stability of the modified electrode was investigated and it was found that the anodic peak current reduced 93.4% of its initial value after 40 consecutive measurements which indicate good performance stability of the proposed sensor. The proposed method was applied for the determination of AMX in pharmaceutical formulation and biological fluids.

New Electrochemical Polymerization of 1-Aminofluorenone

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Electrochemical polymerization of 1-aminofluorenone, AFO, was studied in CH₂Cl₂ solution with tetrabutylammonium perchlorate, TBAClO₄, as the electrolyte, via successive cyclic voltammetry. (PAFO) films obtained from this media showed good redox activity and stability. Factors affecting film formation by successive potential scans like potential limits, scan rate, number of cycles, monomer concentration, and also polymerization techniques were examined in details. Optical properties were studied by UV-vis spectroscopy. To the best of knowledge, this is the first report on direct anodic oxidation of PAFO.

KEYWORDS: polyaminofluorenone, electrochemical polymerization, cyclic voltammetry

Study by FT-IR Spectroscopy of Adsorption onto Activated Carbon

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The adsorption of pollutants from aqueous solutions onto activated carbon prepared from vegetable waste was studied.

The surface characterization of activated carbon was performed using transmission -absorption FT-IR and ATR-FTIR spectroscopy. The use of biomaterials for the removal of colour from its aqueous solution will provide as a potential alternate to the conventional treatment methods.

In this work we use transmission -absorption FT-IR and ATR-FTIR spectroscopy to study spectral characteristics of surface changes and adsorption phenomena. The measured IR spectra of the activated carbon show that there is difference in the surface properties according to the nature of waste use to obtain activated carbon.

The spectra indicate the presence of highly reactive functional group which may explain the values of adsorption capacity of activated carbon.

Removal of Nickel from Aqueous Solutions by Activated Carbon Prepared from Seawater Algae

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Removal of heavy metals from wastewater is one of the major environmental problems because of difficulty in treating by conventional treatment methods. Activated carbon is an effective alternate for the uptake of heavy metals even in the case of lower pollutant concentration. In this work adsorption of Nickel onto activated carbon prepared from seawater was investigated, with respect to contact time, PH and temperature. The seawater alga *Ulva lactuca* and *Cystoseira stricta* modified chemically and physically were used as adsorbents. The Langmuir and Freundlich models fitted well the adsorption isotherms. The surface characterization is performed using iodine number, BET surface analysis and MEB analysis.

To describe the mechanism of adsorption the models of Freundlich and Langmuir are used to fit the experimental data. The calculated values well fitted to the Freundlich model with correlation coefficient, R^2 , attaining value of 0.99. Our results show that activated carbons prepared from seawater algae may be effective adsorbents for the removal of Nickel from aqueous solutions. The Freundlich model better describes the adsorption of Nickel onto activated carbon prepared from seawater alga. The Langmuir model application resulted in maximum adsorption capacities of 64.51mg/g for activated carbon from *Cystoseira Stricta* and 91.70mg/g for activated carbon from *Ulva Lactuca*.

This study shows that heavy metal removal can be carried out by these largely available natural materials.

KEYWORDS: Adsorption, Activated carbon, heavy metal

Solid-Phase Extraction and FAAS Determination of Trace Amounts of Cadmium and Lead in Natural Water Samples

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A new method was developed for pre-concentration of Cd (II) with Pb (II) and their determination by flame atomic absorption spectrometry (FAAS). For this purpose, a new reagent, 1-Phenyl-3-(2-pyridinyl) thiourea, was used as chelating reagent. The influences of the analytical parameters including pH value, the shaking time, the mass of sorbent, sample volume, the elution condition and effect of some matrix elements were investigated. For preconcentration of Pb (II) and Cd (II), the optimum pH values were found to be pH 5 and 7 respectively. The adsorbed metals were quantitatively eluted with 10 mL of 1.0 mol L⁻¹ EDTA. Cd (II) and Pb (II) ions were quantitatively recovered at the rate of 100 % (RSD < 3%) from the studied solutions. The proposed method has been applied for determination of trace amounts of Cd (II) with Pb (II) ions in natural water samples with successful results.

KEYWORDS: solid phase extraction, pre-concentration, trace metals, atomic absorption spectrometry.

The Graphite “Filter Furnace” Atomizer at the Direct Electrothermal Atomic Absorption Analysis of some Plant Matirials

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Capabilities and general analytical characteristics of “furnace-filter” atomizer (FF) at electrothermal atomic absorption spectrometric (ET AAS) determination of selenium (Se), zinc (Zn), arsenic (As), cadmium (Cd) and lead (Pb) in some of plant matirials (coffee, tea, grain, species) are described. For these purpose traditional and slurry sample techniques were used. To eliminate or reduce background absorption and interferences effect on atomic absorption value (Q_A) the main component of materials to be analyzed have been proposed different matrix modifiers (MM): $\text{Pd}(\text{NO}_3)_2$; $\text{Mg}(\text{NO}_3)_2$; $(\text{NH}_4)_2\text{HPO}_4$; $\text{NH}_4\text{H}_2\text{PO}_4$; $\text{Ni}(\text{NO}_3)_2$; ascorbic acid and its mixtures.

The operation heating parameters of graphite FF atomizer on pyrolysis and atomization steps, including at analyte evaporation in presence of universal Pd-Mg MM on analytical signal high listed elements are optimized. At proposed conditions ET AAS determination of Se, Zn, As, Cd and Pb the corresponding pyrolysis step can be raise to 900; 950; 900; 750; 950°C respectively. The graphite FF and Pd-Mg matrix modifier allowed ~ 2-2.5 times to increased sensitivity of Se, Zn, As, Cd and Pb, ET AAS determination and significantly reduced interferences effect from main components of plant materials as well as non-selective absorption of light.

To achieve a aggregative and sedimentation stability some of suspending plant materials the various surface-active agents were used. At ET AAS determination listed elements in some of plant materials were applied its aqua and acid extraction as well as microwave decomposition and slurry sample technique.

The proposed method was successfully used at direct ET AAS determination $\geq 0,0005$; 0,01; 0,001; 0,005; 0,01 ppm of Zn, Pb, Cd, As and Se respectively in coffee, tea, grain, species. The relative standard deviation (S_r) not more then 0.12 and one element determination procedure does not exceed 15-20 min.

Removal of Reactive Black 5 from Aqueous Solutions by TiO₂ Immobilized Onto Activated Carbon

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Adsorption onto activated carbon (AC) and oxidation using photocatalyst are widely used techniques to remove dyes from waste water. The aim of this work is to enhance the removal capacity of activated carbon by combining AC and titanium dioxide (TiO₂) in a Photocatalytically Regenerative Activated Carbon.

Anatase titania were deposited on powder activated carbon made from grape seeds (AGS) by impregnation/mixing method and then the composite photocatalyst was employed for the removal of reactive black 5 from aqueous solution. The TiO₂/AGS was characterized by BET, MEB, XRD and optical absorption spectroscopy. The BET surface area and the pore structure of composite photocatalyst (TiO₂/AGS) and activated grape seeds (AGS) were evaluated from nitrogen adsorption data at 77 K in relation to process conditions. Our results indicate that the photocatalytic activity of TiO₂/AGS was much higher than single phase titania. The adsorption equilibrium of reactive black 5 from aqueous solutions on the examined materials was investigated. Langmuir, Freundlich, and Redlich–Petersen models are in good agreement with the experimental equilibrium data. The degradation kinetics fitted well to the Langmuir-Hinselwood pseudo first order rate law. The photocatalytic activity of TiO₂/AGS was much higher than virgin TiO₂. COD removal was measured at regular intervals to quantify the mineralization of the dye. Above 96% mineralization was observed. These results suggest that UV-irradiated TiO₂ immobilized onto activated carbon may be considered as an adequate process for the treatment of diluted colored textile waste water.

Method Development and Validation for the Simultaneous Analysis of Losartan, Valsartan, Atorvastatin, Pravastatin and Simvastatin Using RP-Hplc and Its Application in Pharmaceuticals

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Since hypertension and hypercholesterolemia are synergistic, co-administration of angiotensin II receptor antagonists, indicated for the treatment of hypertension and statins, a class of drugs that lower the level of cholesterol in the blood, is highly probable, rather, recommended by the physicians. In present Paper, method development and validation of an LC method has been carried out for losartan, valsartan, atorvastatin, pravastatin and simvastatin (most frequently prescribed drugs for both classes of therapeutic) simultaneously. Mobile phase consisted of acetonitrile and water (60:40 v/v) with pH 2.9 maintained at a flow rate of 0.9 mL/min initially for 6.5 minutes then increased to 2.9 mL/min. Analytes were monitored by UV detection at 230 nm, using a gradient acetonitrile/water elution. Calibration curves for all analytes were linear over concentration range of 05–100 µg/mL with correlation coefficients > 0.9990. The results obtained showed a good agreement with the declared contents and successfully employed in quantifying all the analytes in pharmaceutical dosage formulations. The proposed method may be used for the quantitative analysis of pravastatin, losartan, valsartan, atorvastatin and simvastatin alone or in combination from raw materials, in bulk drugs and dosage formulations.

KEYWORDS: Losartan, valsartan, pravastatin, atorvastatin, simvastatin, RP-HPLC, method validation

¹⁸O-assisted ³¹P NMR and Mass Spectrometry for Dynamic Phosphometabolomic Profiling

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Metabolomics, as a new "omics" approach, integrated with proteomic, transcriptomic and genomics is making revolution in personalized medicine, by providing means for early disease detection, deeper understanding of mechanisms, prediction, selecting treatment choices and identifying integrated panel of biomarkers[1-4]. Phosphometabolomics is a new emerging area in metabolomic analyses targeting over 400 phosphometabolites indispensable to life activities, such as genetic inheritance, signal transduction, metabolism and energy transduction. Phosphometabolite levels and turnover rates are most sensitive indicators of body energy and metabolic imbalances such as created by genetic deficiencies, myocardial ischemia, diabetes, aging and obesity.

Here, we explain stable isotope ¹⁸O-assisted ³¹P nuclear magnetic resonance (NMR) and mass spectrometry (GC-MS and LC-MS) for simultaneous measurement of phosphometabolite levels and turnover rates in tissue samples. We have established an expanded dynamic phosphometabolomic platform that includes ¹⁸O-assisted GC-MS, ¹⁸O-assisted ³¹P NMR, 2D ³¹P NMR, ¹H NMR, direct infusion MS, LC-MS and HPLC[1-4]. With these methods, we are able to quantification of ¹⁸O-labeling of mono- or oligo-phosphometabolites. ¹⁸O-assisted ³¹P NMR and MS techniques use ¹⁸O-induced shift in ³¹P NMR spectra and mass increase in spectra in order to determine the percentage of ¹⁸O-labeling of metabolite phosphoryls, respectively. These methods enable simultaneous recording of ATP synthesis and utilization, phosphotransfer fluxes through adenylate kinase, creatine kinase, and glycolytic pathways, as well as mitochondrial substrate shuttle, urea and Krebs cycle activity, glycogen turnover, and intracellular energetic communication. In this study, we summarized the principles and methodology of metabolic profiling and analysis of phosphometabolite turnover rates using stable isotope ¹⁸O and also pros and cons of the methods for phosphometabolomic analysis.

KEYWORDS: ¹⁸O-assisted ³¹P NMR, ¹⁸O-assisted MS, metabolomics

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A Novel Spectrofluorometric Method for Determination of Valsartan in Spiked Human Plasma

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Valsartan (N-(1-oxopentyl)-N-[[2'-(1H-tetrazol-5-yl) [1,1'-biphenyl]-4-yl]methyl]-L-valine) which is described as orally active and specific angiotensin II receptor antagonist is widely used drug for the treatment of hyper-tension [1]. The purpose of this study was to develop a fast and novel spectrofluorometric method which is easier accessible technique than chromatographic methods for determination of valsartan from spiked human plasma. The fluorescence intensities of valsartan are measured at 231 nm (excitation) and 380 nm (emission) wavelength. Experimental procedure for quantitative analysis of valsartan by spectrofluorometric method was as follow: The standard samples and plasma extracts were dissolved in methanol including 50 µL of 1M HCl. Appropriate dilutions that was equivalent to the concentrations of working calibrators and quality control samples were prepared. Extraction was achieved by ether di-isopropyl and back extraction was carried out in order to increase the method recovery.

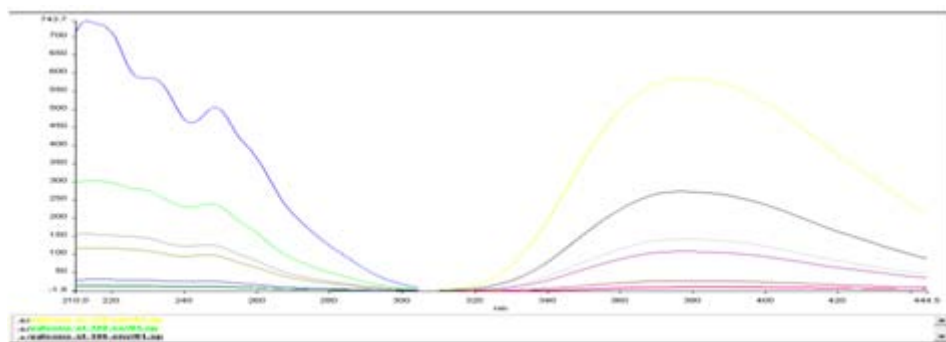


Fig. 1. Emission and excitation spectrum of valsartan extracted from plasma

The proposed method validated by following the FDA guidelines in terms of specificity, linearity, limit of detection, limit of quantification, inter and intra day assay precision, accuracy and recovery. Working calibrators were determined to be 4, 5, 10, 40, 50, 100 and 250 ng/mL where the proposed method was linear with regression equation of $y=2.3722x + 10.825$ and $R^2= 0.9955$. In addition to these, quality control solutions were chosen to be 20, 75 and 250 ng/mL for standard samples. According to the results, accuracy of the method better than 7.47% while intraday and inter day relative standard deviation values were lower than 2.36% and 4.40%, respectively. Limit of quantification (LOQ) were determined to be 4 ng/mL and limit of detection (LOD) was calculated as 1.5 ng/mL. Extraction process was novel, cheap, easy and also have a satisfactory extraction recovery value (average recovery calculated to be 81%). Thus, The proposed method representing a new perspective for determining the valsartan level in human plasma is an alternative method to chromatographic methods and convenient enough for the use in clinical studies.

KEYWORDS: spectrofluorometry, valsartan, spiked human plasma

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Comparison of Univariate and Multivariate Calibration Techniques Using ICP-OES

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Univariate and multivariate (partial least squares 1, PLS1) calibration techniques were compared for the determination of Cu, Ca, Fe, K, Mg, Mn and Zn in the synthetic test solutions. In this study we used synthetic solutions calculated the results obtained using univariate calibration and PLS1 % recovery yield. The recoveries (%) of univariate calibration technique for Cu, Ca, Fe, K, Mg, Mn and Zn were 139,77; 126,92; 103,99; 69,10; 134,16; 124,19 and 171,77 and at the PLS1 method 106,67; 99,75; 94,21; 95,54; 95,02; 99,00 and 106,78 respectively. As a result of student t-test at confidence levels of 95% or 99%, significant differences were found between univariate calibration and PLS1 methods and the PLS1 method was found suitable for ICP-OES.

KEYWORDS: Univariate calibration, multivariatecalibration, PLS1, ICP-OES

Molecularly Imprinted Solid-Phase Extraction of Indapamide

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Molecular imprinting technology is a powerful tool in the development of highly selective analytical methods. Solid phase extraction is a widely used sample preparation technique for isolation, concentration, clean-up of the analytes from environmental and biological samples.

In this study, a molecularly imprinted polymer (MIP) selective for indapamide was prepared via non-covalent strategy and it was used as a molecularly imprinted-solid phase extraction (MISPE) adsorbent for the removal of indapamide in aqueous and organic media. MIP was synthesized using indapamide as a template molecule, 2-(trifluoromethyl) acrylic acid (TFMAA) as a functional monomer, ethylene glycol dimethacrylate (EGDMA) as a cross linker, and N, N'-azobisisobutyronitrile (AIBN) as a thermal initiator in aprotic solvent acetonitrile (ACN) at 70°C. The non-imprinted polymer (NIP) was also prepared in the same way, but in the absence of template. The bulk polymer (MIP/NIP) was crushed, ground, and sieved through 20 µm sieve and then template indapamide was removed from MIP using methanol:acetic acid (MeOH:AA) (9:1, v/v) in a Soxhlet apparatus until no more indapamide could be detected by UV-VIS spectrophotometer. Thereafter, 50 mg MIP and NIP were dry-packed into SPE cartridge and then connected to a vacuum manifold. Eluates from cartridges were analyzed using spectrophotometer for the determination of indapamide.

The proposed MISPE method has been successfully applied to selective extraction of indapamide in organic and aqueous media.

KEYWORDS: molecularly imprinted-solid phase extraction, spectrophotometer, indapamide

The Photocatalytic Removal of *Escherichia coli* and *Aspergillus niger* from Water

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Microbes are the everywhere pollutants in buildings such as hospitals, food industry and bathrooms and present significant health effects [1]. Photocatalysis has been shown to be capable of killing a wide range of organisms including Gram-negative and Gram-positive bacteria, including endospores, fungi, algae, protozoa and viruses. The photocatalytic disinfection of microorganism is based on a strong photooxidation process. In principle, when a photocatalyst, mainly TiO₂, is irradiated with the light source of appropriate wavelength, the electron-hole pair is generated as the electron from the valance band is transferred to the conduction band by leaving a positively charged hole behind. These charge carriers generate highly reactive hydroxyl (·OH) radical and super oxide ions (O₂^{·-}) and these oxidizing agents oxidize the cell membrane and cause the cells to die eventually [2,3].

In the present study, a thermal attachment procedure was employed for the anchoring anatase TiO₂ nanoparticles (44 nm particle size) on waste polystyrene (PS) beads. The aim of the study was to investigate the photocatalytic activity of the produced material for degradative removal of the model pollutants such as *Escherichia coli* (*E. coli*) and *Aspergillus niger* (*A. niger*). TiO₂-PS might be an important composite material with antimicrobial properties. *E. coli* has been used as model bacterial source in order to evaluate the antibacterial efficiency of TiO₂-PS. On the other hand, *A. niger* is a fungus especially grown in humid environments that should also be removed from water and in this regard PS waste can be employed to remove or degrade the pollutant present in various environments. TiO₂ immobilized polystyrene beads seem to be highly promising for succesful removal of studied microorganisms.

KEYWORDS: Waste polystyrene, antimicrobial TiO₂ immobilized polystyrene

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Removal of Ni(II) from Aqueous Solution by Adsorption onto Drinking Water Treatment Sludge

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In this study, the potential to remove nickel(II) ions from aqueous solutions using drinking water treatment sludge (DWTS) was thoroughly investigated. The characterization of DWTS was carried out by X-Ray diffraction (XRD), scanning electron microscope (SEM) and inductively coupled plasma-atomic emission spectroscopy (ICP-AES) methods [1]. And then, the effects of some analytical parameters such as pH, contact time, initial Ni(II) concentration, amount of adsorbent and temperature on the adsorption process were evaluated. From the results, adsorption process was dependent on solution pH and optimum pH was specified as 5.0 (Figure 1) and contact time was determined as 4.0 hour. The sorption data followed the Langmuir and Freundlich isotherms. The results of this study demonstrated that DWTS can be used as an effective adsorbent for removal of Ni(II) from aqueous solutions.

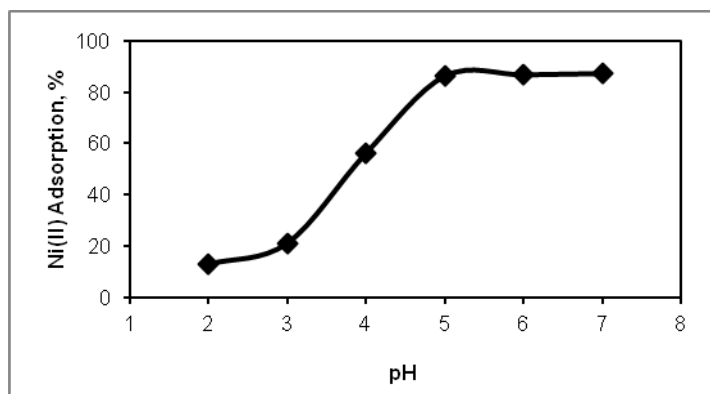


Figure 1. Effect of solution pH on Ni(II) adsorption by DWTS

KEY WORDS: Adsorption, Treatment sludge, Ni(II), Flame Atomic Absorption Spectrophotometry (FAAS)

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POSTER PRESENTATIONS

The Removal of Heavy Metals from Contaminated Sediments by Using Sequential Extraction and Soil Washing/Extraction

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Sediments can be, depending on environmental conditions, either a sink or a source for trace metals in the aquatic environment [1]. Metals are not always permanently fixed by the sediment but may be recycled via biological and chemical agents, both within the sedimentary compartment and back to the water column [2]. Marine and river sedimentary particulate matter consists of many different components and phases, including crystalline minerals, carbonates, hydrous metal oxides, and organic substances. Metals may be bound to particulate matter by several mechanisms such as particle surface absorption, ion exchange, co-precipitation, and complexation with organic substances. The distribution of metals in the various phases of a sediment determines their behavior in the environment: their mobility [3], bioavailability [4], and toxicity. Heavy metals develop significant toxic effect to aquatic organisms; thereby influencing human health through food chain [3]. For this reason, the removal of heavy metals studies are required to determine the extent of contamination, spreading mechanisms and transformations of heavy metals in contaminated sediments to prevent environmental risk factors that may occur. In the main goal of this study, different extraction procedures were investigated for batch methods of sequential extraction [6], and soil washing/extraction methods [7] to remove heavy metals (Cu, Pb, Cd, Fe, Al, Cr, Cu, Zn, Mn, Sr). This study determined average concentrations of ten heavy metals (Cu, Pb, Cd, Fe, Al, Cr, Cu, Zn, Mn, Sr) in sediments of the mid-Black Sea coast of Turkey. Sediment samples were collected seasonally from the Yeşilirmak, Kızılırmak, Mert, Abdal Rivers and Kurupelit sea regions in 2007-2008. The sampling stations were chosen in way to include hotspots of polluted rivers of Samsun city. The digestion of total sediment (fraction <63 µm) were performed in teflon vessel with a mixture of HClO₄-HF at hot-plate and cooling system. Heavy metals concentrations of the solutions were measured by ICP-OES (Perkin Elmer Optima, 4300DV). The analytical performance of the laboratory was evaluated by analysis of Certified Reference Material BCR-701. The data of three replicate analysis obtained for aqua regia extraction (pseudo-total), and sequential extraction procedure. Uncertainty are expressed as Standard deviations. The found values are not significantly ($p>0.05$) different from the certified values. Seasonal studies were also conducted to determine the extent of heavy metal contamination in the samples collected from the Yeşilirmak, Kızılırmak, Mert, Abdal Rivers and Kurupelit sea regions. Findings obtained from 5 stations which were contaminated with heavy metals were compared with the baseline earth crust rock findings and enrichment factors in Abdal region. The extent of heavy metal contamination was as follows; Yeşilirmak>Kızılırmak>Kurupelit>Abdal>Mert. In exchangeable phase (F1), carbonate phase (F2), Fe-Mn oxidation phase (F3), organic phase (F4) and residue phase (F5) which were determined via sequential extraction method, depending on the metals mobility, the removal of heavy metals from sediments was found as; residue>Fe-Mn oxidation>organic>carbonate>exchangeable phase. According to the total concentrations of each Al, Cd, Cr, Cu, Fe, Ni, Pb, Zn, Mn ve Sr metals, a recovery rate of 83-127%, 92-123%, 83-112%, 84-106%, 91-105% were obtained from Kızılırmak, Mert Rivers and Kurupelit sea region, Yeşilirmak and Abdal river sediments, respectively. Soil washing/extraction method was used in a laboratory batch and column system to remove heavy metals from the contaminated sediments using 0.1M Na₂S₂O₅ and 0.01 Na₂EDTA mixture. Depending on the total metal content and the complexation with Na₂EDTA, heavy metal removal rates by applying batch and continuous soil washing/extraction methods were found as; Cu>Ni<Zn>Pb>Mn>Fe>Al, and Mn>Cu>Ni>Zn>Fe>Al, respectively. In conclusion, for the remediation and/or treatment of heavy metal contamination from contaminated sediments; the removal of heavy metals from sediments by sequential extraction and soil washing/extraction was found as 95-110% and 1-43% respectively depending on the metal mobility and mineralogical structure of sediments.

KEYWORDS: Heavy metals, contaminated sediment, sequential extraction, soil washing/extraction

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Development a Proconcentration and Determination Method for Trace Amount of Uranyl Ions Based on Spectrophotometric Detection Flowing Cloud Point Extraction

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Uranium metal in its pure form is chemically active, anisotropic and has poor mechanical properties. On the other hand, uranium alloys are useful in diluting enriched uranium liquid fuel meant for nuclear reactors and pure uranium coated with silicon and canned in aluminium tubes are used in production reactors. However, uranium and its compounds, like lead are highly toxic which cause progressive or irreversible renal injury and in acute cases may lead to kidney failure and death. The tolerable daily intake of uranium established by WHO based on Gilman's studies is 0.6 µg/kg of body weight per day[1-4].

A new micelle-mediated extraction method was developed for preconcentration of ultra-trace Hg(II) ions a prior to spectrophotometric determination. Celestine Blue (CB) and Triton X-114 were used as chelating agent and nonionic surfactant, respectively. U(VI) ions forms a hydrophobic complex with CB in micelle medium. Aliquots of sample or pretreated-sample containing U(VI) ions in the range of 50–2000 µg L⁻¹ was transferred into centrifuge tubes (50 mL in capacity). 2.0 mL of pH 7.0 TRIS buffer, 0.7 mL of 3.0×10⁻³ mol L⁻¹ CB, and 0.5 mL of 5.0 % (w/v) Triton X-114 were added to tube and completed to 50 mL by deionized water. Then, the solutions were mixed and kept in a thermostatic water bath for 15 min at 45 °C. The phase separation was accelerated by centrifugation at 3500 rpm for 5 min. The mixture was cooled in an ice-bath for 5 min in order to increase the viscosity of the surfactant-rich phase and facilitate the removal of the aqueous phase. Then, the aqueous phase was easily separated from surfactant-rich phase by inverting the tube. 1.5 mL of methanol was added to the surfactant-rich phase to reduce its viscosity prior to spectrophotometric detection at 489 nm.

The main factors affecting CPE efficiency such as pH of medium, concentrations of CB and Triton X-114, equilibration temperature and time were investigated in detail. An overall preconcentration factor of 33.3 was accomplished upon preconcentration of a 50 mL sample. The limit of detection obtained under the optimal conditions is 14.3 µg L⁻¹, and the relative standard deviation for five replicate measurements (for 100 µg L⁻¹ U(VI)) was 3.20 %. The method was successfully applied to the determination of uranyl ions in environmental water samples with satisfactory results.

KEYWORDS: Uranium, Cloud Point Extraction, Celestine Blue, Water Samples

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Use of Single Extractions for the Assessment of Metal Mobility in Mine Tailings

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Mining and ore processing industry is one of the major sources of metals releasing into the environment. Although the total metal concentration is commonly used in quality standards, it provides no information regarding the metals chemical nature or mobility. To assess the metals mobility, a great variety of single or sequential extraction schemes have been developed [1-4]. The Apuseni mining area, Romania, has a long mining history of base (Cu, Pb, Zn) and precious metals (Au, Ag) that generated high volumes of mine tailings stored in more than 30 tailing impoundments. Presently, the majority of the tailing impoundments are closed and subjected to different stages of ecologization protocols. The objective of the study was to assess the Cu, Pb, and Zn mobility in tailings resulted from nonferrous mining and ore processing in the Apuseni mining area, Romania. Composite samples from 10 tailing impoundments (Mires, Mialu, Ribita, Sartas, Cutii, Saliste, Sesei, Gura Rosiei, Stefanca and Brazesti) were subjected to selective extraction procedures using water (easily mobilizable fraction), 0.11 M acetic acid (exchangeable fraction) and 0.1M HCl (acid soluble fraction) as extractants at a solid to liquid ratio of 1/20. The total metal content was determined after aqua regia digestion. The metal contents were determined by inductively coupled plasma optical emission spectrometry (ICP-OES) using OPTIMA 5300DV multichannel spectrometer (Perkin-Elmer, Norwalk, USA). The results showed that tailings are highly contaminated with Cu, Zn and Pb, in several tailings the content of metals exceeding the required values for inert wastes. The total metal concentration ranged between 17-1300 mg/kg Cu, 30-1200 mg/kg Zn and 20-1800 mg/kg Pb. About 3% Cu, 4% Zn and 0.5% Pb was found in easily mobilizable form, 8% Cu, 18% Zn and 6% Pb in exchangeable form and 40% of Cu, 25% of Zn and 32% Pb was acid soluble, suggesting that an important fraction of the studied metals can be mobilised from tailing to the surrounding environment. Although measures have been taken to green the tailings impoundments, they continue to act as potential contamination sources of the environment.

KEYWORDS: single extraction, metal mobility, nonferrous mine tailings,

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**Determination of Some Toxic and Nutritive Heavy Metal Contamination
in Grape And molasses samples in Batman and Mardin Region by
AAS and ICP-OES**

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Heavy metal contamination of food especially in fruit and vegetables are becoming more and more important. Some trace metal contamination in Grape and boiled grape juice which is a derivative of Grapeand is a major component in the determination of quality of them. In order to supply organic and healthyfood man is very important. Because it is directly related with human and animal life. Apparently Food qualities in many countries are effected by industrialization and over population.

The main aim of this study was to determine some toxic and nutritive trace metal contamination in some Grape and boiled grape juice (Which is called Pekmez in Turkish) around Batman and Mardin by means of Atomic Absorption Spectrometer and Inductively Coupled Plasma-Optical Emission Spectrophotometers. Grape and boiled grape juice samples were collected ten different parts of Batman and Mardinespecially in rural part ofcities. These samples were collected and determined by a simple preconcentration method which is called activated carbon enrichmentand also another method which is called wet aching was made The toxic and nutritive trace metal analysis was done to determine elements in details. The result that we obtained compared with guidelines for Turkish food quality such as Turkish Standards(TS), World Health Organization (WHO) ,guidelines and European Union Food standards and also we made a comparison between wet aching and activated carbon enrichment.

As a result of this study we concluded that heavy metal contamination of the sample that we take does not have involve a major threat for human and other species and contain enough nutritive elements for health and human bodies.

KEYWORDS: grape and mosaless, toxic metals, nutritive metals activated carbon, AAS ICP-OES

Determination of Chemical and Some Heavy Metalcontamination in Some Spring and Thermal Waters in Eastern and Sout Eastern of Anatolian

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In this study physico-chemical properties of thermal hot waters and some cold water which can be bottled were studied.

Water samples were taken and some physical analyses were performed in during the water sampling. The other major analyses were done in the geothermal laboratory. Water samples were evaluated by both field observations and also taking geology and petrography of the sampling area. Taken data were evaluated by using Aqua Chem soft program under the consideration of the field observations and geology and petrography of the sampling area.

Under the light of obtained data from Aqua Chem and observations of field and geology and petrography of the sampling area, these data used for interpretations of both hot water samples and cold spring water.

Consequently, water samples were characterized for what type of water samples, what their sources which mean if the waters were juvenile magma or meteoric waters, with the help of the isotope studies and taken cat ions and anions through water-rock interaction where the water passed through the system of the East Anatolian Geothermal Field.

Water samples radioactivity results were shown in the range of acceptable limits.

For East Anatolian around hot water resources were determined using Piper diagram.

KEYWORDS: thermal water, geothermometer, geochemistry, ions, reservoir rock, isotope geochemistry, heavy metal

Determination of Some Toxic Traces Metal Contamination in Some Spring and Thermal Waters around Van by AAS and ICP-MS

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Trace toxic metals are a special group of contaminants of water reservoir. They are high ecological significance since they are not removed from water. It is important to remove this contaminants from water but it is not so easy to remove this contaminants by self-purification of water. In order to providing of high quality water for man, is very important. Because it is directly related with human and animal life. Similarly, thermal and spring water qualities in many countries are affected by industrialization and over population.

The main aim of this study was to determine some trace toxic metal concentration in some spring water around Van by means of Atomic Absorption Spectrometer and inductively coupled plasma mass spectrometry after enrichment of activated carbon. Spring water samples were collected from some different parts of city. These spring water samples were determined by a simple pre-concentration method which is called activated carbon enrichment. The trace metal analysis was done to determine, Arsenic (As), Cadmium (Cd), Lead (Pb), Selenium (Se), Zinc (Zn) elements. The result that we obtained compared with guidelines for drinking water quality such as World Health Organization (WHO) guidelines and European Union drinking water standards. As a result of this study, we obtained waters that we studied was generally suitable for the Both criteria of World Health Organization (WHO) guidelines and European Union drinking water standards except for a few samples.

KEY WORDS: Water pollution, toxic metals, activated carbon, AAS, ICP-MS

Characterization and Determination of Some Physicochemical Properties of an Anionic Surfactant

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There is a continuing search for surfactants that possess good detergent properties, biodegradability and low toxicity. With this objective in mind, a great deal of work has been carried on the synthesis and properties of new anionic surfactants. Alkylbenzenesulfonates have been obtained by a photochemical process developed in our laboratory [1 - 3]. The process leads to alkylbenzenesulfonyl chlorides which are separated from the reaction mixture and analyzed by GPC and GC-MS/EI. These Sulfonyl chlorides are then saponified, and after purification they are analyzed by IR and LC-MS. Some physico-chemical properties are determined such as critical micelle concentration (CMC), surface tension at the CMC (γ_{cmc}), the excess surface (Γ_m) and the effective area occupied by molecule (A_m).

KEYWORDS: linear alkylbenzenes sulfonate (LAS), surface properties, gas phase chromatography (GPC), gas phase chromatography coupled to mass spectrometry in electronic impact (GC-MS/EI), liquid phase chromatography coupled to mass spectrometry (LC-MS).

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Ultrasonically Assisted Extraction of Anthocyanins from Red Rose Petals and a New Spectrophotometric Method for Quantitative Determination of Total Anthocyanins

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Anthocyanins are a group of naturally occurring phenolic compounds responsible for the colour of many plants, flowers and fruits. They are responsible for the red, purple, and blue hues present in fruits, vegetables, and grains. Pelargonidin, cyanidin, peonidin, delphinidin, petunidin, and malvidin are the six common anthocyanidins found in nature [1,2]. Recently, this group of compounds have gained a great importance because of their different pharmacological activities. They manifest an array of health promoting benefits such as protecting cells against oxidative stress, anti-inflammatory effects and inhibition of some human tumor cells [3,4]. Anthocyanin pigment content can also be a useful criterion in quality control and purchase specifications of fruit juices, nutraceuticals, and natural colorants. Literature does not report any data on the toxicity of anthocyanins. Interest in the beneficial effects of anthocyanins on human health has stimulated an increased demand for their use in food products and dietary supplements and created a need for an inexpensive and effective method to quantify the total anthocyanin content of a sample, while allowing results to be compared among laboratories [5]. Ultrasonic extraction (UE) followed differential derivative spectrophotometry (DDS) analysis method for the fast, simple and effective extraction and determination of anthocyanins (Acyns) in rose flowers has been developed. Four extraction technologies of anthocyanins from red rose flowers were investigated and compared, including ultrasonic extraction, reflux extraction, soxhlet extraction and marinated extraction. The results showed that UE was most suitable for the extraction of Acyns from red rose flowers because of its high extraction efficiency and short extraction time. The found optimum extraction conditions were that the ethanol concentration was 90 %, solid-liquid ratio was 1/40, extraction time was 15 minutes and extraction number was 3. A new differential derivative spectrophotometry (DDS) was applied for the analysis of Acyns in red rose flowers. Under the optimum experimental conditions, the calibration curve for the Acyns was linear in the range of 12,5-62,5 $\mu\text{g mL}^{-1}$. DDS method validated and compared with the reported derivative and pH-differential methods. Calibration equation and correlation coefficient were found $y = 0,0017x - 0,0319$ and $r = 0,9983$, respectively. The average recovery was 96,7 %, and its RSD was 0,62 % (n: 10). The limit of detection (LOD) and the limit of quantification (LOQ) were found between 0,21 and 1,07 $\mu\text{g mL}^{-1}$, and between 0,69 and 3,58 $\mu\text{g mL}^{-1}$, respectively.

The reliability of the methods was further ascertained by recovery studies via standard addition method.

KEYWORDS: differential derivative spectrophotometry, ultrasonic extraction, anthocyanins, red rose flowers, pH- differential method

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Ecological Dyeing with Some Red Rose Petals on Woolen Fabric by Using Different Mordants

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There are ca. 150 species of plants that could be used as vegetable dye source in Turkey [1]. The extension of the agriculture of these plants will not only provide economic revenue for producers, but also contribute to the development of handicrafts, provide many positive advantages and will not harm the environment, compared to synthetic dyestuffs.

Today, environment friendly products are on the agenda in the world. As well as harming the natural environment, fabric dyes made of synthetic dyestuffs could also contain unhealthy carcinogenic properties. Researchers tend towards natural dyes as an alternative for that. The use of natural colours increasingly spreads on a large area, such as textile, food, home textile and pharmaceutical industry [2]. Although the cost estimates of natural dyeing is greater than synthetic dyeing by 17.39%, natural one is advantageous in terms of human health and environmental aspect [3]. The aim of this study was to determine dyeing properties of anthocyanins which is extracted from red rose petals, using different mordants and dyeing methods on wool fabrics. The effect of mixture of the tannic acid and some selected metal salts were investigated in eight different dyeing methods by using buffer solution at pH 4 for 1 h at 98-100 °C with closed bath dyeing technique. The colour coordinate of dyed samples were found to lie in the yellow-brown quadrant of the colour space diagram. Optimum mordant, dyeing methods and reflectance curves of dyed wool fabrics were determined. CIELAB values have also been evaluated. In this study, good lightfastness (4-8), rubbing fastness (4-5), perspiration fastness (4,5) and antibacterial fibers were obtained.

Dyeing conditions and other characteristics show that the mordant mixture is more beneficial than dye as it shows good lightfastness and antibacteria property. The results of fastness properties of the dyed woolen fabrics were fair to good. The dye obtained from the red rose petals may be alternative source to synthetic dyes for the dyeing of wool.

KEYWORDS: tannic acid, mordant salts, woolen fabric, red rose petals, natural dyeing, light fastness

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Indirect Cloud Point Extraction and Spectrophotometric Determination of Trace Nitrite in Beverages with and without Alcohol

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Nitrite is a versatile chemical agent which has found numerous applications ranging from dye manufacture to food preservation. It produces carcinogenic nitrosamines in the human body through its reaction with amines or amides [1]. Nitrite is one of the pollutants found in the atmosphere and natural water [2] and is an important intermediate in biological nitrogen cycle. Trace amounts of nitrite and nitrate in aqueous beverage and foods as well as drinking water may lead to methemoglobinemia in infants and with long term exposure is a possible cancer risk. Therefore, there is a great need to develop a simple, sensitive, selective and inexpensive method for the determination and continuous monitoring of trace amounts of nitrite in food and beverage samples.

A new indirect micellar mediated cloud point extraction method has been developed for sensitive determination of trace amounts of nitrite by means of spectrophotometry. The method is based on complexation of triiodide ion, I_3^- produced by the reaction of nitrite with excess iodide with acridine orange at phthalate buffer, pH 4.0 and cloud point extraction of ion-pairing complex formed from aqueous solution using Triton X-114. The extracted surfactant rich phase is diluted with acetonitrile and its absorbance is measured at 450 nm. The effects of analytical parameters such as concentration of surfactant, KI and Acridine orange concentration, temperature, incubation time, pH and buffer concentration on the cloud point extraction were studied in details and a set of optimum conditions was obtained. The calibration graph was highly linear in the range of 2–150 $\mu\text{g L}^{-1}$. The limit of detection (LOD) based on ratio of three times the standard deviation of the ten replicate blank measurements to slope of calibration curve ($3SD_{\text{blank}}/m$) was 0.42 $\mu\text{g L}^{-1}$ (n: 6) and the precision (as RSD) for determination of 10, 50 and 100 $\mu\text{g L}^{-1}$ of nitrite was in range of 2.30–4.10% (n: 10). The method was successfully applied to the determination of nitrite in dairy products with fruit aroma and beverage samples.

KEYWORDS: Nitrite; Triton X-114; Cloud point extraction; I_3^- ; Acridine orange; Spectrophotometry

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A Novel Preconcentration Procedure using Cloud Point Extraction for Determination of Inorganic Dissolved Arsenic Species in Some Beverage Samples using Spectrophotometry

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Environmental pollution is the main cause of heavy metal contamination in the food chain. Because of their high toxicities, inorganic dissolve and organic bound arsenic species need to be quantified in food and beverages [1]. Heavy metals composition of foods is of interest because of their essential or toxic nature. Arsenic is a highly toxic element and its presence in food composites is a matter of concern to the humans well-being [2]. After acute and chronic exposures, it causes a variety of adverse health effects to humans such as dermal changes, respiratory, pulmonary, cardiovascular, gastrointestinal, hematological, hepatic, renal, neurological, developmental, reproductive, immunologic, genotoxic, mutagenic, and carcinogenic effects [3]. Diet is the major source of arsenic exposure; therefore, it is important to monitor the dietary intake of arsenic to quantify it. According to the Turkish Food Codex (TFC), the maximum contaminant level of arsenic may not exceed 0.1 mg/kg in soft drinks [4]. Due to the toxic nature of especially As(III), there is a great need to develop a simple, sensitive, selective and inexpensive method for the determination and continuous monitoring of trace levels of inorganic As-species in food and beverage samples.

In this work, a new cloud point extraction (CPE) procedure was developed for the separation and preconcentration of As(III), As(V) and total As in various beverage samples. Selective ternary complex of As(III) with Neutral red (NR⁺) being a cationic azine group dye in presence of citric acid at pH 2.0 were extracted into the surfactant-rich phase of octylphenoxypolyethoxyethanol (Triton X-114) from samples. After phase separation, the preconcentrated As(III) was determined by means of spectrophotometry at 542 nm. Factors affecting cloud point extraction, such as pH, buffer volume, reagents (citric acid and neutral red) and surfactant concentrations, centrifugation rate and time, incubation temperature and time were evaluated and optimized in detail. The interference effect of some cations and anions was also studied. After optimization of the CPE conditions, the limits of detection and quantification (LOD) obtained for arsenic(III) based on the 3SD/m and 10SD/m for twelve replicate measurements of blank with preconcentration factor of 38.5 in linear range of 10-1500 $\mu\text{g L}^{-1}$ were 2.94 and 9.81 $\mu\text{g L}^{-1}$, respectively. The precision of the developed method (as RSD) was in range of 2.15-3.85% (25, 250 and 750 $\mu\text{g L}^{-1}$, n=6). The As(V) contents of samples was calculated from the difference between As(III) and total As after the reduction of As(V) to As(III) with KI and ascorbic acid at HCl media. The presented preconcentration procedure was applied to the determination of arsenic species, As(III), As(V) and total As in certified reference materials (SRM 1575a Pine Needles and SRM-1643e Trace elements in water) and the selected beverage samples.

KEYWORDS: As(III), As(V), Total As; Triton X-114; Cloud point extraction; Citric acid; Neutral red; Spectrophotometry

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Simultaneous Preconcentration of Sb and B in Food and Beverage Samples and Determination by Atomic Absorption Spectrometry

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Boron is a trace mineral element occurring naturally in the environment and in the food supply, although it does not exist as elemental boron in foods or beverages, but rather as one or more inorganic, oxygen-containing borates, such as boric acid. Boron has long been known to be an essential nutrient for all vascular plants, and there is now considerable evidence that it may also be essential for animals and humans [1]. Owing to its use as a catalyst in the fabrication of polyethylene terephthalate (PET) antimony is invariably found in plastic containers made of this material used for water and fruit juices, and consequently fruit juices have been found to contain antimony levels greater than the EU limit [2-4]. The toxicity of antimony is not yet fully understood with respect to human health or the environment. The element is poisonous to humans and animals at high dosage, with symptoms akin to arsenic poisoning. It is not known to serve any biological function [5], but has been administered in the treatment of certain tropical diseases, as have other toxic heavy metals [6,7]. For these reasons, the simultaneous determination of boron and antimony in foods and beverages is important and the method used for their simultaneous determination should be fast, simple, cheap, sensitive and accurate.

A cloud point extraction (CPE) method has been developed for the preconcentration and simultaneous determination of antimony [Sb(III)] and boron [B(III)] using Azomethine H as complexing reagent and CPC as signal enhancing auxiliary ligand at pH 10 and mediated by nonionic surfactant (Triton X-114) by flame atomic absorption spectrometry (FAAS). The analytical variables affecting analytical performance of CPE have been investigated and optimized in detail. The extracted surfactant-rich phase was diluted with (1.0 mol L⁻¹) nitric acid in methanol, prior to subjecting FAAS. The calibration graphs obtained from Sb(III) and B(III) were linear in the concentration ranges of 0.5–180 and 2.5–600 µg L⁻¹ with detection limits of 0.153 and 0.75 µg L⁻¹, respectively. The relative standard deviations for 10 replicates containing 25 and 100 µg L⁻¹ of Sb(III) and B were in range of 2.30 and 3.80 %, respectively. The analytical procedure was verified by the analysis of the standard reference materials MDA-53.5 (water-trace elements) and NIST SRM 1548a (typical diet). The developed method has successfully been applied to the simultaneous determination of total Sb and B in real samples including beverages with and without alcohol.

KEYWORDS: Sb(III), Boron, Simultaneous determination, Azomethine-H; CPC; Triton X-114; Cloud point extraction; FAAS

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Kinetique of Tanins Extraction from Alep Pine

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This work concerns the study of the kinetic of extraction of Alep pine. We have used several solvents: aqueous methanol, aqueous acetone and a mixture of methanol-acetone-water. The study aimed to explore the effect of solvent and duration time on extraction. We determined the operating conditions in another work before (L. Loucif Seiad & R. Derriche) and the Folin –Ciocalteu method was used .

KEYWORDS: Alep pine, tannins, extraction, kinetic

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Development of a New Method on the Basis of “Co-Liquefaction with Organic Solvent” for the Extraction and Pre-Concentration of Trace Volatile Organic Compounds (VOCs) from Gaseous Samples

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Volatile organic compounds (VOCs) are emitted from variety of the industrial sources as potential pollutants [1], insects and plants [2] as the communication or defensive chemicals. Some of these compounds are also released in trace quantities from cancerous cells e.g. lung diseases [3]. These compounds must therefore be monitored at trace levels in gaseous samples for health, environmental, biomedical, biological and scientific studies. For this purpose GC and GC/MS are the most commonly used methods. Considering very low concentration of the target VOC's, use of a rapid, inexpensive and effective samples pretreatment method is indispensable.

In this study we have developed a new extraction method on the basis of co-liquefaction of VOC's with organic solvent. In practice 500 mL of gaseous sample containing BTEX as model compounds were taken in a specially designed and fabricated vessel. 0.5 mL of acetone was added. The vessel is exposed at cold vapor making ultrasonic bath for transformation of acetone to the vapor or aerosol forms. The vessel is then cooled down at -10 °C for co-liquefaction of analytes and acetone vapor. 2 µL of the extract was then analyzed by GC-FID.

The obtained results revealed that under the optimal conditions, the method displays an extraction efficiency of more than 98% and an enrichment factors (EFs) in the range of 1000 for the studied compounds. The limits of detection (LODs) were between 4-8 ng mL⁻¹. Calibration graphs are linear in the concentration range of 6-600 ng mL⁻¹ with a correlation coefficient (R²) of more than 0.99. The overall time for sampling, extraction and pre-concentration of BTEX from gaseous samples is less than 25 min. Low cost, short sample preparation time, less solvent consumption, complete extraction ability and high enrichment factors are the main advantages of the proposed method.

KEYWORDS: Co-liquefaction, VOC's, BTEX, gaseous samples, GC

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Application of Solidified Floating Organic Drop Microextraction Method for Biomonitoring of Chlorpyrifos and its Oxon Metabolite in Urine Samples

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Public health concerns about pesticide exposure to children have received increased attention in recent years [1]. Biomonitoring studies have confirmed that children are widely exposed to pesticides especially including organophosphorus pesticides [2]. Many organophosphates readily undergo conversion from thions (P=S) to oxons (P=O). Conversion occurs in the environment under the influence of oxygen and light and in the body chiefly by the action of liver microsomes [3]. On the other hand, transformation products of OPPs are often more toxic than parent pesticides. These compounds are biotransformed by different reactions that take place within the organisms such as a variety of hydrolyses and oxidations. Hence, the determination of these metabolites in such samples was of great interest. Biological markers of exposure to contaminants afford a direct means of assessing the extent of human contact with chemicals in the environment and they are useful in many aspects of environmental health, including analysis. Chromatographic techniques are widely employed for the determination of organic biomarkers since they are powerful separation techniques but, the sensitivity and selectivity of the method usually depend on the sample preparation method used prior to the analysis. In recent years, simplification and increasing automation of sample preparation steps are one of the modern trends in analytical chemistry. Classical extraction methods (e.g. liquid-liquid extraction, solid phase extraction) were used for the sample preparation steps generally. However, they display some drawbacks such as large consumption of reagent, low enrichment factor, multistage operation [4]. To overcome the drawbacks of the classical extraction methods microextraction methods such as single drop microextraction (SDME) [5], solid phase microextraction (SPME) [6], dispersive liquid liquid microextraction (DLLME) [7] techniques have been developed for the determination of pesticides. Also as an alternative to liquid microextraction techniques a novel liquid phase microextraction method based on solidification of floating organic drop (SFODME) has been introduced by Zanjani et al. [8]. In this study a rapid, simple and cost effective method for the preconcentration and biomonitoring of an organophosphate pesticide that is widely used as an anticholinesterase insecticide namely Chlorpyrifos (CP) and its metabolite Chlorpyrifos-Oxon (CPO) has been developed by using solidified floating organic drop microextraction. In this technique a free microdrop of 2-dodecanol which has a melting point near to room temperature was used as an extracting solvent. Considering the number of parameters those are likely can affect the signal, extraction solvent type, extraction solvent volume, extraction time and temperature, sample volume and salt effect on pesticide extraction were optimized. The analytes were extracted from the 5.0 mL of urine samples by using 10 µL of 2-dodecanol for 40 min at 70°C. Extracts were injected to GC-MS column by applying 100 kPa injection pressure to the system. The separation power of the GC-MS was coupled with the excellent sensitivity of microextraction technique enabling us to determine CP and CPO simultaneously in ppt range with satisfactory RSD values by the help of pulsed splitless injection. The regression coefficients relating to linearity were at least 0.99. Recoveries from spiked well water sample range from 81 to 108% and relative standard deviations were no higher than 10% in the most unfavorable case. Contribute to policies aiming to reduce exposure of pesticides, this study will serve attention due to the sensitivity of the developed method in ppt range. This method can easily be adopted by clinical laboratories that do not have expensive equipment.

KEYWORDS: Solidified floating organic drop microextraction, Urine, Chlorpyrifos, Gas Chromatography, Mass Detector,

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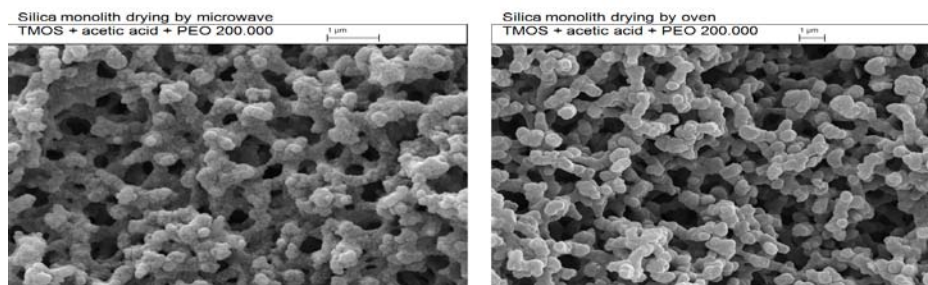
Comparison of Silica Monolith Fabrication and C₁₈ Phase Surface Modification Using Microwave and Conventional Heating Methods for Efficient Extraction of Small Organic Molecules

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Analysis of drugs in biological samples is growing in importance, both in the understanding of their therapeutic and toxic effects and in the development of more selective and effective drugs. Biological matrix however are complex and may contain acids, bases, salts, proteins and other organic compounds with similar properties to the analytes of interest. Despite the development of highly efficient analytical instrumentation for the endpoint determination of analytes in biological samples, sample pre-treatment is usually necessary to extract, isolate and concentrate the analytes of interest from complex matrices, because most analytical instruments cannot handle the sample matrices directly [1]. The interest in using solid phase methodology based on monolithic structures for analyte preconcentration and matrix modification has been growing recently with applications in environmental, food, and biological analyses. This approach has also contributed to the miniaturization of sample preparation, which can reduce the cost and time requirements of sample preparation. This poster, will discuss the use of silica monolithic columns produced using microwave heating during fabrication and C₁₈ phase surface modification in extraction of small organic molecule application, and will demonstrate the development of novel methodology based on micro fluidics which exploits the advantages of miniaturisation for sample preparation and separation for selected drug such as caffeine and eserine [2]. The work presented will focus on the time advantage gained by fabricating silica monoliths and surface functionalizing them with C₁₈ phase using of microwave heating (11 min) compared to conventional oven heating methodology (4320 min) and in the influence of microwave heating during drying in the surface area and pore volume of silica monoliths obtained via sol-gel polymerization process. The results indicated that the monoliths obtained using microwave heating gave an average pore volume of between 1 and 1.4 cm³/g and a surface area between 333 and 574 m²/g compared to an average pore volume of between 0.92 and 0.99 cm³/g and surface area between 460 and 513 m²/g for thermal heating based monoliths. Scanning Electron Microscopy (SEM) confirmed similar structures for both the microwave and conventionally generated silica monoliths were obtained. It was found however, that microwave based fabrication offered a significantly more rapid (11 min) gelation process, compared to those obtained using the thermal heated oven methodology (4320 min). In addition using microwave heating for C₁₈ phase modification of silica monoliths showed very good extraction efficiency between 97 and 111% and reproducibility between (2 and 5.3 CV%). The time of C₁₈ phase modification for silica monolith column using microwave heating (40 min) was much shorter than that monolithic column using conventional thermal heating (550 min). Finally, examples will be presented on how the formation and C₁₈ phase modification of silica monolith using microwave heating has been found to offer a more superior column for the rapid and efficient extraction of caffeine and eserine compared to conventional oven based methodology with a reduce processing times.



KEYWORDS: microwave, silica monolith, surface area, pore size.

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Polyethylene Glycol as a Surfactant for Separation of Some Metal Ions from Aqueous Solutions by Cloud Point Extraction

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Polyethylene glycol as non ionic surfactant with low cloud point is used for separation of silver, copper, ferric and cadmium ions in aqueous media. Addition of ammonium pyrrolidine dithiocarbamate (APDC) as chelating agent is tested. The effect of PH on separation of the metal ions is also examined. A complete separation of silver ions with and without addition of chelating agent could be achieved at PH= 2-3, with decreasing acidity separation up to PH= 8 the efficiency of separation is 95-100%. Copper showed 95% separation at lower PH values (2-6) then the complete separation could be at PH =7-9. Iron showed low separation values at lower PH with about 35-45%, at PH values higher than 6 up to PH = 9 the separation is possible with efficiency of 75-95 %. Cadmium could be extracted with 65% slightly acidic, neutral and slightly basic solutions. The effect of surfactant amount on separation is also investigated. One gram of surfactant is an enough amount for separation of 20 ppm of each metal ion solution. The analysis of metal ions were carried out using flame atomic absorption spectrometer with deuterium lamp background correction and standard curve method.

KEYWORDS: cloud point extraction, surfactant, polyethylene glycol.

Selective Recognition of Copper (II) Ion by a New Phthalocyanine Compound With 2-(4,6-Diphenyl-1,3,5-Triazin-2-YL)-5-(Hexyloxy) Phenol Moiety

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A new phthalocyanine compound carrying 2-(4,6-diphenyl-1,3,5-triazin-2-yl)-5-(hexyloxy)phenol moiety (1) was designed and synthesized [1]. The influence of metal cations such as Mg^{2+} , Ca^{2+} , Sr^{2+} , Fe^{2+} , Fe^{3+} , Cu^{2+} , Co^{2+} , Ni^{2+} , Mn^{2+} , Zn^{2+} , Cd^{2+} , Hg^{2+} , Al^{3+} and Pb^{2+} on the spectroscopic properties of the new fluoroionophore was investigated in acetonitrile-chloroform solution (1:1) by means of absorption and emission spectrometry. The blue shifts on the absorption spectrum were observed for Cu^{2+} , Hg^{2+} , Fe^{3+} and Al^{3+} at 640 nm. Also, the absorption spectrum of the ligand showed quenching in the intensity of the signal at 640 nm for Cu^{2+} , Hg^{2+} , Fe^{3+} and Al^{3+} . The emission spectrum of the ligand showed quenching in the intensity of the signal at 507 nm for Cu^{2+} , Hg^{2+} , Fe^{3+} , Al^{3+} , Mn^{2+} and Fe^{2+} . Especially, interaction of Cu^{2+} with the ligand caused quenching of fluorescence higher than 92 %. According to these results stability constant of complexes with metal cations is calculated. The molar ratio method was used to determinate the complex composition. The fluorescence methods showed good selectivity and sensitivity for Cu^{2+} with respect to other metal cations with linear range of 0.16 mg/L to 0.82 mg/L. The limit of detection (LOD) for Cu^{2+} was 0.01 mg/L. [2,3]

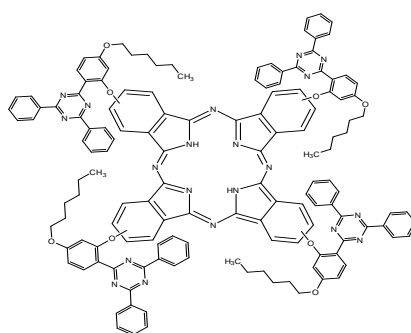


Figure 1. The structure of ligand (1)

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Selective Recognition of Silver (I) Ion by a Ns_3 Crown Ether Ligand Carrying Pyrene Moiety

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The influence of metal cations such as Mg^{2+} , Ca^{2+} , Sr^{2+} , Fe^{2+} , Fe^{3+} , Cu^{2+} , Co^{2+} , Ni^{2+} , Mn^{2+} , Zn^{2+} , Cd^{2+} , Hg^{2+} , Al^{3+} and Pb^{2+} on the spectroscopic properties of the fluorescent NS_3 crown ether ligand [1] was investigated in dimethyl sulfoxide water (1:1) solution by means of absorption and emission spectrometry. The emission spectrum of the ligand showed a regular quenching in the intensity of the signal at 398 nm for Ag^+ . Interaction of Ag^+ with the ligand caused quenching of fluorescence higher than 90 %. According to these results stability constant of complex with silver ion is calculated. The molar ratio method was used to determinate the complex composition. The fluorescence method showed good selectivity and sensitivity for Ag^+ with respect to other metal cations with linear range of 2.5 ppb to 10.5 ppb. The limit of detection (LOD) for Ag^+ was ppb.

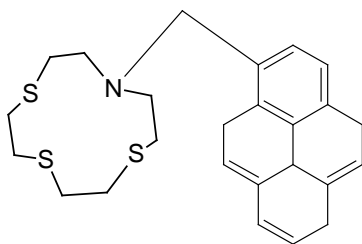


Figure 1. The structure of ligand

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Cancer Diagnosis by Mass Spectrometry

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Mass Spectrometry is widely used by analysts to identify unknown compounds or quantification of known compound in a sample. Mass spectrometry provides useful information unavailable to other types of spectrometry. Mass spectrometry may be capable of providing cancer diagnosis. Cancer is often diagnosed by an abnormal amount of some types of peptide or protein in blood. Protein based diagnostics use to find diagnostic patterns of protein expression. The identifying information provided by mass spectrometry on a peptide or protein is complex. Clinical trials for diagnostic tests are ongoing for early detection of cancer and individualization of therapy and monitoring drug induced toxicity.

Cancer biomarkers are currently used for population screening, diagnosis, prognosis and monitoring therapy. Some established cancer biomarkers are alpha-fetoprotein, carcinoembryonic antigen, immunoglobulins, steroid hormone receptors. Mass spectrometry is now one of the most powerful proteomic tools, many scientists have decided to use mass spectrometry either as a diagnosis tool or as a cancer or disease biomarker discovery.

In this study, mass spectrometric determination of biomarkers and peptide will be discussed. The advantage and disadvantage of mass spectrometry usage of cancer diagnosis will be overviewed.

KEYWORDS: mass spectrometry, biomarker, cancer,

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Analytical Methods for Therapeutic Drug Monitoring

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Therapeutic drug monitoring (TDM) involves the measurement and interpretation of drug concentrations in biological fluids. TDM has been applied different therapeutic classes, such as cardiovascular agents, antiepileptics, antiinflammatory agents, some cancer chemotherapeutics, antidepressants.

A drug will fulfill several criteria in order for TDM to be valuable. These include presence of pharmacokinetic variability, existence of a relationship between concentration and pharmacological (therapeutic) effects. The methods for analyzing drug from biological material are enormous. The fundamental procedures necessary for quantification of the drug in the biological fluids were discussed in this study. The analytical methods should distinguished unchanged drug and metabolites, detect small amounts, useful for routine analysis. Chromatography, radioimmunoassay, enzyme immunoassay techniques were used for TDM. Drugs are usually monitored in venous blood, serum or plasma or urine.

In this study, methods for monitoring drug from biological fluids were discussed.

KEYWORDS: Therapeutic drug monitoring (TDM), mass spectrometry, chromatography

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Methodological Approach to Detailed Analysis of the Unknown Solid Samples

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In different scientific and manufacturing fields there are tasks to determine composition of unknown samples. This subject is especially of interest in analysis of wastes and raw materials as these objects may contain variety of components. General analysis procedure for determination of elemental composition of the unknown samples is described. This procedure is based on consequential use of such methods as X-ray Fluorescence (XRF) analysis, Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES), Atomic Absorption Spectrometry (AAS).

Several objects such as copper-nickel ores, apatite concentrate, solid municipal waste were analyzed to determine their complete elemental composition. XRF analysis was used to obtain a general composition of inorganic part in the samples. Two types of sample preparation were used in this analysis: ground material in the form of loose powder in the cells and pressed pellets. Semi-quantitative content of carbon and oxygen was also obtained by XRF wavelength dispersive analysis. As for the organic part in the samples, loss on ignition was used for its determination. ICP-OES was used to obtain detailed composition of major elements and impurities. AAS was applied for the improvement of obtained results. Depending on the elements to be analyzed different types of sample pretreatment were used in ICP-OES and AAS: heating on a hot plate, microwave digestion method, decomposition by alkali fusion. To get the correct results in determination of content standard samples of the same matrix as the analyzed samples were prepared. The general way for preparation of standard samples from the pure substances was described.

The described scheme was optimized for each kind of object depending on the preliminary results of general composition analysis. The presented methodological approach enables solving two main problems: identification of unknown sample composition and accurate quantitative analysis. Depending on the set task (the range of analyzed elements, specified metrological characteristics) it is useful to modify the analysis scheme to get the required result effectively. XRF analysis is appropriate for major elements determination, ICP-OES enables getting accurate results for impurities content, AAS is suitable for improvement of obtained results. Therefore it is recommended to use complex of the specified methods for effective solution of task to determine complete elemental composition of the unknown samples. The described methodological approach is convenient as it is not necessary to have background information about samples.

KEYWORDS: solid unknown samples, XRF, ICP-OES, AAS, methodological approach

An Extractive Spectrophotometric Method For Uranium(VI) Using Mwcnts and Arsenazo(III)

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Multiwalled carbon nanotubes (MWCNTs) based sorptive extraction method for uranium (U) from aqueous solutions has been developed. The proposed method was optimized by evaluating the analytical parameters including pH, eluent type, flow rates of sample and eluent, etc. The adsorption capacity of MWCNTs was found to be $9.8 \mu\text{g g}^{-1}$, while the detection limit based on 3σ criterion was $1.9 \mu\text{g L}^{-1}$. The presented method was applied for the estimation of U in ore sample with satisfactory results. Effect of potentially interfering ions was also studied and were found to not interfere with U during the analysis. The results suggest that MWCNTs can be used as reliable solid phase for preconcentration and arsenazo-III as chromophore for U spectrometric determination from aqueous solutions.

KEYWORDS: carbon nanotubes, uranium, solid phase, preconcentration, arsenazo-III

Chromium Speciation in Environmental Samples by Using a New Chelating Resin and its Determination by FAAS

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Chromium is extensively used either as alloy or as trivalent or hexavalent salt in a variety of industrial processes such as metallurgical, chemical industries, electroplating, refractories, pigments, tanning industries, oxidative dyeing and cooling water towers [1]. On the contrary, Cr(VI) species are highly toxic as a potential carcinogenic agent due to their high oxidation potential and their relatively small size, which enables them to penetrate through biological cell membranes [3].

In this study, a new method for speciation, preconcentration and separation of Cr(III) and Cr(VI) in different matrices has been developed using solid phase extraction and flame atomic absorption spectrometry (FAAS). Poly-2-(5-methylisoxazole) methacrylamide-co-2-acrylamido-2-methyl-1-propanesulfonic acid-co-divinylbenzene (MAD, see Fig 1), was synthesized and characterized as a new chelating resin for the speciation of Cr(III)/Cr(VI) species. Cr(III) was quantitatively recovered on chelating resin at pH range of 1.5–4.5, while Cr(VI) was not quantitatively recovered in all the pH's. The optimum conditions for the speciation of Cr(III)/Cr(VI) species were investigated on several commonly tested experimental parameters such as pH of the solution, amount of the resin, sample volume, and interfering ions. The preconcentration factor was found to be 200. The limit of detection for Cr(III) corresponding to three times the standard deviation of the blank (3s) was found as $0.01 \mu\text{g L}^{-1}$. Adsorption capacity and binding equilibrium constant were calculated to be 34.3 mg g^{-1} and 1.5 L mg^{-1} , respectively. The method was validated by analysing certified reference materials. The proposed method was applied to the determination and speciation of chromium species in various water and food samples with satisfactory results [3].

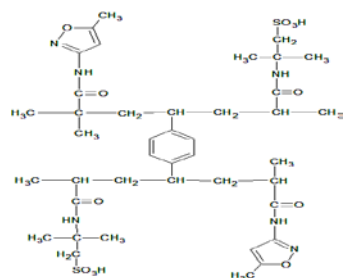


Figure 1. The structure of the chelating resin (MAD)

KEYWORDS: chelating resin, separation, preconcentration, chromium speciation, FAAS

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Determination of Gold and Palladium by FAAS After Dispersive Liquid–Liquid Microextraction Sampling

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Palladium (Pd) is one of the most widely used of the six platinum group metals (PGM). Pd is especially valued for its catalytic functions, conductivity and resistance to corrosion. It is essential in key manufacturing processes in the automobile, chemical petroleum refining, pharmaceutical and electronics industries. Gold (Au) was the first metal known to man [1]. Gold is widely distributed in nature and the chemistry of gold remains an active research area [2]. Gold is one of the precious metals and extensively used in various areas. It is a nonessential toxic element, and some reports about allergic eczematous dermatitis as well as some nephrotoxic effects have been published [3]. The accurate determination of PGMs in environmental solid samples, including soils and sediments is particularly difficult since PGM concentrations are low as little as 1 ng g^{-1} [4]. Simplicity, rapidity, low sample volume, low cost, high recovery and enrichment factors are some advantages of DLLME and the technique has been widely applied for the determination of trace organic pollutants and metal ions in environmental samples [5]. In this study, we developed a new and green dispersive liquid–liquid microextraction (DLLME) procedure combined with FAAS by applying a microsample introduction system for the final measurement of Au(III) and Pd(II). Under the optimized experimental conditions, 10 mL of aqueous sample solution containing 1 mg L^{-1} of Au and 1 mg L^{-1} of Pd was placed into a 50-mL glass test tubes with conic bottom and screw cap. A mixture of 450 μL of acetone (disperser solvent), 250 μL of 1% 5-[(E)-(2,6-diaminopyridin-3-yl)diazonyl]-1,3,4-thiadiazole-2-thiol (DAT) solution (chelating agent, see Fig.1) in ethanol and 250 μL of CHCl_3 (extraction solvent) was rapidly injected into the sample solution by using a microsyringe. A cloudy solution (water, ethanol, and CHCl_3) was formed in the test tube. In this step, the formation and extraction of metal complexes were performed. After the centrifugation for 2 min at 3200 rpm, the organic solvent droplets were at the bottom of the aqueous solution. In this step, the volume of the organic phase was nearly 250 μL . Finally, for the quantitation of each metal ion, 25 μL of the extract was injected into the flame atomic absorption spectrometer by using the micro-injection method [6]. The gold and palladium signals were measured in the peak area mode utilizing the instrument software. The calibration graph was prepared against aqueous standards by submitting to the same DLLME procedure. Blank determinations were carried out as parallel to the measurements made for sample and calibration standards. Finally, the proposed method was successfully applied for the determination of Au and Pd in various environmental samples. The results show that dispersive liquid–liquid microinjection pretreatment is a sensitive, rapid, simple and safe method for the separation/preconcentration of gold and palladium.

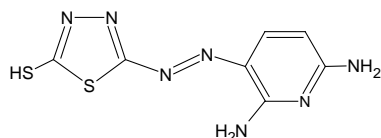


Figure 1. The structure of the chelating agent (DAT).

KEYWORDS: gold, palladium, dispersive liquid–liquid microextraction, chelating agent, FAAS

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Chromium Speciation in Environmental Samples by Solid Phase Extraction on Lewatit Sybron Lonac SR-7

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Chromium is extensively used either as alloy or as trivalent or hexavalent salt in a variety of industrial processes, such as metallurgical, chemical industries, electroplating, refractories, pigments, tanning industries, oxidative dyeing and cooling water towers [1]. The importance of chromium speciation is governed by the fact that the toxicity and reactivity depend on the chemical form or oxidation state of chromium. Cr(III) is relatively non-toxic and an essential nutrient for humans, and trace amounts of Cr(III) are considered as essential to mammals for their maintenance of normal glucose tolerance factor, lipid and protein metabolism, and are therefore essential for human health [2].

Chromium species in water, mainly exist as chromate (CrO_4^{2-}) and cationic hydroxo complexes ($\text{Cr}(\text{OH})_2^+$ and $\text{Cr}(\text{OH})_2^+$ etc.) and organically bound or colloiddally sorbed Cr(III) [3]. Therefore, it is necessary to control the level of Cr(VI) in natural and drinking water, where typical concentrations of total chromium are in the range $0.1\text{--}0.5\text{ }\mu\text{g L}^{-1}$ [4].

In this study, Lewatit Sybron Ionac SR-7 anion exchange resin was used for the separation, preconcentration and speciation of Cr(III) and Cr(VI) species. The analytical parameters including pH, amount of resin, sample volume, etc., were investigated for the quantitative recoveries of Cr(VI). No interferic effects were observed from the concomitant ions which are present in real samples. The detection limit (3s) was $0.003\text{ }\mu\text{g L}^{-1}$. In order to determine the total chromium, first Cr(III) ions were oxidized to Cr(VI) ions in the test solution by using 10 mL of 3% (w/v) H_2O_2 at pH 12 and then the solution was heated on a hot plate adjusted to $80\text{ }^\circ\text{C}$ for 40 min [5]. The solution was allowed to cool at room temperature for 30 min. After the oxidation of Cr(III) to Cr(VI), the pH was adjusted to 3 and the volume of the solution made up to 25 mL with deionized water. The described preconcentration procedure was applied and total chromium was determined by FAAS. The concentration of Cr(III) in samples was calculated by subtracting the concentration of Cr(VI) from the total chromium concentration.

The accuracy of the presented procedure was verified by the analysis of standard reference materials. The method was applied to the determination of the analytes in real samples including natural waters, hair, peritoneal fluid samples, urine, soil and sediment samples etc. and good results were obtained (relative standard deviations $< 2\%$, recoveries $> 95\%$).

KEYWORDS: Lewatit Ionac SR-7, separation, preconcentration, chromium speciation, FAAS

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A New Dispersive Liquid-Liquid Microextraction Procedure for the Determination of Palladium

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Palladium is an element of increasing importance in today's industries. The annual production of palladium is estimated to be 195 tonnes; the majority of this is used in autocatalysts (55%), with other uses including electronics (16%), jewellery (11%), dental (8%), investment (5%) and chemical (4%) [1].

Development of analytical methods for the accurate and precise determination of traces of palladium is meaningful for quality control of industrial products, environmental monitoring as well as palladium ore exploration. In the determination of palladium in industrial materials and environmental samples, serious interferences often occur owing to matrix components [2].

The dispersive liquid-liquid microextraction (DLLME) is a miniaturized sample pretreatment technique based on a ternary component solvent system where the dispersion of fine droplets of the extraction solvent is accomplished within the aqueous phase [3].

In this study, we developed a new DLLME procedure combined with FAAS by applying a microsample introduction system for the final measurement of Pd(II). Under the optimized experimental conditions, aliquots of 10 mL of sample solution containing Pd in 0.1 mol L⁻¹ HNO₃ were placed into 50-mL screw cap glass test tubes with conic bottom. A mixture of 0.4 mL of methanol (disperser solvent), 0.1 mL of 0.1% 2,2'-furyldioxime solution (chelating agent) in methanol and 100 µL of chloroform (extraction solvent) was rapidly injected into the sample solution by using a microsyringe. A cloudy solution (water, methanol, and chloroform) was formed in the test tube. Then, the solution was centrifuged at 3000 rpm for 3 min, and the dispersed fine droplets of chloroform were deposited at the bottom of conical test tube. In order to determine the palladium in the chloroform phase, a 25 µL aliquot of this solution was introduced to the nebulizer of the flame atomic absorption spectrometer by using the micro injection method [4]. The developed method was successfully applied to catalytic converter, anode slime, road sediment, water samples and certified reference material [5].

KEYWORDS: palladium, dispersive liquid-liquid microextraction, 2,2'-furyldioxime, FAAS

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Determination of Gold by FAAS using DLLME Sampling

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Gold is one of the precious metals and extensively used in various areas. It is a nonessential toxic element, and some reports about allergic eczematous dermatitis as well as some nephrotoxic effects have been published [1]. Gold is widely distributed in nature and the chemistry of gold remains an active research area [2]. Gold could be used as a drug in the supervised therapy of arthritis and cancer in the form of different Au(I) and Au(III) compounds, or in radiotherapy of cancer in the form of radioactive isotope ^{198}Au .

The concentration of gold in environmental, geological and metallurgical materials is usually too low to be determined directly by AAS owing to insufficient sensitivity and matrix interferences. Therefore, a separation and preconcentration stage is often necessary for sensitive and interference-free gold determination [3].

In the study, we developed a new dispersive liquid–liquid microextraction (DLLME) procedure combined with FAAS by applying a microsample introduction system for the final measurement of Au(III) ions. Under the optimized experimental conditions, aliquots of 10 mL of sample solution containing Au(III) were placed into 50-mL glass test tubes with screw cap, which have conic bottom. A mixture of 80 μL of methanol (disperser solvent), 0.25 mL of 0.1% 1,5-diphenyl-1,3,5-pentanetrione (DPT) solution (chelating agent) (see Figure 1) in methanol and 20 μL of carbon tetrachloride (extraction solvent) was rapidly injected into the sample solution by using a microsyringe. A cloudy solution (water, methanol, and carbon tetrachloride) was formed in the test tube. In this step, Au(III) reacted with DPT and the formed complex was extracted into the fine droplets of carbon tetrachloride. Then, the solution was centrifuged at 3200 rpm for 4 min, and the dispersed fine droplets of carbon tetrachloride were deposited at the bottom of conical test tube. 20 μL of the sedimented phase was removed using a microsyringe. In order to determine the gold in the carbon tetrachloride phase, a 20- μL aliquot of this solution was introduced to the nebulizer of the flame atomic absorption spectrometer by using the micro injection method [4]. The gold signals were measured in the peak area mode utilizing the instrument software. The developed method was successfully applied to the real samples.

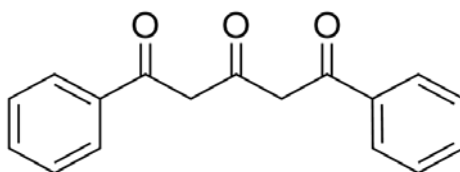


Figure 1. The structure of the chelating agent (DPT).

KEYWORDS: gold, dispersive liquid–liquid microextraction, 1,5-diphenyl-1,3,5-pentanetrione

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Preconcentration of Cu(II) and Ni(II) Ions with Solid Phase Extraction and Determination by Flame Atomic Absorption Spectrophotometry

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Heavy metal concentration levels in seawater are very low, sensitive analytical techniques as well as pre-concentration methods must be used to assess background levels of trace elements. Although flame atomic absorption techniques have maintained high selectivity and sensitivity, there is a crucial need for the preconcentration of trace elements in the seawater. Preconcentration and separation methods such as ion-exchange, co-precipitation, electroanalytical techniques, liquid-liquid extraction are used for different kind of samples. The solid phase extraction (SPE) is an productive approach which has widespread application in the area. The main advantages of solid phase extraction procedure are: high enrichment factor, lower consumption of reagent, no problem with the diffuse of solvent.

In this work, a simple and reliable method has been developed to separate and concentrate trace amounts of copper(II) and nickel(II) ions from seawater samples. The resulting analytes are prepared for flame atomic absorption spectrophotometric analysis. For this purpose, a new reagent, 1-phenyl-3-(2-pyridinyl)thiourea was synthesized and used as chelating reagent for the metals. Effects of pH and interfering ions as well as other critical parameters which control the recovery processes for Cu(II) and Ni (II) were investigated. In order to investigate the influences of matrix components, the recovery studies (R%) for the metals were made by use of synthetic seawater. The optimum pH for preconcentration was found to be 6 for both of the metals. Elutions of metals from the adsorbion material were performed by 1 M EDTA solution. By use of SPE method 1-phenyl-3-(2-pyridinyl)thiourea, enrichment factors of both metals were around 100. The novel SPE reagent and its application method can be satisfactorily used in seawater samples to enable the use of flame atomic absorption spectrophotometry by high sensitivity and accuracy.

KEYWORDS: Solid phase extraction, preconcentration, copper, nickel, atomic absorption spectrometry

A New Application of the Recently Developed Ratio Difference Spectrophotometric Method for the Determination of Ternary Mixtures with Overlapping Spectral Data

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Determination of ternary mixtures with overlapping spectra has always been a challenge facing spectrophotometry. A new application of the recently developed ratio difference spectrophotometric method [1-4] was applied for the determination of a ternary mixture with severely overlapping spectral data at certain points in their ratio spectra (coabsorptive points), a division step directly followed by calibration graphs construction relating the difference between those points and the corresponding concentration of each compound, thus keeping the simplicity and minimal data manipulation advantages offered by the ratio difference method. The proposed method was applied for the analysis of betamethasone, clotrimazole and benzyl alcohol in laboratory prepared mixtures and in their pharmaceutical formulation. The suggested method was validated according to USP 2005 guidelines and acceptable results were obtained indicating that the suggested method can be applied for routine analysis in quality control laboratories.

KEYWORDS: spectrophotometry; ratio difference method; ternary mixtures; betamethasone; clotrimazole; benzyl alcohol; isoabsorptive point and coabsorptive points.

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Spectroscopic Determination of Perlite Containing PVA,PVP,PAA Hydrogel Composites

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Polymer-clay hydrogel composites are one of the newest composite types, which its importance is came out especially after 2000. Polymers are used as matrix in these types of composites and clay minerals act as reinforcement material. By combining these two different structures, new materials can be synthesized which have better physical and chemical properties according to the normal polymers. Polymer-clay hydrogel composites can withstand higher temperature than normal polymer hydrogels. Additionally, physical properties such as impact resistance can be improved. These composites hydrogels can be used in daily life and industry where polymers are used [1]. In this study, Hydrogel composites are prepared by in situ freeradical polymerization. Because of their unique organic (polymer)/ inorganic (clay) network structure, high toughness and excellent optical properties and stimulus-sensitivity are simultaneously realized in hydrogels. Furthermore, NC gels exhibit a number of interesting new characteristics[2].

KEYWORDS: Hydrogel, Perlite, Polyvinyl Alcohol, Polyvinyl Prolidone, Polyacrylic Acid

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Characterization and Spectrophotometric Determination of Mn(II) in Aqueous Medium

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New ternary complexes of Mn(II) with py, bipy, and terpy as primary ligand (L_1) and substituted fluorescein as secondary ligand (L_2) were prepared. The stoichiometry for these complexes was found to be Mn(II): L_1 : L_2 = 1:2:1, and the complex formula proposed is $[Mn(L_1)_2(L_2)]$. The effect of substituent groups of L_2 and the nitrogen atoms of L_1 on complex formation with Mn(II) was studied. Moreover, the interference of some cations and anions in the determination of Mn(II) by this method was investigated and the interference of Cu(II) and Fe(III) with Mn(II) in their corresponding alloys were considered. A simple, rapid, and sensitive spectrophotometric method for determination of Mn(II) in its salts and Mn in its alloys is suggested.

KEYWORDS: Mn(II) - spectrophotometry – complex - fluorescein

Chemical Fractionation of Copper in Malachite Ore (Elazig, Turkey)

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Malachite or basic copper carbonate is a naturally occurring secondary copper mineral with the composition of $\text{Cu}_2(\text{OH})_2\text{CO}_3$. [1]. Determination of total copper in Malachite ore in Elazig (Turkey) was performed in two stage microwave-acid digestion followed by inductively coupled plasma optical emission spectrometer. A seven step sequential extraction process to speciation of copper from Malachite ore was investigated. The conventional method of Sanei et al. with modification was- used for the sequential extraction. Five grams of malachite sample was weighed in a 100 mL PTFE centrifuge tube and the following fractions obtained [2,3]:

Water soluble fraction: Malachite ore sample was leached at room temperature with deionized water. The extract was filtered and diluted.

Exchangeable fraction: the residue from sample (1) was extracted at room temperature with 1 M $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ at pH 7 by shaking. The extracts were centrifuged, and the supernatants were filtered through a GF/C filter membrane (Sartorius AG, Goettingen, Germany) and diluted.

Carbonate fraction: the residue from (2) was extracted with 1 M NaAc, at pH 5, by shaking. The extract was filtered and diluted.

Reducible fraction: the residue from (3) was extracted 0.1 M $\text{NH}_2\text{OH HCl}$ in CH_3COOH , for 6 h by shaking. The extract was filtered and diluted.

Oxidizable fraction: H_2O_2 (30%), at pH 2 was added the residue from (4) at 30 min interval to prevent from foaming. The mixture was heated with NH_4OAc in HNO_3 was added and the sample was diluted to and agitated continuously for 30 min.

Sulfide fraction: the residue from (5) was digested with aqua regia (3 HCl + 1 HNO_3) by shaking. The extract was filtered and diluted.

Residual: the residue from (6) was digested with a mixture of HNO_3 , HF and HCl. HNO_3 was added to the residue. The mixture was gently heated and evaporated on a sand bath. After cooling, HF was added; the mixture was slowly evaporated to dryness. The residue was dissolved by HCl, heated, then deionized water was added, heated and filtered. Rinsing with deionized water was repeated three times.

The accuracy obtained by comparing the determined content of Cu with certified values, using NCS DC73301 Rock – constituents, certified for the extractable contents of Cu, in malachite ore following a seven step sequential extraction procedure, was found to be satisfactory.

KEYWORDS: ICP-OES, copper, sequential extraction, malachite ore, chemical speciation

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Copper Speciation in Malachite Ore by ICP-OES

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Malachite is a bright green mineral consisting of basic copper carbonate. It is an abundant copper ore. It is always found through copper sulphur especially together with chalcopyrite, and at the end of oxidation in the upper parts of their deposits. This oxidation occurs, especially in the presence of calcium carbonate, with the impact of carbon dioxide, water, and air on copper sulfide. Malachite or basic copper carbonate is a naturally occurring secondary copper mineral with the composition of $\text{Cu}_2(\text{OH})_2\text{CO}_3$ [1]. Sequential extraction techniques have been usually used to fractionate metals in solid samples (soils, sediments, sludge, solid wastes, etc.) because of their leach ability. It uses a succession of chemical reagents that sequentially extract various targeted phases in sample. The results are useful for obtaining information about origin, mode of occurrence bioavailability, potential mobility and transport of elements in natural environments [2]. Thus make it the method of choice for the speciation of Cu. A modified Tessier sequential extraction procedure for the fractionation of Cu has been applied to malachite ore in Elazig, Turkey. Analyses were carried out by inductively coupled plasma optical emission spectrometry (ICP-OES). The 327.393 nm line was used because it offers better delectability and was free from major spectral interferences. The fractions extracted were: exchangeable (extraction step 1), Carbonates (extraction step 2), oxidizable-organic matter and sulfides (extraction step 3). The sum of the Cu content in the three fractions plus aqua-regia extractable content of the residue (extraction step 4) was compared to the aqua-regia extractable content of Cu (total copper concentration) in the malachite ore [2]. The accuracy obtained by comparing the determined content of Cu with certified values, using NCS DC73301 Rock – constituents, certified for the extractable contents of Cu, in malachite following a modified tessier four step sequential extraction procedure, was found to be satisfactory.

KEYWORDS: ICP-OES, copper, tessier sequential extraction, malachite ore, chemical speciation

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The Fractionation of Copper with BCR Sequential Extraction Procedure

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Malachite is monoclinic hydroxy carbonate of copper [1]. Malachite or basic copper carbonate is a naturally occurring secondary copper mineral with the composition of $\text{Cu}_2(\text{OH})_2\text{CO}_3$ [2]. It is always found through copper sulphur especially together with chalcopyrite, and at the end of oxidation in the upper parts of their deposits. This oxidation occurs, especially in the presence of calcium carbonate, with the impact of carbondioxide, water, and air on copper sulfide. Total concentration of Cu is still useful in many areas, the knowledge of speciation is of primary importance because the toxicity, mobility, bioavailability, and bioaccumulation depend on the chemical species. The advantages of the technique include a high degree of automation, good reproducibility, and short analysis time and thus make it the method of choice for the speciation of Cu. A revised sequential extraction procedure for the fractionation of Cu, proposed by the Commission of the European Communities Bureau of Reference (BCR) has been applied to from malachit ore in Elazig, Turkey. Analyses were carried out by inductively coupled plasma optical emission spectrometry (ICP-OES). The 327.393 nm line was used because it offers better detect ability and was free from major spectral interferences. The fractions extracted were: exchangeable (extraction step 1), reducible-iron/manganese oxides (extraction step 2), oxidizable-organic matter and sulfides (extraction step 3). The sum of the Cu content in the three fractions plus aqua-regia extractable content of the residue (extraction step 4) was compared to the aqua-regia extractable content of Cu (total copper concentration) in the malachite ore [3]. The accuracy obtained by comparing the determined content of Cu with certified values, using NCS DC73301 Rock – constituents , certified for the extractable contents of Cu, in malachite ore following a modified BCR-four step sequential extraction procedure, was found to be satisfactory.

KEYWORDS: ICP-OES, copper, BCR sequential extraction, malachite ore, chemical speciation

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Determination of Trace Elements in Human Hair by ICP-OES in Diyarbakir, Turkey

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The past several years have seen a rapidly developing interest in the use of hair analysis as a screening tool in medical practice and assessing the nutritional and toxicological status of the body [1]. The concentrations of toxic elements in human hair have been used by many investigators for monitoring environmental or occupational exposure and evaluating heavy metal poisoning. Human hair is an attractive biological material because of the simplicity of sampling, storing, transport and handling, as well as for the fact that it can store the information about contamination over a long period [2]. Another advantage of this material is that some trace elements are considerably more concentrated in hair than in other biological materials (for e.g., hair contains 300 times more mercury than blood), which makes analysis easier [3].

In this study we were collect colored and uncolored hair samples (30 samples) in Diyarbakir, Turkey and we compared with trace elements in colored and uncolored hair samples. Hair samples were washed by a standard procedure proposed by the International Atomic Energy Agency [2,4]. The samples were agitated with acetone, then three times with deionized water and with acetone. The contact time of the cleaning medium with the sample was 10min. The samples were finally dried and 0.5 g of the sample was treated with HNO_3 in the microwave oven. After cooling to room temperature, the solutions were transferred into beakers. To each sample, H_2O_2 was added drop wise and heated for some minutes. The solutions obtained were made up to 50ml with redistilled water and the determination of trace elements was by ICP-OES. The precision and accuracy of this procedure were checked by the use of certified reference materials.

KEYWORDS: Trace elements, human hair, ICP-OES

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Determination of Antimony in Gunshot Residue by GFAAS

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Antimony is an uncommon element and it may be a strong indicator of gunshot firing. It is the major element present in GSR (Gunshot residue). The amount of that element on the hands of shooters depends on several factors, such as the type of weapon and munitions used, the age and condition of the weapon, the suspect's personal hygiene and occupational habits, biometrics, and the time elapsed since the firing. The quantification of the element removed from the hands of shooters depends on both the quality of the sampling protocol and the analytical instrumentation employed[1]

Detection and identification of GSR are commonly performed with the aim of determining whether or not a suspect fired a gun, to determine a bullet entrance hole or to estimate a firing distance [2] and [3]. Little success has been achieved in using GSR to provide investigative leads other than those described [4].

In this research we have studied about 15 different types of adhesive-tape which are used by crime scene investigators and sold in market. Analyzes were based on elemental detection of antimony in samples by graphite furnace atomic absorption spectrometer (GFAAS).

KEYWORDS: gunshotresidue, antimony, GFAAS

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Application of Modified Tessier Sequential Extraction for Copper Fractionation in Dicle (Tigris) River Sediment Polluted by Historic Open-Cast Mining

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The principal copper (Cu) source in eastern Anatolia is in the Ergani mining area north of modern Diyarbakir, SE Turkey. It is well-known for its cupriferous pyrite ore deposits associated with ophiolite, but the reserve is on the decrease recently. A Cu smelter and a Cu ore processing factory located here. The world's oldest and Turkey's largest open cast copper mine is located close to the upstream of Dicle (Tigris) river. Processing of Cu ore caused man-made heavy metal pollution of the local environment. The principal environmental impacts of Ergani Copper Co. include pollution by liquid effluents discharges to Dicle (Tigris) river, infiltration of soils, contamination of underground waters, residue disposal, and threats from tailings dams [1]. Sediments are highly complex mixtures of minerals and organic compounds in which ions are associated by adsorption, absorption, or complexation [2]. River surface sediments play an important role as pollutants and they reflect the history of the river pollution. In sediments, heavy metals are present in a number of chemical forms, and generally exhibit different physical and chemical behaviors in terms of chemical interaction, mobility, biological availability and potential toxicity. Measurement of the total concentration of Cu provides inadequate information to assess the bioavailability or toxicity of Cu. The toxicity of Cu depends especially on its chemical forms rather than its total elemental content. Sequential extractions can be useful to have an operational classification of metals in different geochemical fractions. Cu in river sediments can be bound to various compartments; adsorbed on clay surfaces or iron and manganese oxyhydroxides; present in lattice of secondary minerals like carbonates, sulphates or oxides; occluded in amorphous materials such as iron and manganese oxyhydroxide; complexed with organic matter or present in lattice of primary minerals such as silicates [3]. The goal of the study is to determine the total and fractionation of Cu occurrence in Dicle (Tigris) river surface sediments. Determination of total Cu in river surface sediment was performed in two stage microwave-acid digestion followed by inductively coupled plasma optical emission spectrometer at 327.393 nm. The modified Tessier sequential extraction technique [4] was used to study the mobility and dynamics of operationally determined chemical forms of copper in the river surface sediment samples collected from Dicle (Tigris) river basin, Turkey. Total Cu concentration in the sediment is 130.04 mg kg⁻¹ dry weight (d.w). The most abundant Cu fraction in studied sediment sample was found as residual fraction of Cu (71.83 mg kg⁻¹). Relative abundances of the remaining Cu fractions in river surface sediment are as follows: organic matter and sulfides (38.98 mg kg⁻¹) > carbonates (11.39 mg kg⁻¹) > exchangeable (7.84 mg kg⁻¹). Cu compounds are mainly bound to the organic matter/sulfides and residual fractions (85.21 % of total copper extracted). The results reveal that high environmental risk of Cu, are due to their higher availability in the exchangeable fraction. Substantial amount of Cu, is observed as carbonate bound, which may result due to their special affinity towards carbonate and their co-precipitation with its minerals. Even though Cu is generally adsorbed to a greater extent than other metals with the exception of lead, the high affinity of Cu²⁺ ions for soluble organic ligands may greatly increase their mobility in sediments. Cu can easily complex with organic matters because of the easy formation of high stability constants of organic-Cu compounds. The residual fraction represents the Cu that have strongest association with the crystalline structures of the minerals. It is always not easy to extract Cu in this fraction [5]. The modified Tessier sequential extraction scheme allows quantitative knowledge of Cu distribution in Dicle (Tigris) river surface sediment historically contaminated with acid mine drainage.

KEYWORDS: copper mining, Tessier sequential extraction, Dicle (Tigris) river, sediment, ICP-OES

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Direct Determination of Silver by SQT –FAAS Technique

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Silver has soft, white, lustrous transition metal; it possesses the highest electrical conductivity of any element and the highest thermal conductivity of any metal. Today, silver metal is also used in electrical contacts and conductors, in mirrors and in catalysis of chemical reactions. Its compounds are used in photographic film, and dilute silver nitrate solutions and other silver compounds are used as disinfectants and micro biocides (oligodynamic effect). While many medical antimicrobial uses of silver have been supplanted by antibiotics, further research into clinical potential continues [1].

Since the early days of the flame AAS technique, two important negative aspects of this approach came to the attention of researchers. One was the relatively low efficiency of the sample introduction system; nebulization is only 1–10% efficient, therefore most of the sample is not transported to the atomizer and there is a great dilution of the sample by flame gases. The resulting analyte concentration in the measurement zone is relatively low where the source lamp beam and atoms occupy the same volume for signal formation. The second deficiency noted was the short residence time of analyte atoms in the measurement zone; this value, considering flame velocities and beam geometry, could be calculated to be in the order of few milliseconds. Both of these deficiencies limit the sensitivity of the flame AAS technique. *Slotted quartz tube atom trap (SQT-AT)* is one of the atom trap technique [2]. SQT has also been employed as a preconcentration device or an atom trap, where the analyte species introduced to flame by nebulization are trapped on the inner SQT surface, followed by rapid revolatilization and atomization effected by introducing 10–50 µL of an organic solvent [3], [4] and [5].

In this study, analytical parameters, namely composition of the aqueous medium, sample flow rate, flame conditions, distance between burner head and SQT, sampling period and type of organic solvent and its volume have been optimized for the determination of silver. So, the method described requires very simple and inexpensive equipment.

KEYWORDS: SQT, FAAS, silver, atom trap

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Interference Studies of Lead by SQT-FAAS

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FAAS is an analytical technique with high sensitivity is required for detection of a lot of metals. A nebulizer is used to produce fine droplets in FAAS. It was reported that typical nebulization efficiency that is the ratio of the sample amount transported to flame to the sample amount introduced to nebulizer is in the range of among 1–10% [1]. Therefore, a significant part of the sample is not transported to the atomizer. For this reason, several analytical techniques have been used to improve the sensitivity of FAAS. One of the attempts to improve the sensitivity of FAAS was suggested by Watling [2,3]; a quartz tube with two slots was placed on flame and the atomization signal was monitored in this tube by using ordinary nebulization. As one of these slots was designed to allow the laminar flame in, the upper one was also found to be necessary for reduced turbulence. For some elements such as Ag, As, Bi, Cd, Pb, Sb, Se and Sn, the increase in sensitivity was 2–5 folds depending on the element. Among the reasons suggested to improve the sensitivity are reduced flame speed, longer optical path and the increased lifetime of free analyte atoms in flame [1]. This device and the relevant technique were called slotted quartz tube (SQT) and SQT-FAAS, respectively. Among these recent reports by SQT-FAAS, a sensitivity increase for lead and cadmium was obtained as high as 6 and 10 fold, respectively [4]. In organic solvent aspiration technique, 10–50 μL of an organic solvent, most often isobutyl methyl ketone (IBMK), is introduced and nebulized into the flame; the momentary change in the flame fuel/oxidant ratio is believed to be the reason of re-atomization from the quartz surface [5,6]. From these studies, SQT-AT-FAAS has evolved as an efficient alternative for sensitivity enhancement with FAAS[7].

In this study, a sensitive analytical method for lead determination will be reported by using SQT-FAAS and then SQT-AT-FAAS. was used as an atom trap (AT) where the analyte is accumulated in its inner wall prior to re-atomization. The signal is formed after re-atomization of analyte on the trap surface by introduction of 10 μL of isobutyl methyl ketone (IBMK). Sensitivity was improved using SQT-AT-FAAS system with respect to conventional FAAS and with respect to SQT-FAAS without any collection. Characteristic concentration (C_0) and limit of detection values were found. In addition, interference effects of some elements on lead signal were studied.

KEYWORDS: SQT, FAAS, Lead, Atom trap

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Trace Metals and Minerals in Some Spices and Herbs

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Spices and herbal plants contain metal ions over a wide range of concentrations. Metals can have important positive or negative roles in human life. Twenty-three elements have known physiological activities in humans and other mammals. Some of these elements, including iron, zinc and copper, are considered essential. Other metal ions such as cadmium, lead and mercury have toxic roles in biochemical reactions on our body. The metals vanadium, chromium, manganese, iron, cobalt, copper, zinc and molybdenum; and the non-metals selenium, fluorine, and iodine are trace elements that belong to the category of micronutrients, which are needed by the human body in very small quantities (generally less than 100 mg/day). Other elements are considered to be macronutrients, e.g. sodium, calcium, magnesium, potassium, chlorine, etc., which are required in larger quantities. Some trace elements are essential components of biological structures, but they can also be toxic at concentrations beyond those necessary for their biological functions. Examples of these metals include cobalt, copper, chromium and nickel [1,2].

Herbs and spices (ginger, curcuma longa, Prunusmahaleb, fennel, clove, rhus, laurus, equisetum, achilleamillefolium, senna, camomile, mint, cinnamon and achilleamillefolium etc.) were analysed using FAAS and ICP-OES. So, their trace metallic analyte concentrations (As, Ba, Ca, Cd, Co, Cr, Cu, Fe, Mg, Mn, Ni, Sr, Zn, etc.) in acid digests of these materials were determined. To ensure that the results obtained for the analyses were accurate, a certified reference material was analyzed.

KEYWORDS: Herbs, Spices, Trace elements, FAAS, ICP-OES

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Simultaneous Spectrophotometric Determination of Phenolic Antioxidant (BHA and BHT) in Capsules and Chewing Gums by Using H-Point Standard Addition Method

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Antioxidants and preservatives are commonly added to food, drugs and cosmetic products to prevent alteration and degradation due to microbial contamination or oxidation. Antioxidants are used to inhibit lipid oxidation [1]. Synthetic phenolic antioxidants (SPAs), such as propyl gallate (PG), tertiary butyl hydroquinone (TBHQ), butylated hydroxyanisole (BHA), and butylated hydroxytoluene (BHT), are increasingly used instead of natural antioxidants due to their high stability [2]. To ensure food safety and safeguard the health of the general public, the use of SPAs in food is strictly controlled in many countries, whether singly, which is the usual case, or in combinations, the corresponding permitted levels range from 100 to 200 mg kg⁻¹ [3]. The regulatory amounts of SPAs are primarily based on the acceptable daily intake for a healthy individual [2].

In this study, a simple, rapid and sensitive spectrophotometric method was described for the simultaneous determination of binary mixtures of BHA and BHT in pharmaceutical capsules and chewing gums, without prior separation steps using the H-Point standard addition method (HPSAM). In this method, the concentration of one antioxidant was calculated from overlapping spectra at two appropriate wavelengths, where the other antioxidant was selected as interferent present the equal absorbance relationship. These wavelength pairs are generally easily found and can be selected to give the most precise analytical results.

Absorbances at two pairs of wavelengths, 265 and 288 nm (when BHA acts as analyte) or 288 and 295 nm (when BHT acts as analyte) were monitored, while adding standard solutions of BHA or BHT, respectively.

The calibration graphs were linear in the for BHA and for BHT were 4-20 and 20-100 µg.mL⁻¹, respectively. The correlation coefficients of BHA and BHT were 0,9999 and 0,9997, respectively. The accuracy and reproducibility of the determination method for various known amounts of BHA and BHT in their binary mixtures were evaluated. The proposed method was validated successfully applied to the determination of synthetic antioxidants (BHA and BHT) in synthetic binary mixtures with different concentration ratios and commercial products (pharmaceutical capsules and chewing gums). The results were statistically compared with the derivative spectrophotometric method which has been previously reported, and very similar values were found between the methods.

Quantification of Synthetic Phenolic Antioxidants in Capsules and Chewing Gums by Derivative-Differential UV Spectrophotometry

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Synthetic phenolic antioxidants (SPAs) are widely used in food systems for prevention of lipid oxidation during processing and storage. This oxidation is responsible for the production of volatile compounds forming unpleasant flavours. The use of SPA in foodstuffs is strictly regulated and in the European Communities (EU) the directive 95/2/ EC lays down the rules for their use [1]. The synthetic compounds butylated hydroxyanisole (BHA), and butylated hydroxytoluene (BHT) are the antioxidants most frequently used as additives in lipid-containing foods [2]. They have been used both alone and in mixtures in oils. The conclusions of research carried out on the effects of these substances on consumer health are contradictory. On one hand, it has found that these synthetic antioxidants exert toxic effects in some animal tissues [3] and that even at low dose levels phenolic compounds may produce additive/synergistic effects as regards carcinogenesis [4] and therefore their use is being questioned [5]. By contrast, these substances have also been found to have anti-mutagenic and anti-tumour properties [6]. Consequently, the analytical control of these compounds in foods is of considerable importance. The use of synthetic antioxidants is regulated in the legislation of most countries, the limit amounts that can be added to foods being strictly defined [7].

In this study, a method is presented for the direct determination of BHA and BHT in medicine capsules and chewing gums, without the need for any separation step. The derivative-differential spectrophotometry, comprised of measurement of the difference absorptivities for BHT and derivatized in the first order (DD₁) for BHA of a capsule or chewing gum extract in 0,1 N NH₄OH relative to that of an equimolar solution in methanol at wavelengths of 281 nm and 305 nm, respectively. Linear calibration graphs of differential first derivative values (at 305 nm for BHA) and absorbance values (at 281 nm for BHT) versus concentration (in the ranges 10-40 and 20-100 µg.mL⁻¹ for BHA and BHT, respectively) were obtained with negligible intercepts. The detection and quantification limits were also calculated. The relative standard deviations were found to be less than 2,8 and 1,75 % for BHA and BHT, respectively, indicating reasonable repeatability of the method. The proposed method is found to be selective, linear ($r > 0,998$), accurate (recovery: 65% to 88% and 93,45% to 101,99% for BHA and BHT, respectively) and precise (%RSD < 3%) in the respective linear concentration ranges. The method is successfully applied for the analysis of these antioxidants in the laboratory prepared mixtures with different concentration ratios, capsules and chewing gums. The reliability of the method was further ascertained by recovery studies via standard addition procedure. The results obtained were compared with the results of the derivative spectrophotometric method which has been previously reported and very similar values were found between the methods.

KEYWORDS: synthetic phenolic antioxidant, BHA, BHT, derivative-differential UV-spectrophotometry, medicine capsules, chewing gum

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Simultaneous Analysis of Binary Mixtures of Allura Red (E 129) and Carmine (E120) By Using First Derivative Spectrophotometry

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Natural or synthetic food colorants are often added to foodstuffs and soft drinks in order to maintain the natural color during process or storage and to create the desired colored appearance. However, synthetic colorants have more advantages than natural dyes such as low price and high stability. At present, synthetic colorants are widely used to make food more attractive and appetizing. Due to their toxicity, especially when consumed in excess, synthetic colorants are strictly controlled by laws, regulations and acceptable daily intake (ADI) values for food safety. Food colorants can cause serious disorders and diseases like nausea, headache, ulceration, lung cancer, hyperactivity, anemia, and also have effect on eye, skin, mucous membrane etc. That's why there is a necessity to control the content of these dyes in food. For that purpose many analytical methods have been developed like: Derivative spectrophotometry [1], H-point standard addition method [2] and Cloud point extraction [3] Derivative spectrophotometry offers a useful approach for the analysis of binary and ternary mixtures of synthetic food colorants. Objective of the current study was to develop simple and rapid simultaneous method for the determination of Allura Red (E 129, AR) and Carmine (E 120, CAR) which are used for coloring the chewing gums.

Derivative spectrophotometric method was based on first derivative absorption at 529.5 nm for AR (zero-crossing for CAR) and 509.8 nm for CAR (zero-crossing for AR). The method applied in the concentration range of 4-20 $\mu\text{g.mL}^{-1}$ for AR and 10-50 $\mu\text{g.mL}^{-1}$ for CAR. The results showed higher correlation coefficient ($r_{\text{AR}} = 0.9991-1.000$ and $r_{\text{CAR}} = 0.9997-0.9999$) in the proposed method. Further, the method was validated for precision, accuracy and assessed the synthetic colorant contents in laboratory prepared mixtures with different concentration ratios and in chewing gum sample. The method do not require any separation step. The detection limits (LOD) for AR and CAR were found 0.705 and 0.65 $\mu\text{g.mL}^{-1}$, respectively; while the quantification limits (LOQ) were found 2.35 $\mu\text{g.mL}^{-1}$ for AR and 2.16 $\mu\text{g.mL}^{-1}$ for CAR. The relative standard deviations were found to be less than $\text{RSD} < 2\%$, indicating reasonable repeatability of the method. The proposed method is found to be selective, linear ($r > 0.999$), accurate (recovery= 95% to 108%) and precise ($\text{RSD} < 4\%$) in the respective linear concentration ranges. The method is successfully applied for the analysis of these colorants in chewing gum samples without pretreatment. The reliability of the method was further ascertained by recovery studies via standard addition procedure.

KEYWORDS: derivative spectrophotometry, simultaneous determination, chewing gum, Allura Red, Carmine, food colorants

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Cloud Point Extraction and Spectrophotometric Determination of Synthetic Colors in Tablets Using Nonionic Surfactants

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Synthetic dyes are used in textile, leather, paper, rubber, plastics, cosmetics, pharmaceuticals and food industries. Generally, synthetic dyes have complex aromatic structures that make them stable and difficult to biodegrade [1]. In recent years, natural food colors have been increasingly used for the consumer preference. However, they are relatively unstable and the costs are higher than synthetic food colors. Therefore, synthetic food colors are still used instead of natural colors in many pharmaceuticals [2]. Many countries have regulated the use of some of azo dyes in pharmaceuticals because they pose a potential risk to human health and are even carcinogenic [3]. Therefore, the development of a simple, sensitive and accurate test method for the analysis of these chemicals in pharmaceuticals is an important task [4]. For this purpose, any method should be inexpensive, environmentally friendly, easy and should allow fast sample preparation and detection of permitted and banned colors in different types of pharmaceutical products. In the last few years, there has been much interest in the use of cloud point extraction (CPE) with non-ionic surfactants because of the use of inexpensive solvents, less toxicity and more ecologically friendly characteristics compared to organic solvents. Non-ionic surfactants in water become cloudy at a surfactant specific temperature (cloud point), which results in phase separation. Separation of a surfactant micelles-rich layer enables the extraction of compounds from water. This technique has been described for the extraction and preconcentration of metals, phenols and some permitted and illegal food colors. There are a number of important parameters that have to be optimized for CPE to increase recovery of target compounds. These parameters are the type of surfactant, concentration of surfactant, extraction temperature, addition of salt, concentration of salt, pH, heating time, and centrifugation time [5]. In this study, CPE is carried out to extract synthetic dyes from pharmaceutical products using two different non-ionic surfactants, TX-100 and TX-114. The effect of different operating parameters, e.g. concentrations of surfactant, dye and salt, temperature, pH on extraction of both dye and surfactant, incubation and centrifuge times have been studied in detail. Under the optimal conditions, the analytical characteristics of the method (e.g. limit of detection and quantification, linear range and preconcentration factor) were obtained. The proposed method was successfully applied to the determination of synthetic dyes in the laboratory prepared mixtures with different concentration ratios and in the pharmaceutical products.

KEYWORDS: cloud point extraction, pharmaceutical, erythrosine, quinoline yellow, indigo carmine, synthetic dyes

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A Simple Flow Injection Spectrophotometric Procedure for the Direct Determination of Copper (II) in Environmental Samples

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Copper is essential element with an important role in living organisms and one of the main toxic elements in the environment [1]. Several methods such as graphite furnace atomic absorption spectrometry (GF-AAS) [2], inductively coupled plasma optical emission spectrometry (ICP-OES) [3], and ion selective electrode (ISE) [4] have been developed to determine the copper(II) ions in solutions depending on its concentration. In our previous studies [5,6] we developed simple flow-injection analysis methods for the selective and sensitive determination of copper (II) in sea and river water samples by using different complexing agents.

In this study, a new simple, rapid and very sensitive flow-injection spectrophotometric detection has been developed for the on-line determination of copper (II) in environmental water samples. The method is based on the measurement of the absorbance of the coloured complex formed by copper(II) with the Alizarin Red S (also known **3,4-dihydroxy-9,10-dioxo-2-anthracenesulfonic acid sodium salt (ARS)**) in an acidic medium. The optimum conditions for the reaction of Cu (II) with ARS is studied and the complex is selectively monitored at max 510 nm. With the reagent carrier solvent (3.5×10^{-5} M ARS solution and 0.1 M acetate buffer, pH 5.0) flow-rate of 1.0 mL min^{-1} . The calibration graph was linear in the Cu (II) concentration range $2\text{--}110 \text{ } \mu\text{g L}^{-1}$ with the detection limit of $0.6 \text{ } \mu\text{g L}^{-1}$ (RSD=3.3 %, n=6) was obtained at a sampling rate of 80 sample h^{-1} . The detailed study of various interferences confirmed the high selectivity of the developed method. The proposed method was successfully applied to determination of copper(II) in real samples including river water and seawater. The accuracy of the method was demonstrated by the analysis of standard reference material MBH-C31XB20.

KEYWORDS: Flow-injection spectrophotometric method; Cu (II) determination; Alizarin Red S

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Determination of Nizatidine-H2 Receptor Antagonist in Pharmaceutical Dosage Form by Reversed Phase Liquid Chromatography

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Nizatidine, a histamine H₂-antagonist, is known to ACE inhibitor used clinically generally used for patients with stomach ulcer and gastro-esophageal reflux disease in daily clinics. Nizatidine works by decreasing the amount of acid produced by the stomach. Nizatidine; stimulate the release of stomach acid, reduces stomach acid by blocking chemicals called histamines [1-2].

In this study, a method was developed for analysis of nizatidine. It is well separated on X-Terra RP-18 (250 x 4.60 mm ID x 5µ) column by using the mobile phase consisting of a mixture of acetonitrile (15:85; v/v, 20 mM H₃PO₄; pH=7) at a flow rate of 1.0 mL/min and 25 °C. Very well sensitivity for all analytes was observed with DAD detection. The internal standard method was used to draw the calibration graph, ranitidine was chosen as internal standard. After, anaysis of nizatidine was carried out in pharmaceutical dosage form.

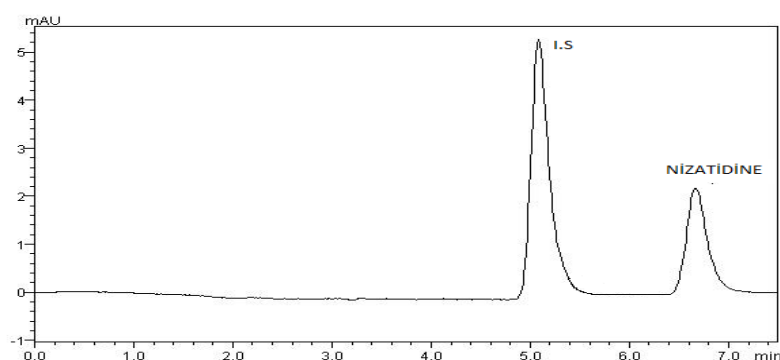


Figure 1. Chromatograms obtained from standards mixtures: Chromatogram of standard mixture; Nizatidine (1 µg/mL) and Internal standard (2 µg/mL)

KEYWORDS: Nizatidine, ACE, RP-HPLC

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The Investigation of the Effects of the Interferences on the Determination of Fe in Food, Glass and Water Samples by ICP-MS

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Inductively Coupled Plasma Mass spectrometry (ICP-MS) is a powerful technique for the determination of elements with a high accuracy and precision. Large linear dynamic range and simultaneous determination of elements are some of the many advantages of ICP-MS. But, interferences are the most formidable complications when analyzing samples with a complex matrices. Molecular interferences are the most complicated interferences in ICP-MS. For avoiding the interferences different technologies are developed by different commercial ICP-MS manufactures such as collision reaction cells, dynamic reaction cells, sector field ICP-MS. The Universal Cell Technology combines patented dynamic reaction cell and collision in the same reaction cell. This cell consists of four rod like a quadrupole and located between ion deflector and mass analyzer. By pressurizing the cell with ammonia, methane, hydrogen or oxygen several molecular reactions has occurred in the cell. These reactions are charge transfer, atom transfer and collision induced dissociation. In collision mode helium is used as a collision gas. Collision mode uses kinetic energy discrimination for eliminating interferences by using non-active gas. Without using any reaction mode, the results of the analyses could be incorrect in the presence of interferences.

Iron can be effected by molecular interferences. The molecular species can effect the determinations of iron isotopes ^{54}Fe , ^{56}Fe , ^{57}Fe and ^{58}Fe by ICP-MS are shown in table 1.

The table 1 the potential interferences of iron.

Isotope	Abundance	Potantiel Interferences
^{54}Fe	5.82	$^{37}\text{Cl}^{16}\text{O}^+\text{H}^+$, $^{40}\text{Ar}^{14}\text{N}^+$, $^{38}\text{Ar}^{15}\text{N}^+\text{H}^+$, $^{36}\text{Ar}^{18}\text{O}^+$, $^{38}\text{Ar}^{16}\text{O}^+$, $^{36}\text{Ar}^{17}\text{O}^+\text{H}^+$, $^{36}\text{S}^{18}\text{O}^+$, $^{35}\text{Cl}^{18}\text{O}^+\text{H}^+$, $^{37}\text{Cl}^{17}\text{O}^+$
^{56}Fe	91.66	$^{40}\text{Ar}^{16}\text{O}^+$, $^{40}\text{Ca}^{16}\text{O}^+$, $^{40}\text{Ar}^{15}\text{N}^+\text{H}^+$, $^{38}\text{Ar}^{18}\text{O}^+$, $^{38}\text{Ar}^{17}\text{O}^+\text{H}^+$, $^{37}\text{Cl}^{18}\text{O}^+\text{H}^+$
^{57}Fe	2.19	$^{40}\text{Ar}^{16}\text{O}^+\text{H}^+$, $^{40}\text{Ca}^{16}\text{O}^+\text{H}^+$, $^{40}\text{Ar}^{17}\text{O}^+$, $^{38}\text{Ar}^{18}\text{O}^+\text{H}^+$, $^{38}\text{Ar}^{19}\text{F}^+$
^{58}Fe	0.33	$^{40}\text{Ar}^{18}\text{O}^+$, $^{40}\text{Ar}^{17}\text{O}^+\text{H}^+$

In this study, the iron concentrations in glass, food and water samples with ICP-MS by using different working modes were determined. The results were compared then the possible interferences and the elimination conditions of interferences were investigated. For this purpose, collision mode, reaction mode and standard mode are used for the determination of Fe isotope concentrations in different matrices. Different kinds of certificated materials glass and food samples were used for verification.

KEYWORDS: ICP-MS, Interferences, iron isotopes

Parameters to Optimize the Residual Stresses on the Surface of The Deposited Layer Under Beam

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The surface coating by laser opens up new possibilities for repairing and rebuilding of worn parts. This technique has already been applied to a wide range of alloys for various cases such as anti-wear deposits, corrosion, thermal barrier differs from other means of thermal spraying competitors by its ability to generate fine microstructures.

It is well established that the quality of a coating produced by powder spraying under power laser beam requires optimization at both the geometrical parameters (dilution, dimensions) and morphological (appearance, cracks) than that of the residual stresses [1]. The technical and economic benefits of this type of treatment have stimulated many optimization studies. Many of them have been devoted to the control of residual stresses [2-3]. While the feasibility of these treatments is well established, the problem is related to residual stresses, meanwhile, very poorly understood.

If we want to control the level of these constraints and search, which is usually the most beneficial, it is essential, first, to understand the mechanisms involved in their creation and, secondly, to quantify stresses thus generated. To achieve this goal, we have developed a phenomenological approach to character based on decomposition into blocks of stress fields and their mutual interactions. After introducing the method of making deposits and the determination of stress fields, we study the influence of each parameter separately on the level of this surface of the deposited layer. The results will be discussed and compared with those obtained experimentally.

KEYWORDS: laser deposition - coating - residual stresses - modeling of residual stresses

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Simultaneous Separation of Arsenic and Selenium Species by Anion Exchange Chromatography and ICP-MS Detection

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Selenium is an essential element for animals and humans over a narrow concentration range [1]. It is in the structures of glutathione peroxidases, phospholipid hydroperoxide glutathione peroxidase, type I 5' iodothyronine deiodinase and thioredoxin reductases. Low activities of enzymes could result in elevated concentration levels of peroxides and free oxygen-containing radicals. Over the range, it shows toxic effects, and below the range, deficiency is observed [2].

On the other hand, Arsenic is a nonessential element for both animals and plants. It mainly occurs as arsenite and arsenate in the environment. Arsenate is a phosphate analog, and therefore it can compete with phosphate in the cytoplasm, replacing phosphate in ATP, leading to the disruption of energy flows in cells [3].

In the present study, simultaneous separation of five selenium species, namely Se(IV), Se(VI), selenomethionine, selenocysteine, selenomethyl selenocystine, and two arsenic species, As(III) and As(V), was performed by using anion exchange chromatography coupled to ICP-MS. Different mobile phase compositions were studied. First mobile phase was ammonium phosphate buffer in 5% (v/v) methanol at pH values of 5.0, 7.0 and 9.0. At pH 9.0 As(III) and As(V) was successfully separated within 8 min. However, selenocystine and selenomethionine were strongly retained in the column and did not elute within 40 min. A lower pH value, namely pH 7.0, was studied and a better separation was achieved but peaks were not baseline separated. Lowest pH value, pH 5.0, resulted in full separation but Se(VI) could not be eluted within 30 min.

Second mobile phase system was ammonium citrate buffer at pH values 5.0, 5.5 and 6.5. At pH 6.5, all the analytes were separated except Se(IV) and Se-(methyl) selenocysteine. These two species were co-eluted. At pH 5.5, peaks were separated but cannot be baseline resolved. Lowest pH value resulted in best separation of five selenium and two arsenic species.

KEYWORDS: Selenium, Arsenic, Speciation, Anion exchange chromatography

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Indium Determination by Volatile Compound Generation Atomic Absorption Spectrometry

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In this study, volatile compounds of Indium were generated prior to atomization using NaBH₄ as a reducing agent. However, reproducibility of the results was not enough for optimization of the parameters due to high memory effect. A new flow injection volatile compound generation system was used in order to overcome this problem. In this design, reaction coil was removed from an ordinary hydride generation system and volatile compounds were rapidly separated and transported to the quartz T-tube atomizer [1]. In this system, it was realized that hydrogen flame inside the quartz T-tube constitutes a convenient atmosphere for atomization of In species and absorption read-out drops sharply when hydrogen flame is removed. Using this system, a trapping technique was developed. During collection of analyte, oxygen is introduced into the inlet arm and an oxygen-hydrogen flame formed is used to consume hydrogen generated. At the end of the collection cycle, oxygen gas is stopped and atomization is realized. An external hydrogen gas flow is integrated into the system for further minimization of memory effect during atomization. In order to maximize the sensitivity of system, O₂ gas flow rate, Ar gas flow rate for transportation of volatile compounds generated, collection time, injection loop volume and temperature of the quartz T-tube were optimized and the values found were 80 mL min⁻¹, 300 mL min⁻¹, 60 s, 1.0 mL and 980°C, respectively.

Applying this technique, limit of detection was found to be 12 ng mL⁻¹, which is described as 3 times the standard deviation of the signal for 100 ng mL⁻¹ standard solution. Precision was 4.9% in terms of RSD, for 1.00 mg L⁻¹ In standard, n=6. The detection limit can be further improved if the collection time and/or injection loop volume is increased.

KEYWORDS: indium, hydride generation, atomic absorption spectrometry

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Inorganic Tellurium Speciation Using Tungsten-coil Atom Trap and Hydride Generation Atomic Absorption Spectrometry

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Tellurium belonging to group 16 in the periodic table is one of the rarest elements on the Earth's crust with an abundance in the order of $\mu\text{g/kg}$ [1]. The most common forms of this element in the nature are Te(IV) and Te(VI). It is known that toxicity of Te(IV) is 10 times higher than Te(VI) [2]. Since tellurium has a low abundance, its concentration cannot be determined by common analytical methods such as spectrophotometry or conventional flame atomic absorption spectrometry (AAS). Hydride generation AAS using tetrahydroborate is considered to be one of the most widespread techniques for determination of trace amounts of hydride forming elements including Te. *In situ* hydride trapping has also become popular in recent years as lower limits of detections can be obtained by this approach [3]. Speciation analysis of tellurium can be realized by means of HGAAS on the basis of different treatments of Te(IV) and Te(VI). While Te(IV) forms hydride readily with sodiumborohydride, Te(VI) does not [4].

In this work, a continuous flow hydride generation AAS system combined with a tungsten-coil atom trap system was used. Optimization parameters affecting analytical signals were tested and optimized. Calibration curves were plotted for both systems. Using continuous flow HGAAS system, LOQ and LOD values are 3.73 ng/mL and 1.12 ng/mL, respectively. In tungsten-coil atom trap system, LOQ and LOD values were found to be 0.97 ng/mL and 0.29 ng/mL, respectively. In addition, reduction of Te(VI) to Te(IV) was carried out by microwave assisted prereduction using HCl. Total concentration of Te was determined after reduction procedure. Amount of Te(VI) was determined by subtracting Te(IV) concentration from total Te.

KEYWORDS: tellurium, atom trap, speciation, hydride generation, atomic absorption spectrometry

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Highly Efficient Proteolysis of Proteins by Trypsin-Encapsulated Magnetic Sol-Gel for Mass Spectrometry Based Proteomics

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Proteomics studies are required to detect sequences of peptides and proteins due to determine the structure and function of proteins. Mass spectrometry is an essential instrument for the identification of proteins and determination of peptide sequences. Digestion of proteins using a proteolytic enzyme is the most significant step in bottom-up proteomics [1]. However, the conventional digestion procedure is needed time-consuming incubation step due to form an adequate amount of peptides. Moreover, numerous auto-digestion products can be supposed as the proteolytic enzyme is in mixture together with the protein [2]. For the elimination of these types of problems, development of fast, efficient and easy technique and reusable material for high-grade proteolysis is required. Repeated use without much loss of its activity, the ability of easily separation from the reaction mixture and reduce cost and time are the main advantages of an encapsulated enzymes.

In this study, a novel trypsin-encapsulation technique using the sol-gel method was developed for determination of proteins sequence. With this aim, trypsin and magnetic Fe_3O_4 encapsulated sol-gel materials were developed via tetramethoxysilane-based sol-gel method. Magnetic nanoparticles (Fe_3O_4) were also encapsulated due to provide fast and east separation by affecting magnetic field. Several experimental conditions were optimized, and also trypsin encapsulated magnetic sol-gel materials were tried to for fast, efficient and easy application. To evaluate the trypsin encapsulated magnetic sol-gel's activity, various proteins such as BSA, α -casein and β -casein, which have different molecular weight and isoelectric points, were used. Proteolytic products of proteins that obtained by various protein using trypsin encapsulated magnetic sol-gels were monitored by MALDI-MS. The highest signal intensities of the proteolytic products of proteins were observed in MALDI mass spectra using trypsin and magnetic Fe_3O_4 encapsulated sol-gels. Reusability of the trypsin encapsulated magnetic sol-gels was also examined by MALDI-MS and found to be encapsulated trypsin maintains its activity up to 10 digestions. Additionally, natural samples such as milk, tear and saliva were digested by trypsin encapsulated magnetic sol-gel for evaluation to its digestion performance into complex biological samples. These results showed that the trypsin encapsulation sol-gel material is very beneficial to achieve fast and efficient proteolysis of various proteins without formation of auto-digestion products.

KEYWORDS: sol-gel, proteolysis, enzyme encapsulation, mass spectrometry, proteomics

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Investigation of Mineralogical Matrix Effect on XRF Analysis of Geological Samples

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X-ray fluorescence spectrometry (XRF) is one of the mostly used instrumental techniques for elemental analysis of rocks, cements, metallurgical samples and paint samples [1]. It can be expressed as a non-destructive technique that allows the direct measurement of a sample without vaporization and/or prior digestion. This technique has extremely good precision in a wide range of sample matrices and has a dynamic range of up to six orders of magnitude.

Sample preparation is crucial in XRF analysis [2]. There are many methods for sample preparation for XRF analysis and the most important ones are the pressed pellets preparation and fused beads preparation. Pressed pellet is the method to get a solid disc where the sample powder, with or without binding agent, is compressed. In fused beads preparation method, the sample is mixed with suitable flux, which is then fused in a platinum crucible. Fused beads and pressed pellets may show significant differences in XRF microstructure, micro heterogeneity and mineralogy [3].

Mineralogical matrix effects are due to the differences in composition of grains of the sample. This study shows the effect of mineralogical matrix differences in semi-quantitative measurements by XRF of the major elements of different geological samples such as bauxite, dolomite, soil, iron ore and lake sediment. Fused beads were prepared by mixing lithium tetraborate / lithium metaborate flux with the sample in ratio of ten-to-one and by fusion at 1050 °C. Samples were also pressed in pellets with binding agent. In order to check the XRF results, other analytical techniques such as ICP-OES and ICP-MS were also used.

KEYWORDS: XRF, ICP-OES, ICP-MS, Geological Samples, Mineralogical Matrix Effects

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On-line Preconcentration of Ni(II), Cd(II) and Cu(II) Ions on Polyamine Silica Gel for Their Determination by FAAS

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Many modern instrumental techniques including flame atomic absorption spectrometry (FAAS) cannot measure trace heavy metal levels in environmental samples due to insufficient detection limits and/or matrix effects. For solving these problems a preconcentration methods have been widely employed to increasing of concentration of the analytes [1-5].

On-line solid phase extraction procedure is very effective method for the preconcentration and separation of the analytes in several samples such as water, food, ore and etc [6-8].

In this study, silica gel was chemically functionalized with pentaethylenhexamine group (PEHA-SG). The obtained sorbent was characterized by C,H,N elemental analysis and FT-IR spectroscopy. PEHA-SG was used as an sorbent for the enrichment of Ni(II), Cd(II) and Cu(II) ions using on-line preconcentration system. The procedure was optimized by searching a several parameters effecting the retention and/or elution of the analytes including pH, flow rate, matrix ion, sample and loop volume, concentration of the eluents and etc. The developed method was validated by analyzing a reference material and applied to environmental water and several food samples. Also, adsorption capacity of PEHA-SG for Ni(II), Cd(II) and Cu(II) ions was calculated after their batch adsorption.

In conclusion, PEHA-SG loaded mini column could successfully utilized for the enrichment of Ni(II), Cd(II) and Cu(II) ions for their trace level determination using FAAS.

KEYWORDS: On-line preconcentration, solid phase extraction, modified silica gel, chelating resin, trace elements

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Spectrophotometric Determination of Some Amino Acids in Aqueous Solution Using Tetracyanoethylene Reagent

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A simple and sensitive Spectrophotometric method has been developed for the determination of some amino acids namely; glycine, glutamine, serine, methionine and hydroxyproline. The method is based on the reaction of these amino acids in aqueous solution with tetracyanoethylene reagent in the presence of sodium hydroxide to produce a yellow colored species measurable at λ_{\max} 335 nm for serine and hydroxyproline and 328, 325 and 322 nm for methionine, glycine and glutamine respectively. Beer's law is obeyed over the concentration range 0.5-24 $\mu\text{g/ml}$ for glutamine, serine and methionine and 1-24, 1-20 $\mu\text{g/ml}$ for glycine and hydroxyproline respectively, and the molar absorptivities are ranged between 3.855×10^3 and $7.435 \times 10^3 \text{ l.mol}^{-1}\text{cm}^{-1}$ for all the studied amino acids. The different experimental parameters affecting the development and stability of the color were carefully studied and optimized. A proposal of the reaction pathway has been postulated.

KEYWORDS: Spectrophotometry, amino acids, aqueous solution, tetracyanoethylene

The Use of Oxidative Coupling Reaction for Spectrophotometric Determination of Mesalazine

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I develop a sensitive spectrophotometric method for the determination of microgram amounts (0.16-8 µg/ml) of Mesalazine (5-aminosalicylic acid) based on the oxidative coupling with 2,6-xylenol in the presence of sodium metaperiodate in alkaline medium to form a blue indophenol dye which has maximum absorption at 610 nm. The molar absorptivity is $13316 \text{ l.mol}^{-1} \cdot \text{cm}^{-1}$ with LOD 0.042 µg/ml and LOQ 0.139 µg/ml. The accuracy (average recovery) is 100.91% and precision (RSD) is less than 2.5%. The method has been applied successfully to the assay of mesalazine in pharmaceutical preparations (enteric coated tablets and extended release capsules). The analytical results are compatible with certified values of pharmaceutical preparations and with standard addition procedure.

Application of H-point standard addition method in simultaneous spectrophotometric determination of isoniazid and mesalazine via Schiff's base formation reaction

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Isoniazid (INH), is the most potent and selective tuberculostatic antibacterial agent in the therapy of tuberculosis [1]. Mesalazine (5-ASA) is used to treat inflammation of the digestive tract (crohn's disease) and mild to moderate ulcerative colitis [2]. H-point standard addition method (HPSAM) has been applied to the simultaneous determination of INH and 5-ASA drugs in binary mixtures. The method is based on the Schiff's base formation of drugs with 1,2-naphoquinone sulphonate (NQS) as a chromogenic reagent in the presence of micellar cetyltrimethyl ammonium bromide (CTAB) and sodium carbonate. The results showed that simultaneous determinations could be performed with the ratios 0.4:1.4 and 1.6:0.2 measured at pair of wavelengths (438 and 521) nm with recovery % range 94.5-105 % and precision better than 2.95%. The method was applied successfully for determination of above drugs in their pharmaceutical formulations and the obtained results were compared statistically by a Student's *t*-test for accuracy and a variance ratio *F*-test for precision with the official method.

KEYWORDS: isoniazid; mesalazine; Spectrophotometry; HPSAM

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Electrocatalytic Oxidation of Hydrazine at Poly(4-Aminobenzene Sulfonic Acid)-Modified Glassy Carbon Electrode

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Hydrazine (HZ) is important compound of interest in chemical and pharmaceutical industries. It is employed in areas such as fuel cells, herbicides, catalysts, rocket propellants and so on [1]. HZ can be absorbed through skin has carcinogenic and hepatotoxic effect. It affects the liver, the kidney and the brain and is very important in pharmacology [2]. There are several electrochemical methods for determination of HZ in the literature with different detection limit, pH, linear range and the potential of hydrazine oxidation [1-6]. In this study, a stable modified glassy carbon electrode based on poly (4-aminobenzene sulfonic acid) (poly(4-ABSA) film was prepared by electrochemical polymerization technique in phosphate buffer solution (PBS) (pH 7.0). The poly(4-ABSA) modified glassy carbon (poly(4-ABSA/GC) electrode has very high catalytic ability for electrooxidation of HZ, which appeared in a wide operational pH range of 5-10. The electrocatalytic oxidation of hydrazine at (poly(4-ABSA/GC) electrode was studied by cyclic voltammetry (CV) and chronoamperometry (CA) techniques. The poly(4-ABSA/GC) electrode showed excellent electrocatalytic activity for electrooxidation of HZ in pH 7.0 PBS (0.1 M). So, pH 7.0 PBS (0.1 M) was chosen for electrocatalytic oxidation of HZ at the polymer film-modified electrode. The oxidation peak potential value of 3×10^{-4} M HZ was obtained at poly(4-ABSA/GC) electrode at 380 mV by CV technique. The scan rate studies were carried out. The nature of the oxidation process was found to be diffusion controlled in the buffer system studied, as evidenced from the linear plots of the peak current (i_p) versus square root of the scan rate ($v^{1/2}$) with correlation coefficient, $R^2=0.9983$ and slope (0.4765) of $\log i$ versus $\log v$ [1,7]. A linear calibration curve for CV and CA analysis was constructed at poly(4-ABSA/GC) electrode in the HZ concentration range 5×10^{-6} - 1×10^{-4} M. Limit of detection (LOD) and limit of quantification (LOQ) were obtained as 1.305×10^{-7} M and 4.35×10^{-7} M for CV; 7.89×10^{-8} M and 2.63×10^{-7} M for CA, respectively. The electrocatalytic oxidation of hydrazine was determined by applied techniques satisfactorily. The stability, sensitivity and reproducibility of the poly(4-ABSA/GC) electrode studied by cyclic voltammetry and repetitive chronoamperometry. The results of experiments showed that prepared modified electrode have good stability, sensitivity and reproducibility for at least one month if stored dry in air.

KEYWORDS: hydrazine, 4-aminobenzene sulfonic acid, modified-glassy carbon electrode, electrochemical polymerization, electrocatalysis, voltammetry, chronoamperometry.

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Effect of Lead Alloys on the Electrochemical Behavior of the Plate of the Positive Lead Acid Battery

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Battery technology is the lead answered as part of electrical energy storage. The lifetime of a battery depends especially positive electrode whose capacity decreases during charge-discharge cycle [1, 2]. The results of the kinetic study of the reduction of PbO_2 formed on both types of alloys (Pb-5% Sb and Pb-1.7% Sb-0.02% Se) have shown that the best and discharge capacity obtained for the PbO_2 formed on the alloy Pb-1.7% Sb-0.02% Se. Reducing the lead dioxide formed on the two electrodes is limited by the diffusion of H^+ ions through the layer of PbO_2 and the values of the diffusion coefficients are given as the diffusion of H^+ ions in the network PbO_2 formed on the alloy Pb-1.7% Sb-0.02% Se is fast compared to that formed on the alloy Pb-5% Sb. Therefore concluded that the electronic conductivity and proton PbO_2 is improved for PbO_2 formed on the alloy Pb-1.7% Sb-0.02% Se.

KEYWORDS: battery, lead alloy, lead dioxide, capacity, diffusion coefficient

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An Ionic Liquid Modified Carbon Paste Electrode And Investigation of Its Electrocatalytic Activity to Hydrogen Peroxide

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This paper reports on the preparation and advantages of novel amperometric biosensors in the presence of hydrophobic ionic liquid (IL), 1-methyl-3-butylimidazolium bromide ([MBIB]). Carbon paste biosensor has been constructed by entrapping horseradish peroxidase in carbon + IL mixed with paraffin oil as a binder. The resulting IL/graphite material brings new capabilities for electrochemical devices by combining the advantages of ILs composite electrodes. The influence of the IL and horseradish peroxidase (HRP) loading upon the amperometric and voltammetric data. Amounts of H₂O₂ were amperometrically detected by monitoring current values at reduction potential of K₃Fe(CN)₆ -0.15 V. Decreases in biosensor responses were linearly related to H₂O₂ concentrations between 10 μ M and 100 μ M with 2 seconds response time.. Limits of detection of the biosensor for H₂O₂ were calculated to be 3.98 μ M, respectively. In the optimization studies of the biosensor some parameters such as optimum pH, optimum temperature, enzyme amount interference effects of some substances on the biosensor response, reproducibility and storage stability were carried out. The promising results are ascribed to the use of an ionic liquid, which forms an excellent charge-transfer bridge and wide electrochemical windows in the bulk of carbon paste electrode.

KEYWORDS: ionic liquid (IL), 1-methyl-3-butylimidazolium bromide ([MBIB]), carbon paste electrode, horseradish peroxidase (HRP)

Investigation of Electrochemical Behavior of Benzophenone Hydrazone on Glassy Carbon Electrode Surfaces

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Hydrazones are a versatile class of compounds with several applications[1]. Hydrazones, especially acyl and aroyl hydrazones, are multipurpose class of ligands having great biological and chemical activities[2]. Hydrazones of aromatic carbonyl compounds of the type $\text{ArRC}=\text{N-NR}'\text{R}''$, where R, R' and R'' are carbon substituents, are reduced in aprotic media to the radical anion, which may cleave to an amine anion and an imine radical; the reduction is analogous to the reduction of vinyl halides of the type $\text{ArR}=\text{CR}'\text{X}$. For R' and R'' equal to methyl the rate of cleavage is a linear function of the reversible reduction potential of the hydrazone[3].

In this study, the electrochemical behavior of Benzophenonehydrazone (BPH) on the Glassy Carbon (GC) electrode surface in aqueous media was investigated with cyclic voltammetry (CV). Pt wire, Ag/AgCl and glassy carbon electrode were used as counter, reference and working electrode, respectively. In order to provide aqueous media for the modification experiments, Britton Robinson (BR) buffer solution with proper pH was chosen. On the other hand, negative and positive potential range, 100 mV/s scan rate and 100 cycle were determined as optimum conditions for the modification experiments. Electrochemical characterization was realized with CV technique in the presence of redox probes as potassium hexacyanoferrate (III) (HCF(III)), Ferrocene and Ruthenium hexamine (III) chloride in the suitable conditions of their own potential range, scan rate and solvent.

This study reports the results of electrochemical investigation of BPH for the first time. It is thought that the characterization and the application of these bare and modified surfaces will be investigated in our following studies.

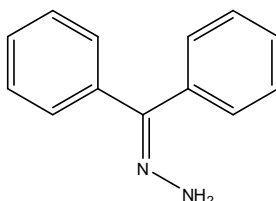


Figure 1. Structure of BPH

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The Investigation of Electrochemical Behavior of Co(II) Arginine Complex

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Metal complexes of amino acids or peptides are also important as model systems in the understanding of biochemical processes in living organisms and for drugs production [1]. The variety of inorganic compounds and their applications in medicine surround cancer chemotherapy, arthritis, antimicrobial agents, antitumor agents and many others [2]. Metal complexes of biologically important ligands are sometimes more effective than the free ligands. Cu(II), Ni(II), Co(II) and Zn(II) metal cations are recognized as essential elements that are distributed in biological systems including cells and body fluids. [3-5]. Also, copper exists in nuclei and plays a key role in determining DNA quaternary structure. There are a few studies on the electrochemical investigation of arginine complexes of metal cations.

In this study cobalt(II)-Arginine complex was synthesized and characterized firstly and then the electrochemical behavior of this complex has been investigated by the use of several electrochemical methods in DMSO on glassy carbon electrode. The number of electron transferred (n) and diffusion coefficient (D) in the reduction of the complex were calculated by cyclic voltammetric and chronoamperometric results for both the complex and ferrocene with ultramicro electrode.

The mechanism confirmed by comparing experimental cyclic voltammogram to the theoretical one drawn with simulation software. On the other hand the standard rate constant (k_s) and transfer coefficient (α) of the electrochemical reaction were also calculated from this simulation study.

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Investigation of Electrochemical Behaviour of Zinc(II) Glycine Complex

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Amino acids are essential building blocks of biological molecules [1] and play key roles in many neurochemical response mechanisms, such as memory, appetite control and pain transmission [2–4]. The oxidation and adsorption behaviors of amino acids on electrode surfaces are relevant to the interfacial behaviors of proteins and also to the medical and industrial problems associated with the proteins adsorption on the surfaces [5–7]. There are a few studies on the electrochemical investigation of glycinato complexes of metal cations. The electrocatalytic oxidation of alanine, l-arginine, l-phenylalanine, l-lysine and glycine on poly-Ni(II)–curcumin film (curcumin: 1,7-bis [4-hydroxy-3-methoxy phenyl]-1,6-heptadiene-3,5-dione) electrodeposited on a glassy carbon electrode was investigated in alkaline solution [8]. The process of oxidation and its kinetics were established by using cyclic voltammetry, chronoamperometry and electrochemical impedance spectroscopy techniques[8].

In this study Zinc(II)-Glycine complex was synthesized and characterized, and then electrochemical behaviour of the complex has been investigated by several electrochemical methods in DMSO on glassy carbon electrode. The number of electron transferred (n) and diffusion coefficient (D) in the reduction of the complex were calculated by cyclic voltammetric and chronoamperometric results for both the complex and ferrocene with ultramicroelectrode. The mechanism also confirmed by simulation studies. The standard rate constant (k_s) and transfer coefficient (α) of the electrochemical reaction were calculated from simulation study.

KEYWORDS: Zinc(II)glycine complex, electrochemistry, cyclic voltammetry, ultramicroelectrode

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A New Differential Pulse Polarographic Method for the Determination of Trace Elements in Tea Samples

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Tea is used in large quantities in Turkey. It is known that it has ability to lower the fever and head ache and to decrease the risks from some cancer types. The presence of Zn protects from the taste problems of tongue. In this work a new and simple DPP method has been established for the determination of trace elements in tea. For this purpose tea samples are first dried until constant weight and then wet digested using nitric acid [1] and it was evaporated until nearly dryness. After digestion a few ml HCl acid was added in order to reduce the selenate formed into selenite for selenite determination. For the determination of elements HAc electrolyte (pH 2, 4, 6, 9) and ammonia buffer (pH 9.8) with or without EDTA has been studied. For the selenite determination the sample digested with HCl was used. Cu and Fe could be determined at pH 6-7) in HAc and in the presence of EDTA [2]. Zn and Ni peaks on the other hand could be separated in ammonia at pH 9.8 [3]. Selenite in HAc in acidic medium was determined.

KEYWORDS: Tea, trace elements, polarography,

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**Determination of Fluoride and Iodide in Brassica oleraceae
var.acaphale Using Ion Selective Electrodes**

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In this work iodide and fluoride determinations have been made using ion selective electrodes, prepared in our laboratories. The brassica is planted and used in high quantities as a food at the black sea shore. It contains most probably high amounts of important elements. However, as known in this area goiter disease is observed at high percentages, it maybe because of insufficient iodide. On the other hand the deficiency of fluoride is important for the teeth health. Thus we decided to measure the fluoride and iodide in brassica because of its high usage in this area. For this purpose our newly established fluoride[1] and iodide electrodes[2] have been used. The slope of fluoride electrode was 28 mV and it was 59 mV for iodide electrode between 10^{-5} – 10^{-1} M concentrations. There was no interference of most common cations such as K⁺, Na⁺, Ca²⁺ and Mg²⁺ and anions such as Cl⁻, NO₃⁻, SO₄²⁻ and PO₄³⁻. The results are compared with the results obtained with commercial electrodes.

KEYWORDS: fluoride determination, iodide determination, brassica, polarography,

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Voltammetric Determination of Cadmium in Some Vegetables

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The presence of heavy metals in plants is expected to be in low levels. As a result of polluted environments, heavy metal concentrations may increase and/or metals which are not normally present in plants can be found [1]. Cadmium is a non-essential element for plants and could be up taken and accumulated by plant tissues. Cadmium is very harmful to human health when it enters the food chain [2–6]. So determination of cadmium in vegetables has an increasing importance.

Many methods have been used for the determination of cadmium, such as atomic absorption spectrometry, inductively coupled plasma atomic emission spectrometry, and mass spectrometry, X-ray fluorescence spectrometry, neutron activation analysis, differential pulse anodic stripping voltammetry. Voltammetry is an important method for the determination of cadmium due to simplicity and low cost.

The aim of this research is to determine cadmium concentrations in boiled liquors of vegetables; namely, spinach, leek, lady's finger, lamb's quarters and mad parsley. These vegetables were selected because they are either cultivated or naturally grown in Samsun and in the Middle Black Sea region.. It is known that metal ions can be transferred to the solution after heat treatment of vegetables. Since, there is a conflict about using or throwing away of boiled vegetable liquors, the data of this work would help to solve this food usage behaviour.

The adsorptive stripping square wave voltammetric experimental conditions were selected as: initial potential 0.0 V, final potential -1.0V, accumulation potential (-0.5V), pulse size 25mV, frequency 25 Hz, accumulation time 60 s while using a hanging mercury drop electrode as working electrode. The supporting electrolyte was 0.5M acetate solution at pH 4.5. Cadmium gave a single peak at -0.64V versus Ag/AgCl. Calibrations have performed by using standard addition method.

The levels of cadmium in the vegetables were obtained compatible with literature and smaller than WHO's permissible values.

KEYWORDS: Cadmium, vegetables, voltammetry

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A Highly Sensitive Humidity Sensor Made of Quartz Crystal Microbalance Coated with Conductive Polymer (PSDA)- Al_2O_3 Nanocomposite Films

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Different sensing techniques such as capacitive, resistive, optic, thermal and gravimetric have been explored to detect the humidity [1]. Among the gravimetric techniques, the Quartz Crystal Microbalance (QCM) is a very sensitive and stable tool that is able to measure small mass change. The working principle of QCM sensors depends on frequency shift of quartz oscillation frequency under molecules coated or adsorbed onto quartz electrode. Therefore, the most important step in the QCM sensors is the modification of the quartz surfaces. Many kinds of sensing materials including polymers, metal oxides and inorganic/organic hybrite materials have been coated on the QCM electrode to detect humidity [2-3]. In particular, conductive polymers are appropriate materials on QCM sensor surfaces due to their electrical, adsorption and desorption properties, long-term stability and reliability. In this work, the nanohybride thin films composed of a water soluble conductive polymer poly(sulfonic diphenylamine) (PSDA), (3-mercaptopropyl) trimethoxysilane (MPTMS) and nano Al_2O_3 were coated on quartz crystal and used as humidity sensor. The frequency shifts and the change of resistance due to the adsorption and desorption of water vapor on the surface of the modified QCM electrodes were simultaneously measured by using SRS QCM100 device. Humidity sensing properties of the films to relative humidity ranging from 5% to 97% were studied at room temperature. The sensor exhibits excellent humidity sensing properties such as fast response/recovery time, good repeatability (Fig.1), good linearity with high correlation (Fig. 2) and low hysteresis.

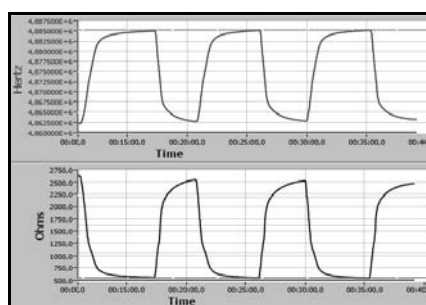


Figure1. Repetitive response of PSDA-MPTMS-nano Al_2O_3 nanocomposite at a humidity of 97% RH and 5%RH

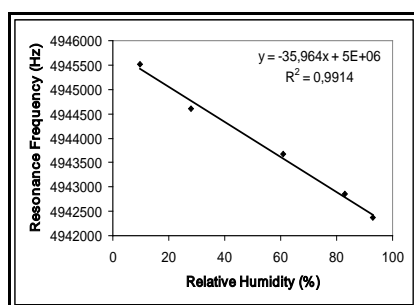


Figure 2. Calibration plot between the values of relative humidity and the resonance frequency

KEYWORDS: Quartz Crystal Microbalance, humidity sensor, conductive polymer, nanocomposite

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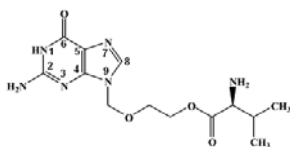
An Electroanalytical Approach for Voltammetric Determination of Antiviral Drug Valacyclovir using Boron-Doped Diamond Electrode in Different Electrolyte Media: Comparison with Glassy Carbon Electrode

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Antiviral medications are the standard of practice in the management of herpes viral infections. For decades, substituted purines, such as guanosine analogues (acyclovir and its *L*-valyl ester pro-drug valacyclovir) have been primarily used to treat and/or prevent the infections caused by herpes simplex virus type 1 and 2 and varicella zoster virus. After oral administration, valacyclovir, which is administered as a hydrochloride salt is well absorbed from the gastrointestinal tract and undergoes rapid and extensive metabolism in the liver to give acyclovir and an essential amino acid, *L*-valine.



Most of the works related with analytical methods for the detection and quantification of valacyclovir in pharmaceutical preparations or in biological fluids either alone or simultaneously with acyclovir involve the use of liquid chromatographic techniques. Generally, these reported methods offer a high degree of sensitivity and selectivity; however, these are rather time-consuming methods and require expensive instrumentation and large number of complicated steps to follow on for analysis. Although valacyclovir is an electrochemically active compound, to the best of our knowledge, no literature data were found on its electrochemical behaviors, except in a recent work of our group dealing with its differential pulse and square-wave voltammetric determination in pharmaceuticals and human biological fluids using glassy carbon electrode [1]. In keeping with limited data available, the goal of the present work was to throw a more light upon the redox behavior of valacyclovir by application of a boron-doped diamond electrode (BDDE) without any electrode surface modification, in the presence of surfactants. Glassy carbon electrode (GCE) was also used for comparative purpose under identical experimental conditions. The electrochemical oxidation of valacyclovir was first investigated in aqueous and aqueous/surfactant solutions by cyclic and linear sweep voltammetry using BDDE and GCE. The compound was oxidized in one, two or three steps at high positive potentials, resulting in the formation of a several reduction and re-oxidation waves at less positive potentials, depending on the nature of the electrode material, pH and composition of the supporting electrolyte, scan rate, surfactant type and applied potential range. It underwent irreversible oxidation, which was a diffusion-controlled process. Using differential pulse waveform, valacyclovir yielded a well-defined voltammetric response in 0.2 M sulphuric acid solution containing 1×10^{-3} M sodium dodecylsulfate (anionic surfactant) at +1.18 V (vs. Ag/AgCl). The process could be used to determine valacyclovir in the concentration range of 0.1 to 6 μ M, with a detection limit of 0.02 μ M. The suggested method was successfully applied to the commercial formulations. From the biological point of view, surfactants can stabilize radicals or other intermediate reaction products. Bearing this important knowledge in mind, in addition to the practical application of the voltammetric technique described in this study, the data obtained may be useful, at least in part, and shed considerable light on the fundamentals of very complex in vivo oxidation pathways of purines with antiviral or other types of biological activity.

KEYWORDS: Valacyclovir, boron-doped diamond electrode, anionic surfactant, voltammetric determination, tablet

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Determination of Ascorbic Acid Based on Electropolymerized-Molecularly Imprinted Polypyrrole Modified Pencil Graphite Electrode

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Interest in ascorbic acid (AA) or vitamin C has been persisted since its discovery, due to its important roles in the body, such as collagen synthesis, hormone synthesis, anticoagulant and antioxidant activities [1]. A couple of review articles were reported for AA determination, which include titrimetry, fluorimetry, flow-injection analysis, spectrophotometry, chromatography, and atomic absorption spectrophotometry [2,3]. These techniques are having complications of limited endurance, tedious fabrication procedures involving specific and expensive reagents and materials, and poor separation of peaks for the simultaneous determination of analyte mixtures. Despite the molecularly imprinted polymers (MIP) being a well established analytical tool to produce artificial recognition element of lower price and high stability. [4,5]. Furthermore, MIPs provide a simple and rapid technique of controlling the thickness of the conductive polymer film grown adherent to a transducer of any size and shape [6].

In this work, we describe the electrochemical determination of ascorbic acid at molecularly imprinted polypyrrole (PPy) sensing layers at modified pencil graphite electrode (PGE). The MIP was obtained electrochemically on the surface of the PGE in aqueous solution of 0.1M LiClO₄, 0.01M pyrrole and 0.001M ascorbic acid. After the electropolymerization process, the embedded AA was then extracted to give a surface complementary in shape and functionality to the original template AA and this was in 0.2M phosphate buffer solution using potential cycling between -0.6 and +1.00V.

Then the recognition of the target molecule was studied in PBS solution containing ascorbic acid for different concentrations. The results show that electrodeposition of polypyrrole film on PGE in the presence of extracted ascorbic acid has been successfully fabricated. A linear relationship between ascorbic acid concentration and current response was obtained with excellent reproducibility of the current and a low detection limit < 10⁻⁷ M using square wave voltammetry.

These MIPs are very selective to ascorbic acid without any influence of interferences molecules as dopamine and quercetin. The proposed low cost chemical sensor could find application in the measurement of ascorbic acid and many molecules level in biologic fluids as well as in pharmaceutical industry.

KEYWORDS: molecularly imprinted polypyrrole, ascorbic acid, detection limit, square wave voltammetry.

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Manganese-oxide/Platinum Modified Glassy Carbon Electrode: An Electrocatalytic Platform for the Monitoring of Electrochemical Reduction of Oxygen and Its Biosensing Application

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The reduction of molecular oxygen plays a vital role in electrochemical energy-conversion systems and biosensing studies therefore, several attempts have been made at the development of efficient electrocatalysts [1]. The use of transition metal oxides has been proposed as novel electrocatalyst for the oxygen-reduction reaction (ORR).[2]. Alloys of Pt with other metals, mostly first row transition metals as Co, Ni, Cr, V and Fe, were found to be more active for ORR than pure Pt. [3] Manganese can hold a number of oxidation states, Mn(II) Mn(III) and Mn(IV) being the most common for the oxides [1]. Manganese oxides with various valence states and crystalline structures are currently under investigation for electrochemical, electronic, catalytic and other applications [2]. Studies of the direct electron transfer processes between redox proteins and electrodes can not only provide information about the electron-transfer mechanisms in biological systems, but can also lay the foundations for preparation of biosensors and bioanalytical devices [4]. In this study mixed valance manganese oxide and platinum modified GCE surfaces are obtained by cycling the potential between 1.05 - (-0.25) V. Then the response of the modified electrode for dissolved oxygen is studied in pH : 4.50 AcH/Ac- buffer. The results showed that manganese oxide and platinum has an effective catalytic activity for dissolved oxygen reasonably this electrode is used for glucose biosensing.

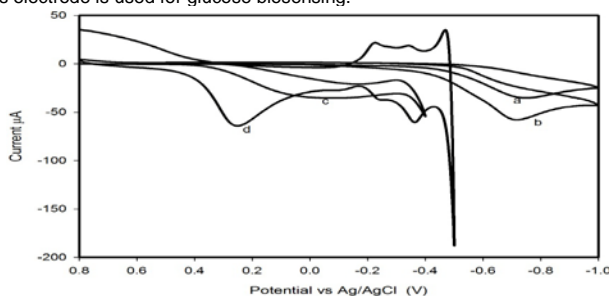


Figure 1 Cyclic voltammograms recorded in pH 4.50 acetate buffer saturated with oxygen gas at a) bare GCE b) Mn modified GCE, c) GCE modified stepwise with Mn and then Pt, d) GCE modified with Mn and Pt simultaneously.

KEYWORDS: manganese oxide, platinum, oxygen reduction, glucose biosensor

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Investigation Of Oxygen Reduction On Nickel-Copper Modified Poly (3,4-ethylenedioxythiophene)(PEDOT) Film Glassy Carbon Electrode

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The electrochemical behavior of oxygen is particularly important for clean energy generation systems like hydrogen-oxygen fuel cells, metal air batteries, industrial electrolytic process, and electro-organic reactions. Fuel cells are evaluated promising power sources because of their high-energy transform efficiency, reliability and environmental compatibility. The reaction mechanism includes multi-electron reduction in aqueous solution proceeding in two overall pathways depending on electrode material and solution pH. Bare electrode surfaces generally induce oxygen reduction via a two-electron reduction process at two different potentials. Numerous different materials have been proposed to prepare a catalytic electrode surface on which a four-electron reduction takes place in one step [1-5]. In this study, as a type of conductive polymer, PEDOT film electrode was prepared by electrochemically synthesis and modified with nickel-copper nano particles on glassy carbon electrode in alkaline solution especially high activity catalyst for oxygen reduction reaction (ORR). Electroreduction of oxygen was investigated at bare glassy carbon (GC), poly3,4-ethylenedioxythiophene (PEDOT/GC), copper- poly3,4-ethylenedioxythiophene /GC (Cu-PEDOT/GC),nickel-copper-poly3,4-ethylenedioxythiophene/GC(Ni-Cu-PEDOT/GC), electrodes. The best electrocatalytic activity for oxygen reduction was observed Ni@Cu nano particles deposited PEDOT modified electrode because of the highest peak current and more negative potential value. The surface morphology of GCE before and after the electropolymerization of PEDOT and Ni@Cu /PEDOT/GCE was characterized by SEM (*scanning electron microscope*) and XRD (*X-ray Diffraction*). SEM images of the PEDOT/GCE and Ni@Cu/PEDOT/GCE and XRD image of Ni@Cu/PEDOT/GCE were given in Fig.1. In order to achieve optimal conditions for electrocatalytic reduction of oxygen, main parameters related to the film formation and solution characteristics were studied. These parameters were selected as cycle number of polymerization, cycle number, deposition and concentration order of Ni@Cu particles and NaOH concentration. Influence of H₂O₂ on oxygen reduction was also studied. The electrochemical measurements illustrate that the Ni-Cu particles modified PEDOT film electrode have great electrocatalytic activity and stability toward oxygen reduction reaction (ORR) in alkaline media. The enhanced electrocatalytic property may be attributed to the cooperative effects between metals and polymer film in the presence of a large number of active sites on the electrode surface.

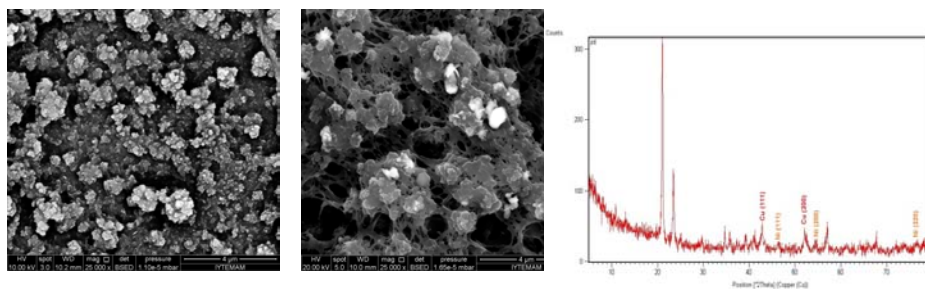


Fig. 1 SEM images of the A) PEDOT/GCE, B) Ni@Cu/PEDOT/GCE and C) XRD image of Ni@Cu/PEDOT/GCE

KEYWORDS: nickel and copper core-shell particles, polymer film electrode, electroreduction of oxygen, full cell

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An Enzymatic Glucose Sensor Based on Multi-Walled Carbon Nanotubes Decorated with 1-Aminoindan

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The development of sensitive, selective, reliable, low-cost and simple analytical systems for the determination of glucose is important in various fields as food quality control, fermentation process monitoring and clinical diagnosis. Among various analytical methods, enzyme-based electrochemical biosensors are attractive choice, due to its simplicity, low-cost, high sensitivity and selectivity. Glucose oxidase (GOx) which catalyzes the oxidation of glucose in the presence of oxygen and/or various redox-active electron transfer mediators, instead of oxygen, is useful and mostly selected model enzyme for the determination of glucose due to its high bioelectrocatalytic activity and biochemical stability [1, 2, 3].

In recent years, nanostructured materials from metal nanoparticles to any form of carbon nanostructures have attracted attention in the field of enzyme-immobilized biosensors, as they provide a suitable matrix for enzyme immobilization and also their effect for prevention the leaching of enzymes [4]. Carbon nanotubes (CNTs) are interesting class of nanostructures offering high electrical conductivity, high surface area, significant mechanical strength and good chemical stability [5, 6]. Therefore, CNTs are an attractive material for Li ion batteries, supercapacitors, gas sensors, humidity sensors, biosensors, and solar cells. Nowadays, the combination of CNTs with other nanostructures, organic/inorganic molecules and polymeric films are the attractive applications, especially in biosensing systems [7, 8].

The main aim of this study was to apply multi-walled carbon nanotubes (MWCNT) for the design of an enzyme based glucose biosensor. The system was the combination of MWCNT and 1-aminoindan as an electron transfer mediator. The proposed biosensing system showed excellent selectivity towards glucose and demonstrated good reproducibility and stability.

KEYWORDS: Cyclic voltammetry, Glucose sensor, Glucose oxidase, Multi-walled carbon nanotube, 1-Aminoindan.

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Rapid ICP-AES Monitoring of Lead Content in Plates Used in Lead-Acid Battery Manufacturing

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The analysis of PbSO₄ content in lead plates is one of the main tasks of analytical laboratories that are involved in controlling the quality of lead-acid batteries. It is usually determined with the gravimetric method, which is accurate, but at the same time laborious and time-consuming. The aim of the project was to elaborate a procedure for the determination of lead sulfate in lead-acid battery plates by means of a relatively novel and fast technique – inductively coupled plasma atomic emission spectroscopy (ICP-AES). A rapid, accurate and precise ICP-AES procedure for the determination of lead sulfate in lead-acid batteries plates was elaborated based on the measurement of the sulfur emission line. The optimal parameters of the spectrometric measurements were selected, and accuracy, repeatability and reproducibility were estimated. The proposed ICP- AES analytical procedure was validated through the analysis of certified reference materials, and good agreement between the ICP AES results and the reference values was obtained. It was proved that the ICP-AES method is more accurate and precise than the routine gravimetric one. Additional advantages of the elaborated method include the high speed of total analysis and the elimination of the toxic barium chloride, which is applied in the routine method. When determining PbSO₄ with the ICP-AES technique, the time of analysis is cut down to about 20 minutes, and the stage in which BaSO₄ is precipitated by means of the highly toxic BaCl₂ solution using the classical gravimetric method may be eliminated altogether. The elaborated method has been applied for routine and fast determination of PbSO₄ in active positive and negative battery plates, essential in industrial plants that produce batteries. The advantages this method offers in comparison to the laborious and time-consuming gravimetric method are especially obvious when analyzing a high number of samples.

KEYWORDS: lead sulfate, ICP AES, lead-acid batteries

Application of Antimony Film Electrode Plated in a Potassium Tartrate Solution for Anodic Stripping Voltammetry

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Stripping voltammetry is one of the most sensitive analytical methods. The type of working electrode greatly affects the deposition of analytes and, consequently, the sensitivity of metal determination by means of anodic stripping voltammetry (ASV). The best analytical results have always been achieved using liquid mercury electrodes thanks to their excellent electrochemical performance; consequently, for many decades they were the type of electrodes applied most frequently in stripping voltammetry. However, restrictions connected with the toxicity of mercury have forced researchers to search for electrode materials that would replace mercury. Some of the solid metallic film electrodes developed in response to this challenge provide a wide range of useful potentials, mechanical stability, easily renewable surface and effective preconcentration in stripping procedures.

In the present work, the performance of an antimony film electrode (SbFE) prepared in situ on a glassy carbon (GC) support from a new complexing supporting electrolyte – a saturated solution of hydrogen potassium tartrate – is presented. In this medium, Sb(III) ions form complexes with tartrate, which prevents the precipitation of SbOCl that would otherwise occur in diluted hydrochloric acid. Moreover, the solution of hydrogen potassium tartrate is less acidic than solutions of HCl; as a result, hydrogen ions are reduced at more negative potentials and less interference with stripping voltammetric curves of Zn(II) is observed (Fig.1). The applied supporting electrolyte was investigated during square-wave anodic stripping voltammetric (SW ASV) detection of Cd(II), Pb(II), Zn(II), Tl(I), In(III) and Cu(II). The concentration of antimony ions and the experimental parameters of the SW ASV procedure were optimized.

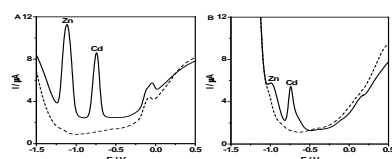


Fig. 1. SW ASV curves recorded for 50 $\mu\text{g/L}$ Zn(II), Cd(II) and 1.2 mg/L Sb(III) in the solutions: (left) tartrate (pH = 3.6) (solid line) and (right) 0.01 M HCl together

The ASV voltammetric curves of Zn(II), Cd(II) and Pb(II) or Zn(II), Tl(I) and Pb(II) are well-separated and can therefore be detected simultaneously in the whole range of the investigated concentrations, i.e. from 2 to 100 $\mu\text{g/L}$. Taking into account the fact that the differences between peak potentials of Tl(I) and Cd(II), Cd(II) and In(III), or Tl(I) and In(III) range from 30 to 80 mV, the simultaneous determination of these species is not possible due to the strong overlap of their voltammetric signals. The detection of Cu(II) at the SbFE is possible because the voltammetric curves of Cu(II) are sufficiently separated from the curve of Sb(III). The calibration plot of Cu(II) was linear over the 2–50 $\mu\text{g/L}$ concentration range. The ASV method with the use of the SbFE deposited in situ from the solution of hydrogen potassium tartrate provides high sensitivity, low limits of detection (from 0.5 to 3.8 $\mu\text{g/L}$), and satisfactory repeatability. The elaborated procedure was validated by determining trace concentrations of lead in the certified rainwater reference material (CRM TMRain – 95). Satisfactory agreement was obtained.

KEYWORDS: anodic stripping voltammetry, antimony film electrode

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Lead Film Electrode Exploited for Chronopotentiometric Determination of Ni and Co

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Stripping chronopotentiometry (SCP) is one of the most effective tools for metal traces' determination, but it is less frequently used than stripping voltammetry. SCP involves two steps: potentiostatic preconcentration, followed by stripping accompanied by oxidation, reduction or desorption of the preconcentrated analyte. During the latter step, two different stripping mechanisms can be exploited: chemical oxidation/reduction generated by oxidants/reductants present in the solution (Potentiometric Stripping Analysis, PSA), or oxidation/reduction by means of an applied constant current (Constant Current PSA or Stripping Chronopotentiometry). The second of these mechanisms ensures more standardized conditions and better control of the stripping process. Over the course of the second SCP step, the potential of the working electrode varies with time, and the potential vs. time curve is usually recorded and then transformed into the dt/dE vs. E form.

In this work an electrode consisting of lead film plated in situ on glassy carbon (PbFE/GC) was used for the determination of Co and Ni traces by means of constant current adsorptive stripping chronopotentiometry (CC-AdSCP). The supporting electrolyte, which simultaneously acted as the plating solution, contained Pb(II) ions, 0.1 M ammonia buffer, 10^{-5} M nioxime and 0.1 M nitrite. The application of negative potential during preconcentration caused the reduction of Pb(II) ions and the formation of a lead layer, which adsorbed nioximate complexes of Co and Ni. Finally, the reduction of Ni(II) and Co(II) complexes was induced with constant current and the potential vs. time dependence was recorded (Fig. 1). When using the PbFE the separation of Co and Ni peaks was considerably better than that observed at the hanging mercury film electrode.

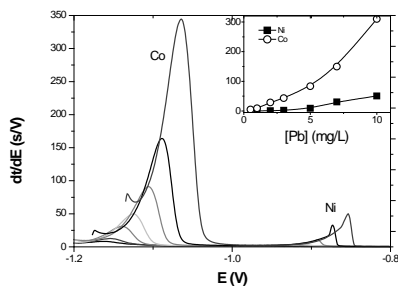


Fig.1. CC-AdSCP curves recorded for increasing concentrations of Pb in the solution of $5 \cdot 10^{-9}$ M Co, $5 \cdot 10^{-8}$ M Ni, 0.1 M ammonia buffer, $5 \cdot 10^{-5}$ M nioxime, 0.25 M NaNO_2 at the PbFE *in situ*. Preconcentration: -1.45 V for 20 s, accumulation: -0.75 V for 60 s; stripping current: 2 μA .

The presence of nitrite causes the catalytic enhancement of the Co analytical response, resulting in a great increase in sensitivity and a lower detection limit [1]. Thanks to this catalytic amplification, Co traces at the level of 10^{-10} M were determined in the presence of a significant excess of other elements, e.g. Ni and Zn. The analytical characteristics (linearity, limit of detection, reproducibility, selectivity) of the investigated CC-AdSPC procedure were evaluated. The recovery study of Co(II) determination in mineral water confirmed the usefulness of the designed electrode as a replacement for the hanging mercury electrode.

KEYWORDS: stripping chronopotentiometry, lead film electrode, nickel, cobalt

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Perchlorate-Selective Membrane Electrode Based on a New Calix[4]arene Derivative

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In recent years, improper storage and disposal of perchlorate salts has lead to the emergence of perchlorate ion as one of the major environmental contaminants. Out of different salts of perchlorate ion, ammonium salts are frequently used in explosives, rocket propellants, fireworks, airbag inflators, and other relevant applications of defence/aerospace sector [1]. Recent research has shown that perchlorate anions may be found at high concentrations in surface water and ground water around the world. The determination of perchlorate in different samples such as ground water or urine in the presence of other anions is of vital importance [2]. Various analytical methods such as volumetric titrations, gravimetry, spectrophotometry, atomic absorption spectrometry and ion chromatography have been used for determination of perchlorate. Most of these methods are susceptible to interference from different cationic or anionic species, are either time-consuming and/or need sophisticated instruments and require the expensive instrumentation and/or extensive sample pretreatment. An ion-selective electrode due to its unique advantages such as speed and ease of preparation and procedures, simple instrumentation, wide dynamic range, non destructive analysis, reasonable selectivity, low cost, low detection limit and enhanced possibility of miniaturization has been widely applied to the reliable *in situ* estimation of perchlorate levels in environmental samples [2]. The wide uses of ion-selective electrode in routine chemical analysis have been accompanied by a search for ionophores that can chemically recognize specific anions and offer either a new or improved selectivity to different ions [3, 4]. Most of the reported ClO_4^- ion-selective electrodes are ion exchanger based liquid membranes, where the electro-active species including perchlorate ion-association complexes with cations and metal chelates, long chain quaternary ammonium ions and organic dyes have been dissolved in various organic solvents. In these liquid membranes, ion-pair formation between ClO_4^- and the cationic site may occur with some selectivity but none of these electrodes can be considered to be carrier based [2]. Calixarenes are very popular as attractive and excellent ionophores in poly(vinyl chloride) (PVC) membrane electrodes because they provide a platform for the attachment of convergent binding groups to create host molecules, mainly for the attraction of simple ions and small molecules [5]. The purpose of this work was the development of perchlorate-selective electrodes based on plasticized PVC membranes, containing 25,27-bis(4-ethyl-piperazine-1-yl-1-propoxy)-26,28 dihydroxy calix[4]arene as the membrane active material (Scheme 1). In this work, the selectivity for a variety of ions and the effect of membrane matrix, ionophore concentration, additives and pH on the potentiometric response properties of the proposed electrode were investigated. The proposed electrode exhibited Nernstian slope for perchlorate ions over a wide concentration range. It has fast response time, good reproducibility and repeatability. This electrode was used for the determination of perchlorate in various sample with satisfactory results without complicated and time consuming pretreatment.



Scheme 1. 25,27-bis(4-ethyl-piperazine-1-yl-1-propoxy)-26,28 dihydroxy calix[4]arene

KEYWORDS: perchlorate, calix[4]arene, ion-selective electrode

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Ion-Selective Membrane Electrode Based on a New Calix[4]arene Derivative for the Determination of Dichromate

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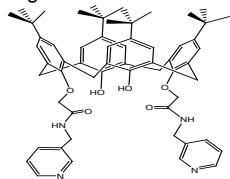
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Chromium is an element widely used in industrial activities. It exists as two major species, Cr(III) and Cr(VI) in natural waters and soils. Cr(III) is a stable and slightly soluble cation considered as an essential microelement, while Cr(VI) (as dichromate) is highly water soluble and mobile anion, known as a toxic pollutant, with mutagenic and carcinogenic effects [1]. Due to the different toxicities of these two species, it is essential to determine hexavalent chromium rather than the total chromium concentration by using a rapid and simple method that can be applied in industrial and environmental fields [2]. An alternative method for the determination of dichromate ion is potentiometry using ion-selective electrodes.

Several compounds have been used as a neutral carrier in dichromate-selective electrodes. In this study, new dichromate-selective electrode based on 5,11,17,23-Tetra-*tert*-butyl-25,27-bis[(3-amidopyridine)carbonyl]methoxy-26,28-bis-hydroxy-calix[4]arene (Scheme 1) was developed and its lifetime, response time, optimum working range and other performance characteristics were determined. The effect of membrane composition and the pH of test solutions on the potentiometric response of the electrode were investigated. The electrode exhibited linear response with a super-Nernstian slope in the working range 1.0×10^{-1} - 1.0×10^{-6} M at ambient temperature. It showed good selectivity for dichromate ions in the presence of some cations and anions. The proposed electrode has fast response time, good reproducibility and repeatability.

The influence of different construction techniques and the question whether this electrode can be used for other analytical purposes were also investigated.



Scheme 1. 5,11,17,23-Tetra-*tert*-butyl-25,27-bis[(3-amidopyridine)carbonyl]methoxy-26,28-bis-hydroxy-calix[4]arene

KEYWORDS: chromium(VI), dichromate, calix[4]arene, ion-selective electrode

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Using a Calix[4]arene Derivative Based Ion-Selective Electrode for Potentiometric Determination of Iodide

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Various analytical methods reported for the determination of anions reveal that most of the instrumental techniques are complicated and expensive for routine analysis. On the other hand, ion-selective electrodes offer an inexpensive and convenient method for fast analysis with high selectivity, and have emerged as one of the most promising tools for direct determination of various anionic and cationic species in biological and industrial analysis [1].

An important group of ion-selective electrodes is anion-selective electrodes, just like cation-selective ones. However, the number of anion-selective electrode is lower than that of the cationic sensors, due to reasons like the relative larger size of anions, and their various shapes [2]. Although the preparation of anion-selective membrane electrodes has been related primarily to the use of metallomacrocyclic ionophores as Schiff base complexes of metal ions, cobyrinates, porphyrins, and phthalocyanines, we introduce a new calix[4]arene derivative as an unmetallated macrocyclic compound used as an ionophore for an anion-selective electrode.

Iodide is essential for human health as it helps to ensure proper thyroid gland function and serves as an antiseptic for skin wounds and for the emergency disinfection of drinking and swimming pool waters. Iodide is present in food, drug compounds and in drinking water and it is often added to table salt as a source of iodine for preventing iodine deficiency disorders. An excess of iodine or iodide ingestion can produce goiter and hypothyroidism as well as hyperthyroidism. Therefore, the determination of iodide and iodine species in a variety of fields such as food, clinical, biological and environmental samples is an important analytical task [3].

In this study, we developed an iodide ion-selective PVC membrane electrode based on 5,11,17,23-Tetra-*tert*-butyl-25,27-bis(pyren-1-yl methylimido-propoxy)-26,28-dihydroxy-calix[4]arene as an ionophore and its optimum working range, response time, lifetime, slope, selectivity coefficients towards variety of ions were determined. An optimum membrane composition of 2 % ionophore, 68.3 % plasticizer, 29.7 % PVC was found for the proposed electrode. The electrode exhibited linear response to iodide ions in the concentration range of 1.0×10^{-1} - 1.0×10^{-5} M with a near Nernstian slope at pH 4.0. The electrode was found to work well under laboratory conditions by utilizing it as an indicator electrode to determine iodide content in samples.

Furthermore, it can be possible to prepare a potentiometric biosensor with the help of H_2O_2 forming enzymatic reactions and peroxidase as the catalyst by using the proposed iodide-selective electrode.

KEYWORDS: Iodide-selective electrode, potentiometric sensors, PVC membrane electrode

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Poly(vinyl chloride) Membrane Electrode Based on a New Calix[4]Arene Derivative for Salicylate

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Salicylate derivatives are commonly used as effective antimicrobial, antipyretic and analgesic agents. It is also employed in analytical practice, such as in synthesis of dyes and in preservation of foods. Therefore salicylate and its derivatives require suitable detection in clinical medicine and pharmaceutical analysis. There are many methods for the detection of salicylate anions. Most of the methods are time consuming and expensive. However, potentiometric detection based on ion-selective electrodes (ISEs) as a simple method offers great advantages such as speed, and ease of preparation and procedure, wide linear dynamic range and low cost[1,2].

The aim of the present work was to develop poly(vinyl chloride) membrane electrode for salicylate based on 5,11,17,23-tetra-tert-butyl-25,27-bis(pyren-1-yl methylimido-propoxy)26,28-dihydroxy calix[4]arene (Scheme 1) as an ionophore. The effect of the amount of the ionophore, type of plasticizer and lipophilic additive on the potential response of the electrode were investigated. The electrode prepared with bis(2-ethylhexyl)sebacate as a plasticizer exhibited linear response to the salicylate ions in the concentration range of 1.0×10^{-1} – 1.0×10^{-5} M. The selectivity coefficients of the proposed electrode towards various anions and cations were determined by using separate solution method recommended by IUPAC.

The proposed electrode was also successfully employed as an indicator electrode for the potentiometric determination of salicylate in drug and food samples.

Scheme 1. Calix[4]arene

KEYWORDS: salicylate, calix[4]arene, ion-selective electrode

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Determination of Phenol Using Modified Electrode Poly(3-methylthiophene) in Methylene Chloride

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Phenol is main structure of phenolic compounds such as catechol and hydroquinone. Phenol and its chemical derivatives are used in many fields like industry, pharmaceutical drugs [1] food antioxidants of polymerization inhibitors and cosmetic industries [2,3]. Phenol and its vapors are corrosive and the substance may cause harmful effects on the central nervous system and heart [4] so it is important to determine phenol.

Conductive Poly 3-methylthiophene films are prepared electrochemically on solid substrate material (Pt, Au, Glassy carbon) [5]. Determination of phenolic compounds using Poly 3-methylthiophene (P3MT) modified electrodes give better responses when compared to uncoated electrode [6]. It was stated that P3MT films have electrocatalytic effect on phenolic compounds [7].

In this study P3MT film was synthesized by electrochemically on Pt disk electrode in methylene chloride solution containing 500 mM 3-methylthiophene and 0.10 M TBAP between 1.80 V and -0.40 V, -0.20 V, 0.0 V, 0.20 V potential. Cyclic voltammetric behavior of these electroactive films were taken in methylene chloride solution containing 0.1 M TBAP (blank solution). The most electroactivity film was determined as film deposited between potential from 1.80V to -0.40 V. This film was used for determination of phenol in solution consisting of NaHSO₄/Na₂SO₄ (pH 2.0). We studied at 0.70, 0.80, 0.90 V potentials for amperometric determination of Phenol with this modified electrodes. Results show that the best potential was 0.90 V. The linear response range, Limit of Detection (LOD) and Limit of Quantification (LOQ) were found to be between 4.51×10^{-7} – 4 mM (R^2 : 0.9932), 1.35×10^{-7} mM and 4.51×10^{-7} mM at 0.90 V vs saturated calomel electrode (SCE), respectively. This linear range is similar to tyrosinase-modified core-shell magnetic nanoparticles supported at a carbon paste electrode (Tyr-MgFe₂O₄-SiO₂) 2.5×10^{-3} – 0.1 mM [8] and a tyrosinase-colloidal gold modified carbon paste electrode (Tyr-Au-CPE) 4×10^{-3} – 48×10^{-3} mM [9] for phenol.

KEYWORDS: 3-methylthiophene, phenol, P3MT, amperometric determination;

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Analysis of Tap Water Samples in The Eastern Black Sea Regions

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In this study, water hardness (with complexometric titration method), conductivity and pH values of 40 different tap water samples taken from city centers, township and villages in the Eastern Black Sea regions were measured. Compared hardness and conductivity values these tap water samples; it was observed that when hardness degrees increased, values of conductivity increased. The hardness degrees of these tap water samples were determined using France hardness degree parameter. The hardness degree (502.94 mg CaCO₃ / L) and conductivity (734 μ S) of the tap water sample that was taken from inik village, Akaabat, Trabzon region were detected to be the most value in the other samples and one that was taken from Pınarca village, Of, Trabzon region was found as a the most soft (21.54 mg CaCO₃ / L) and of least conductivity of 22.20 μ S.

KEYWORDS: tap water, water hardness, conductivity, pH

Determination of Hydroquinone Using A New Poly (3,3'-diaminobenzidine)- Poly(3-Methylthiophene) (PDAB-P3MT) Modified Electrode

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Hydroquinone (HQ), 1,4-dihydroxybenzene, is derivative of benzene which have two hydroxyl groups which is used many different fields such as dye, photography and cosmetic industries [1]. Determination of HQ is important because of its toxicity and environmental pollution [2]. So, there are many methods for determination HQ and its isomers such as chromatography[3], spectrophotometry [4], electroanalysis [1,5]. Electrochemical methods are faster and not required pre-separations than the others. Previous study showed that like Se (IV) or Te (IV) metals give specific reaction with o-amines like 3,3'-diaminobenzidine (DAB) [6]. Modified electrode which has been prepared DAB on solid substrate is used metal analysis [7,8], cell marker, determination phenolic compounds [9] and immunoassay studies [10]. Poly (3-methyl thiophene) is widely investigated for modified electrode due to its stability and high electrical conductivity [11]. There are many study for determination of phenolic compounds and catecholamines which environmental and biologically important compounds with P3MT modified electrode [12,13]. In this study P3MT film was synthesized on Pt electrode in methylene chloride containing 0.10 M tetrabutyl ammonium perchlorate (TBAP), 500 mM 3MT and then PDAB film was deposited on this film in acetonitrile containing 0.10 M TBAP, 1.0 mM DAB between -0.40 V and 1.80 V (20 cyclic) vs. Ag/AgCl electrode. This film was used amperometric determination of hydroquinone in solution consisting of NaHSO₄/Na₂SO₄ (pH 2.0). We studied at 0.40 V, 0.45 V, 0.50 V, 0.55 V and 0.60 V potentials for amperometric determination of HQ with this modified electrodes. Results show that the best potential was 0.55 V. The linear response range, Limit of Detection (LOD) and Limit of Quantification (LOQ) were found to be between 8.833x10⁻⁷ – 75.0 mM (R²: 0.9949), 2.65x10⁻⁷ mM and 8.833x10⁻⁷ mM at 0.55 V vs saturated calomel electrode, respectively. This linear range is similar to graphene/BMIMPF₆ nanocomposite on the glassy carbon electrode 5.0x10⁻⁷-5.0x10⁻⁵ M [14], a graphitic mesoporous carbon on the glassy carbon electrode 0.3–90 µM [15] for hydroquinone

KEYWORDS: Hydroquinone, Poly (3,3'- diaminobenzidine), Poly (3-methylthiophene), Amperometric determination

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Electrocatalytic Reduction of Dissolved Oxygen at Molybdenum-Oxide and Pt Nanoparticle Modified Glassy Carbon Electrodes

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The reduction of oxygen to water is one of the most important reactions in electrochemistry with regards to the wide range of applications in electrocatalysis, metal corrosion, metal-air batteries, fuel cells and mostly in biosensor [1]. The reaction mechanism includes multi-electron reduction in aqueous solution proceeding in two overall pathways depending on electrode material and solution pH. Bare electrode surfaces generally induce oxygen reduction via a two-electron reduction process at two different potentials. Numerous number of studies deal with developing catalytic surfaces for one step reduction of oxygen including four electron [2]. Transition metals are widely used as mediator to modify the electrodes' surfaces. These metals have several stable oxidation states and they are able to form polymeric films by their oxide forms including mixed valence metals. Therefore these mediators provide a great catalytic activity towards to oxygen reduction.

In this study molybdenum and platinum were electrodeposited onto glassy carbon surface by cycling the potential 1.05 – (-0.25) V from aqueous solution sodium molybdate and platinum as well or molybdate and platinum individually. The response of electrodes were recorded in pH:5.0 AcH/Ac⁻ buffer.

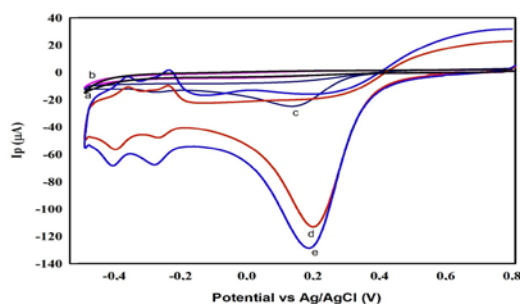


Figure 1. Cyclic voltammograms obtained in pH 5.0 acetate buffer saturated with oxygen gas a) bare GCE, b) GCE modified with MoO_x, c) Pt disk electrode, d) GCE subsequently modified with Mo and Pt respectively, and e) Simultaneous modification of GCE with MoO_x and Platinum from the same solution.

KEYWORDS: molybdenum oxide, oxygen reduction, cyclic voltammetry

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Anodic Behaviour and Voltammetric Determination of Levodopa on Poly(Nile Blue A) and Multiwalled Carbon Nanotube Modified Glassy Carbon Electrodes

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Levodopa (LD, 3,4-dihydroxy-L-phenylalanine) is a drug used for the treatment of Parkinson's disease (PD). LD is used to increase levels of dopamine in the brain and in this way slow down the progression of the disease, since motor symptoms such as tremor, rigidity, slowness of movement, and postural instability are produced by a lack of dopamine.

Poly(Nile blue A) (PNB) is obtained by electrochemical polymerisation of Nile blue A. PNB has been used as a redox mediator, especially for the electrocatalytic oxidation of the nicotinamide coenzymes NADH and NADPH.

Carbon nanotubes (CNTs) have recently become important due to their properties such as high electrical conductivity, chemical stability, and high surface area. CNTs have been used in electrochemical sensors and biosensors, since they have good chemical stability to biomolecules e.g. [1,2].

Modification of glassy carbon electrodes was carried out by electropolymerisation of PNB films using potential cycling in 0.1 M phosphate buffer solution (PBS) at pH 6.0 and deposition of functionalised multi-walled carbon nanotubes (MWCNT). The anodic behaviour and determination of LD on the PNB/MWCNT modified electrodes was investigated using cyclic and differential pulse voltammetry in 0.1 M PBS at different values of pH between 5.0 and 8.0. A diffusion-controlled irreversible oxidation peak was observed in cyclic voltammetry at ~240 mV vs SCE.

The quantitative determination of LD was carried out using differential pulse voltammetry in 0.1 M PBS at pH 6.0. The peak currents of LD were linear over the concentration range from 2×10^{-6} to 1×10^{-4} M.

The repeatability, precision, and accuracy of the method were also investigated. High sensitivity and a low detection limit of 0.77 μ M for LD were obtained using this new modified electrode.

KEYWORDS: levodopa, nile blue A, carbon nanotubes, cyclic voltammetry, differential pulse voltammetry, glassy carbon electrode

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Electrooxidation of Hydrazine on Metal Nano Particles and poly(L-Serine) Modified Glassy Carbon Electrode

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The energy requirement of the world is increasing depending on the increasing population, industrialization and technological developments. The fuel cells based on the main of the production of the electric and heat energy with the fact that a fuel is oxidized in the anode and oxygen is reduced in the cathode. The fuel cells used of hydrazine as a fuel is called direct hydrazine fuel cells [1-2]. The electrocatalytic activity can be increased by using the modified substances in the both electrode so that chemical energy can be highly converted to the electric energy. The main target in this studies, it is needed to the modified surfaces to provide the possibility to the fact that the fuel in the anode is oxidized in the so low (negative) potentials. The use of some expensive metals (Pt, Au) known that the electrocatalytic activity increase is increasing the cost of the fuel cell. To remove this problem, it is needed to the new electrode materials to prepare with more low costs [3]. The conductive polymers synthesizing with the electrochemical method in the electrode surface are using in recent years. Moreover, metal nanoparticle electrodes modified on this polymer surfaces are densely the subject of the researches in recent years. In this work, L-serine monomer was polymerized electrochemically at glassy carbon electrode surface by repetitive potential cycles using cyclic voltammetry and obtained electrode donated as poly(L-serine)/GCE. After L-serine polymerization, metal nano particles (MNP) (Cu, Mo, Pt, Au, etc) were doped by electrochemical reduction from 1mM metal ions solution on poly(L-serine)/GCE surface. Modified electrodes were characterized by using scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX) techniques. The electrochemical behavior of hydrazine oxidation was investigated at all prepared electrodes in 0.1 M pH 7.0 phosphate buffer. The obtaining results were comparing with bare GCE, poly(L-serine) modified glassy carbon and MNP-poly(L-serine)/GCE. As shown the Fig.1, the peak potential of hydrazine oxidation on bare and poly(L-serine)/GCE were observed at 767 mV and 469 mV, respectively. Therefore, the peak current of hydrazine on poly(L-serine)/GCE was increased. A high catalytic activity was observed towards 1.0 mM hydrazine oxidation at -380 mV on Pt_{nan}-poly(L-serine)/GCE. At this electrode, the peak potential of hydrazine was shifted at 1.1 V negatively direction more than bare GCE.

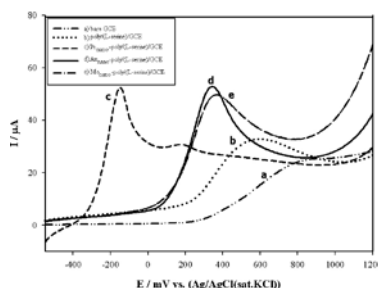


Fig. 1 Linear sweep voltammograms of 1.0 mM hydrazine oxidation in 0.1 M pH 7.0 phosphate buffer solution at different modified electrodes. Scan rate 50 mV/s

KEYWORDS: hydrazine, metal nano particle, cyclic voltammetry

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Electrooxidation of Hydrazine on Metal Nano Particles and poly(Alanine) Modified Glassy Carbon Electrode

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The necessity to the renewable alternative and clean energy sources because the fossil origin fuels create the environment pollution are rapidly increasing in recent years. The fuel cells which are one of the steady with the environment clean energy sources are been heavy working in recent years aiming at this aim. The fuel cells based on the main of the production of the electric and heat energy with the fact that a fuel (hydrogen, methanol and hydrazine) is oxidized in the anode and oxygen is reduced in the cathode. The fuel cells hydrazine is used as a fuel called direct hydrazine fuel cells. Hydrazine doesn't create the effect of intoxication because carbon isn't in its structure and hydrazine isn't form the product of CO and CO₂ in a consequence the reaction [1,2]. The main working principle of the fuel cells, as hydrogen or different fuel substance feeds to the anode, the oxygen in air is sent to the cathode. As the fuel is dispersing along the anode, oxidation is occurring in the anode electrode, reduction of oxygen carry out in the cathode electrode. Therefore, the electrons passing from the outside circuit from the anode to the cathode are converted to the energy. The electrocatalytic activity can be increased by using the modified substances in the both electrode so that chemical energy can be highly converted to the electric energy. The main target in this studies, it is needed to the modified surfaces to provide the possibility to the fact that the fuel in the anode is oxidized in the so low (negative) potentials and oxygen in the cathode is reduced in more positive potentials. The use of some expensive line metals (Pt, Au) known that the electrocatalytic activity increase is increasing the cost of the fuel cell. To remove this problem, it is needed to the new electrode materials to prepare with more low costs [3]. The conductive polymers and metal nanoparticle electrodes are densely the subject of the researches in recent years. In the nanodimensions, because of changing both physical and chemical characteristics of the substance and very increasing the unit surface field of the substance, active surface area also increase. More pure metal nanoparticle can be obtained with the electrochemical method. In this work, alanine monomer was polymerized electrochemically at glassy carbon electrode surface by repetitive potential cycles using cyclic voltammetry and obtained electrode donated as poly(alanine)/GCE. After alanine polymerization, metal nano particles (MNP) (Pt, Au, etc) were doped by electrochemical reduction from 1mM metal ions solution on poly(alanine)/GCE surface. Modified electrodes were characterized by using scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX) techniques. The electrochemical behavior of hydrazine oxidation was investigated at all prepared electrodes in 0.1 M pH 7.0 phosphate buffer. The obtaining results were comparing with bare GCE, poly(alanine) modified glassy carbon and MNP-poly(alanine)/GCE. As shown the Fig.1, the peak potential of hydrazine oxidation on bare and poly(alanine)/GCE were observed at 767 mV and 313 mV, respectively. Therefore, the peak current of hydrazine on poly(alanine)/GCE was increased. A high catalytic activity was observed towards 1.0 mM hydrazine oxidation at -270 mV on Pt/poly(alanine)/GCE.

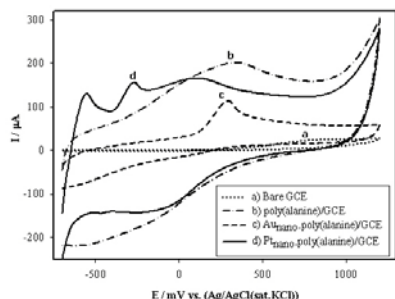


Fig.1 Cyclic voltammograms of 1.0 mM hydrazine oxidation in 0.1 M pH 7.0 phosphate buffer solution at different modified electrodes. Scan rate 50 mV/s.

KEYWORDS: hydrazine, poly(alanine), metal nano particle, cyclic voltammetry

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- [3] P. Paulraj, N. Janaki, S. Sandhya, K. Pandian, Colloids and Surfaces A: Physicochem Eng. Aspects 377 (2011) 28

Voltammetric Investigation of Lapatinib at Glassy Carbon Electrode

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Lapatinib (LPT) is a new active drug for breast cancer and other solid tumours. To date only two LC-MS/MS methods has been reported for LPT assay in the literature. In this study, the oxidation mechanism of LPT at a glassy carbon electrode (GCE) has been studied using cyclic voltammetry (CV), differential pulse (DP) and square-wave (SW) voltammetry. The pH-dependent oxidation of LPT was studied in the range of pH 0.3-10.0 and the number of electrons and protons transferred of LPT were determined.

According to the repetitive CVs of $20 \mu\text{g mL}^{-1}$ LPT at GCE in pH 2.0 phosphate buffer, LPT exhibited two anodic peaks, first peak at 0.94 V, second peak at 1.17 V and one cathodic peak at 0.57 V (100 mV s^{-1}). After first cycle, new peak was occurred at 0.62 V on anodic branch. On further successive CVs, while the two anodic peak currents were decreased, the new peak current was increased.

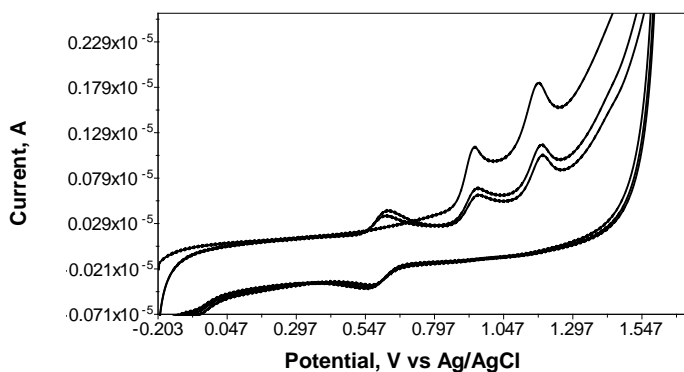


Figure. Repetitive cyclic voltammograms of $20 \mu\text{g mL}^{-1}$ LPT

LPT exhibited three anodic peaks by DPV and SWV. The third peak at about 1.40 V could be seen only in DP and SW voltammetric studies. When SWV was compared with DPV, currents of three anodic peaks were significantly enhanced by means of SWV.

The oxidation of LPT was compared with model compounds which contain aromatic amine moiety. Especially CV measurements of the LPT, fosamprenavir, aniline, 2-aminophenol, amisulpride, clenbuterol and ambroxol were used in this study for the comparison of the aromatic amine group oxidation. LPT was oxidized at similar potentials with model compounds on GCE. Taking into account all the studies performed so far, it was suggested that the oxidation process may occur on the aromatic amine group.

Possible interference effects of uric acid (UA) and dopamin (DA) to the electrochemical response of LPT was studied under the optimum conditions. Different amounts of UA and DA were added to the constant amount of LPT. There is no significant decrease with addition of DA and UA.

KEYWORDS: lapatinib, voltammetry, glassy carbon electrode, oxidation

Sensitive Determination of Antiviral Drug Valganciclovir Based On Multi-Walled Carbon Nanotube Modified Glassy Carbon Electrode in Pharmaceutical Dosage Forms

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Valganciclovir (VAL) is a pro-drug of ganciclovir which has been developed for the treatment of cytomegalovirus retinitis in patients with AIDS. Some methods based on the use of chromatographic techniques such as HPLC, and LC/MS have been reported for the determination of VAL. No previous electrochemical studies were available neither concerning the electrode behavior nor the sensitive electroanalytical determination of VAL in its dosage forms. To demonstrate the benefits of the multi-walled carbon nanotubes (MWCNTs) modified glassy carbon electrode (GCE) for the determination of VAL, which may offer advantages for the use of such electrodes as nanosensors, voltammetric behavior of VAL on MWCNTs modified GCE was investigated in details.

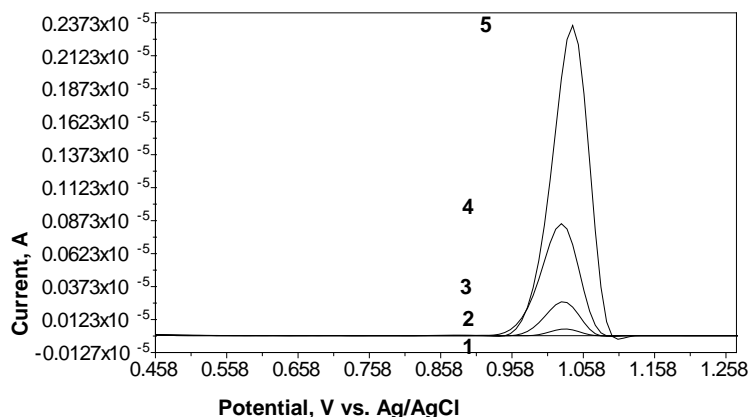


Figure. AdSDP voltammograms on MWCNTs modified GC electrode in pH 4.00 BR buffer for the determination of VAL; (1) blank, (2) containing 2.5×10^{-8} M, (3) 1.0×10^{-7} M, (4) 5.5×10^{-7} M, (5) 1.0×10^{-6} M

In this study voltammetric oxidation of VAL was investigated at MWCNTs modified GCE using cyclic and differential pulse voltammetry over a wide pH range. The results revealed that the oxidation of VAL is an irreversible pH-dependent process in an adsorption-controlled mechanism. The results show that the oxidation signal was remarkably enhanced to provide down to the ultra trace levels. Operational parameters have been optimized. The calibration curve was linear in the concentration range of 7.50×10^{-9} – 1.00×10^{-6} M with the detection limit of 1.52×10^{-9} M. The reproducibility of the peak current was found 2.07% ($n=5$) RSD value in pH 4.0 BR buffer for the modified electrode. A probable reaction mechanism is discussed. The modified electrode showed good stability and reproducibility, and also it was successfully applied to the sensitive and selective determination of VAL in its dosage forms.

KEYWORDS: valganciclovir, carbon nanotubes, voltammetry, modified electrode

Hydrazine Oxidation at Au Nano Particles and Poly(Bromocresol Purple) Carbon Nanotube Modified Glassy Carbon Electrode

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Hydrazine (N_2H_4) and its derivatives are widely used in industrial applications and agriculture as fuel cells, explosives, antioxidants, rocket propellants, corrosion inhibitor, insecticides and plantgrowth regulators. Hydrazine is an ideal fuel for a direct fuel cell system because it does not exhaust environmentally loading materials such as CO_2 . In addition, studies have shown that the hydrazine electro-oxidation process does not suffer from any poisoning effect [1,2]. The conductor polymers synthesizing with the electrochemical method in the electrode surface are using in recent years. Moreover, metal nanoparticle electrodes modified on this polymer surfaces are densely the subject of the researches. In the nanodimensions, because of changing both physical and chemical characteristics of the substance and very increasing the unit surface field of the substance, active surface area also increase. More pure metal nanoparticle can be obtained with the electrochemical method. Noble metal nanoparticles have been extensively utilized in recent years, owing to their extraordinarily catalytic activities for both oxidation and reduction reactions. Due to the unique properties of gold nanoparticles, such as good conductivity, useful electrocatalytic ability, several researchers have been devoted to fabricate electrochemical sensors [3,4]. In this study, bromocresol purple monomers were polymerized electrochemically at glassy carbon electrode surface and obtained electrodes were donated as poly(BCP)/CNT/GCE. After electrochemical polymerization, Au nano particle were doped on the polymer film carbon nanotube(CNT)/GCE surface by electrochemical reduction from their acidic solutions. Modified electrodes were characterized with electrochemical impedance spectroscopy (EIS), scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX) techniques. The electrochemical behaviour of hydrazine oxidation was investigated at metal nano particals modified poly(BCP) electrodes in phosphate buffer solution (PBS). The obtaining results were comparing with other modified electrodes. The best catalytic activity was obtained at $Au_{nano}/poly(BCP)/CNT/GCE$ due to the shift of oxidation peak to more negative values than other electrodes with a highest current value (Fig. 1). The best catalytic activity towards hydrazine oxidation obtained at $Au_{nano}/poly(BCP)/CNT/GCE$ due to the great peak shift to the more negative values. The peak potential and current oxidation of hydrazine obtained at $Au_{nano}/poly(BCP)/CNT/GCE$ (-28 mV, 138,4 μA), $Au_{nano}/CNT/GCE$ (-38 mV, 154,7 μA) $Au_{nano}/poly(BCP)/GCE$ (173 mV, 41,4 μA).

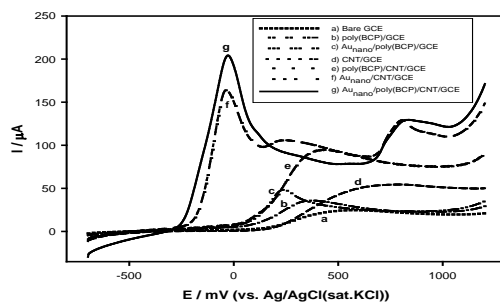


Fig.1 Linear sweep voltammograms of 1.0 mM hydrazine oxidation in 0.1 M pH 10 phosphate buffer solution at different modified electrodes. Scan rate 50 mV/s

KEYWORDS: Nano Au, hydrazine, bromocresol purple, cyclic voltammetry

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Electrocatalytic Hydrazine Oxidation at Pt Nano Particles and Poly(Bromcresol Purple) Carbon Nanotube Modified Glassy Carbon Electrode

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Hydrazine (N_2H_4) is an ideal fuel for a direct fuel cell system because it does not exhaust environmentally loading materials such as CO_2 . In addition, studies have shown that the hydrazine electro-oxidation process does not suffer from any poisoning effect [1,2]. Hydrazine is a compound with high hydrogen content (12.5 wt.%). The direct hydrazine fuel cell demonstrate higher electromotor force of 1.61 V which is close to that of then direct borohydride fuel cell (1.64 V) and higher than that of then direct methanol fuel cell (1.21 V) [3,4]. Noble metal nanoparticles have been extensively utilized in recent years, owing to their extraordinarily catalytic activities for both oxidation and reduction reactions. Due to the unique properties of metal nanoparticles, such as good conductivity, useful electrocatalytic ability, several researchers have been devoted to fabricate electrochemical sensors [5]. Carbon nanotubes (CNTs) are new kinds of carbon nanostructure materials possessing properties such as high surface area, high electrical conductivity, chemical stability and significant mechanical strength. They can be used to promote electron transfer reactions when applied as electrode materials in electrochemical devices. Metal nanoparticles such as Pt, Au and Ag are demonstrated the catalytical effect on the anodic oxidation of hydrazine [6]. Bromocresol purple (BCP) is a pH indicator. It is also used as dye to measure albumin in medical laboratories. Its electropolymerization at the electrode surface and its function as an electrocatalyst have been reported in the literature [7]. In this study, bromcresol purple monomers were polymerized electrochemically at glassy carbon electrode surface and obtained electrodes were donated as poly(BCP)/GCE. After electrochemical polymerization, Pt nano particle were doped on the polymer film carbon nanotube GCE surface by electrochemical reduction from their acidic solutions. Modified electrodes were characterized with electrochemical impedance spectroscopy (EIS), scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX) techniques. The electrochemical behaviour of hydrazine oxidation was investigated at Pt nano particles modified poly(BCP)/CNT/GC electrodes in phosphate buffer solution (PBS). The obtaining results were comparing with other modified and bare electrodes (Fig.1). The best catalytic activity was obtained at $Pt_{nano}/poly(BCP)/CNT/GCE$ due to the shift of oxidation peak to more negative values than other electrodes with a highest current value. The peak potential and current oxidation of hydrazine obtained at $Pt_{nano}/poly(BCP)/CNT/GCE$ (-465 mV, 168,1 μA), $Pt_{nano}/CNT/GCE$ (-461 mV, 133,1 μA) $Pt_{nano}/poly(BCP)/GCE$ (-470 mV, 59,2 μA).

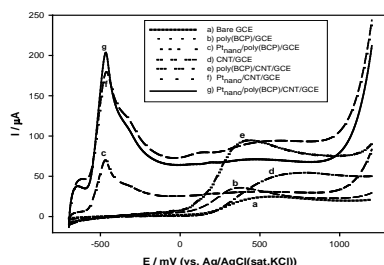


Fig.1 Linear sweep voltammograms of 1.0 mM hydrazine oxidation in 0.1 M pH 10 phosphate buffer solution at different modified electrodes. Scan rate 50 mV/s

KEYWORDS: Hydrazine, Pt, carbon nanotube, bromcresol purple

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Voltammetric Determination of Anticancer Drug Irinotecan on Poly(Methylene Blue) and Multi-walled Carbon Nanotubes Modified Glassy Carbon Electrode

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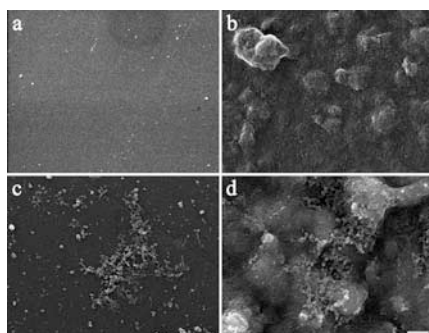
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Irinotecan HCl is a new anticancer drug, which has antitumor activity in a wide range of malignancies, such as metastatic colorectal cancer, upper gastrointestinal, pancreatic, lung, breast cancer, and gynaecological malignancies [1,2]. Irinotecan (IRT) is a potent inhibitor of topoisomerase I. IRT is activated by hydrolysis of SN-38 (7-Ethyl-10-hydroxy-camptothecin) an inhibitor of topoisomerase I. The inhibition of topoisomerase I by the active metabolite SN-38 eventually leads to inhibition of both DNA replication and transcription.

The voltammetric behavior of anticancer drug IRT was investigated at poly (methylene blue) / multi-walled carbon nanotube (PMB/MWCNT) modified glassy carbon electrode (GCE). As yet, there has been no report for the redox properties of IRT on neither bare nor modified electrodes. The PMB/MWCNT modified GCE exhibits a distinct shift of the oxidation potential of IRT on the cathodic direction and a considerable enhancement of the peak current compared with bare electrode. The modified electrode surface was characterized by a scanning electron microscope (SEM). The calibration curve was linear between the concentration range 8.0×10^{-6} and 8.0×10^{-5} M with the detection limit of 2.14×10^{-7} M by differential pulse voltammetry in pH 10.0 Britton-Robinson buffer solution. The proposed differential pulse voltammetric method was used for the determination of IRT in its pharmaceutical dosage forms. Precision and accuracy of proposed methods were also checked.



Surface morphology of bare GCE (a) MWCNT modified GCE (b) PMB modified GCE (c) PMB/MWCNT modified GCE (d) obtained by SEM. Scale bar=2 μ m. Electrodes were initially coated with AuPd in 15 nm thickness using sputter coater and viewed at 20 keV, x20000.

KEYWORDS: modified electrodes, irinotecan, voltammetry, validation.

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Electrochemical Oxidation of Alpha-2-Macroglobulin on Carbon Electrodes

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Many disease biomarkers are proteins, which may be emitted by cells under different physiological conditions such as when they are diseased and/or stressed. Measuring proteins at low levels is also crucial for investigation of protein syntheses and functions in biological system. Electrochemical mechanisms are significant to all redox chemistry including biological systems relating to electron transport chains. The research of direct electron transfer between proteins and electrodes can provide a model for understanding the real protein electron transfer mechanism in biological system. The electrochemical biosensor for protein detection is important as tools for disease study and diagnosis. As seen in the literatures, among the 20 amino acids presented in proteins only tyrosine, tryptophan, histidine, cysteine and methionine were oxidized at carbon electrodes. Alpha 2-Macroglobulin is the largest major nonimmunoglobulin protein in plasma. The alpha 2-macroglobulin molecule is synthesized mainly in liver, but also locally by macrophages, fibroblasts, and adrenocortical cells. A common variant (29.5%) (Polymorphism) of α_2 -macroglobulin leads to increased risk of Alzheimer's disease.

The direct electrochemical behavior of α_2 -macroglobulin adsorbed on glassy carbon, edge plane pyrolytic graphite, boron doped diamond and gold electrodes surface, were studied by differential pulse voltammetry in different pH values (pH 4.0-8.0). The oxidation mechanism of α_2 -macroglobulin was occurred in two signals related to the pH values and electrodes. These signals were compared with the oxidation of tryptophan and histidine amino acid. Also using glassy carbon electrode, the native and denatured forms of alpha 2-macroglobulin could discriminated by square wave voltammetry in pH 7.0 phosphate. The different urea concentration range 0.5-10 $\mu\text{g/mL}$ was tried for α_2 -macroglobulin denaturation. The peak current of native α_2 -macroglobulin was increased as for 20 folders by treatment with 8.0 M urea. The protein concentration range of 0.5-120.0 $\mu\text{g/mL}$ was applied both native and denatured protein. It can be expected that the electrochemical method will be applicable to a large number of proteins and may become useful in biomedicine and proteomics.

Electrochemical Evaluation of Testosterone Hormone at Bismuth Film Electrode

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Testosterone chemically known as 17-hydroxyandrost-4-en-3-one is the principal endogenous androgenic-anabolic steroid in humans. It is the principal male sex hormone which plays a key role in health and well-being as well as in osteoporosis[1]. Testosterone may be given to treat medical conditions like breast cancer in female, hypogonadism in male, cryptorchism and menorrhagia[3].

The reduction process was irreversible and adsorption-controlled. Special attention was given to the use of adsorptive voltammetry on bismuth film electrode in aqueous solutions over the pH range of 1.0-9.0. Addition of cationic surfactant (tetraethyl ammonium bromide,) to the testosterone -containing electrolyte enhanced the current signal. The process could be used to determine testosterone in the concentration range of 10 to 70 nM. The suggested method was also applied to the determination of testosterone in different drug formulations and spiked human urine samples

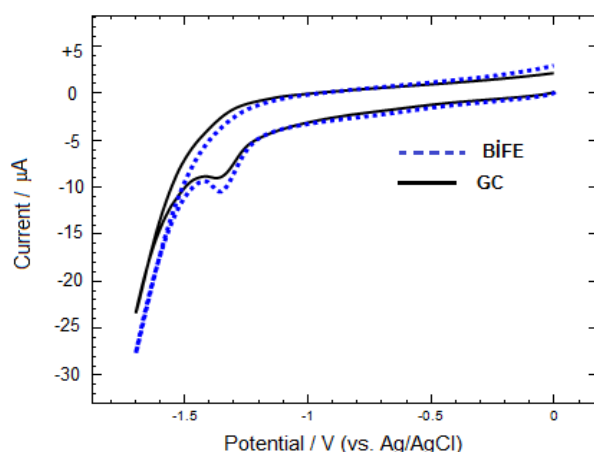


Figure 1. The CVs of 1.0×10^{-4} M testosterone solutions in 0.1 M Britton-Robinson, pH 5.0 for glassy carbon electrode (GC) and bismuth-film electrode (BiFE). Scan rate, 100 mV/s.

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Electrochemical Determination of Isoniazid by using PEDOT Modified Gold Electrode in Pharmaceuticals

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Isoniazid (pyridine-4-carboxylic acid hydrazide or isonicotinic acid hydrazide) is one of the widely used effective tuberculosis drug, which has acted against mycobacterium strains [1]. Poly(3,4-ethylenedioxythiophene) (PEDOT) is a widely investigated electronically conducting polymer, which can be easily electrodeposited onto surface by electrooxidation of its monomer. PEDOT modified electrodes have been extensively reported and showed excellent electrocatalytic effect on phenolic compounds [2,3]. The electrochemical behavior of isoniazid on a polycrystalline gold electrode and PEDOT modified gold electrode were investigated by using cyclic voltammetry and controlled potential techniques. Electrocatalytic performance measurements of this composite electrode toward oxidation of isoniazid showed an increase of 4-fold in reduction peak densities compared to the bare gold electrode. Central composite design method was used to obtain optimum experimental conditions. Under the optimum conditions, there was a good linear relationship between anodic peak current and isoniazid concentration in the range of $2.0 \times 10^{-8} - 3.0 \times 10^{-7}$ M with correlation coefficients of 0.998. This developed method had been applied to the direct determination of isoniazid in pharmaceutical formulations with satisfactory results.

KEYWORDS: Isoniazid, PEDOT, cyclic voltammetry.

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Preparation of QCM Electrode Having Metabolomics Nanoparticle Memory for Early Diagnosis of Ovarian and Prostate Cancer

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Tumor markers are molecules which can be synthesized by the cancerous tissue or could be observed by increased levels of them in tissue or serum as a result of destroyed of cancer tissue [1]. The level of lysophosphatidic acid (LPA) molecule increases in blood serum when the ovarian cancer occurs. After ovarian cancer cells appear, the increases of this marker in blood can provide early diagnosis of ovarian cancer [2]. Similarly, due to the occurrence of prostate cancer, the level of sarcosine molecule increases in urine and early diagnosis of prostate cancer is possible by measuring level of sarcosine [3].

In this study, LPA and sarcosine inprinted nanoparticles have been synthesized using MAA (methacrylic acid) functional monomer by molecular imprinting technique. Surface morphology of synthesized nanoparticles has been performed with scanning electron microscope (SEM) and atomic force microscope (AFM). Then, nanoparticles have been uniformly coated on the surface of quartz crystal microbalance (QCM) electrodes by using spin coater. The modified electrodes have been placed on the QCM instrument and they interact with different concentrations of LPA and sarcosine solutions. Versus increasing of biomarker concentrations, calibration graphs have been obtained by using frequency shift. The limit of detection, selectivity, reusability, and binding constants of the nanoparticles have been determined for cancer biomarkers.

KEYWORDS: ovarian cancer, prostate cancer, LPA, sarcosine, molecularly imprinted polymers, QCM

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Electrochemical Preparation of New Surface with 2-Nitroaniline

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The improvement of novel electrode materials for use in the definition of clinically, industrially and environmentally important compounds is currently an area of very active observation [1]. New surfaces can be obtained by modification of electrode. Modified electrodes have a great deal of attention, largely because they have a wide range of potential applications in electrochemical technology, energy conversion, and, particularly, chemical analysis, as well as possible practices in information storage, electrochromism equipment, and displays [2–4]. Modified electrodes are prepared by various methods [5].

The main aim of this study was to determine the electrochemical modification method for platinum electrode by 2-nitroaniline (2-NA) and apply it for determination of Cu(II). Electrochemical surface modification was applied by cyclic voltammetry at various scan rate by 50 cycles in aqueous media. Pt wire, Ag/AgCl/(sat.KCl) for aqueous media and Ag/Ag⁺(in 10 mM AgNO₃) for non-aqueous media, and platinum electrode were used as counter electrode, reference electrodes and working electrode, respectively. The modified surface was then characterized electrochemically by means of different mediators such as potassium ferricyanide and ferrocene. The sensitivity of modified platinum electrode towards Cu(II) was investigated in Britton-Robinson (BR) buffer solution at pH 5.0.

The characterization of both bare and modified surfaces will be completed by using Electrochemical Impedance Spectroscopy (EIS) and Scanning Electron Microscopy (SEM). Then, applicability of the modified electrode for the determination of Cu(II) in wastewaters will be investigated.

KEYWORDS: cyclic voltammetry, modified platinum electrode, surface modification, 2-Nitroaniline

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Preparation and Characterization of 2-Nitroaniline Modified Gold Electrode

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Electroanalytical methods are widely studied in many areas such as medical compounds and pharmaceutical [1], metals in industrial wastes [2], etc. Modified electrodes are prepared by various methods such as self-assembled monolayers (SAM) on commonly gold electrode surface [3], amine oxidation [4] and reduction of diazonium salts [5] on commonly glassy carbon (GC) electrode surface as using the electroanalytical method. Several studies about nitroanilines have been performed by this method. It was performed that electrochemical modification of GC electrode by poly-4-nitroaniline (P4NA) with cyclic voltammetry [6,7]. Nitroanilines are important pioneers to create azo dyes, pesticides, antioxidants and fuel additives [8]. A variety of analytical methods have been reported for the examination of selected nitroanilines.

In this study, electrochemical modification of gold electrode by 2-nitroaniline (2-NA) and applicability of electrode modified in this way for determination of Cu(II) was investigated. Electrochemical surface modification was performed by cyclic voltammetry at various scan rate by 50 cycles in aqueous media. Pt wire as counter electrode, vs. Ag/AgCl/(sat.KCl) for aqueous media and vs. Ag/Ag⁺(in 10 mM AgNO₃) for non-aqueous media as reference electrode, and gold electrode as working electrode were used. The modified surface was then characterized electrochemically by means of different mediators such as potassium ferricyanide and ferrocene. The sensitivity of gold electrode modified in defined way towards Cu(II) was investigated in Britton-Robinson (BR) buffer solution at pH 5.0.

In addition to electrochemical study, spectroscopic and microscopic characterization of these bare and modified surfaces will also be performed by using Electrochemical Impedance Spectroscopy (EIS) and Scanning Electron Microscopy (SEM) in our following studies, respectively. The ability of the complex to modify surfaces with metal ion will be researched. Finally, the modified gold electrodes prepared by described way in here will be exploited for the determination of Cu(II) in technological waste water and/or some other solutions containing Cu(II) ions.

KEYWORDS: 2-Nitroaniline, Cyclic voltammetry, Gold electrode, Modification of gold surface

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Potentiometric pK_a Values of Some Sulfonylureas in Thf-Water

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Diabetes mellitus and its abnormalities constitute a major health problem in the modern society. It is characterized by disrupted insulin production, leading to high blood glucose concentration and other complications [1]. Diabetes mellitus is classified into two types (type 1 and type 2) based on individual etiologies. Around 95% of diabetic patients are diagnosed with type 2 diabetes [2]. Many oral antidiabetic drugs with different mechanisms of action have been developed to lower blood sugar and delay the occurrence of serious complications in patients with type 2 diabetes [1].

Glimepiride is a third generation and glipizide is a second generation sulfonylurea oral antidiabetic drugs that commonly prescribed in the treatment of type 2 diabetes [3]. Since these molecules show poor solubility in water, hydro-organic mixture solvents are necessary for determination of pK_a values. In this study, the dissociation constant of glimepiride and glipizide have been determined in tetrahydrofuran–water binary mixtures at five different percentages (40, 45, 50, 55, and 60% (v/v)) by potentiometrically.

Potentiometry has been the most useful techniques for the determination of equilibrium constants in hydro-organic mixture, because of their accuracy and reproducibility. Moreover, the use of computer program for the refinement of equilibrium constants allows the different pK_a values in polyprotic substances. Dissociation constants of glibenclamide and gliclazide have been calculated by using PKPOT program [4]. The pK_a values obtained in aqueous medium have been compared with the values predicted by the SPARC on-line pK_a calculator ACD Lab, Marvin Sketch [5]. The potentiometric titration of sulfonylureas allows the calculation of dissociation constants for these compounds.

KEYWORDS: potentiometric titration, pK_a , glimepiride, glipizide

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Electrochemical Determination of Dopamine Based on Poly(1-Chrysen-6-YL-1H-Pyrrole) Modified Pencil Graphite Electrode

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It is essential to develop simple, sensitive, accurate and inexpensive analytical methods for detection of chemical or biological species [1]. Dopamine (DA) is a substance which has importance for central nervous system [2]. The measurement of DA is essential due to deficiency of it can cause several diseases and neurological disorders such as Schizophrenia, Huntington's disease, and Parkinson's disease [3]. Electrodes prepared with conducting polymers provide new advantages for instance, good mechanical stability, simplicity and possibility of miniaturization to determinate the substances like DA [4].

In this study, 1-chrysen-6-yl-1H-pyrrole was electropolymerized onto pencil graphite (PG) electrode with using cyclic voltammetric technique for determination of DA. The voltammetric behavior of conducting polymer film coated PG electrode and determination of DA were investigated by differential pulse voltammetry (DPV) in phosphate buffer solution (PBS) at pH 7.4. The response current increased with the increase of DA concentration (Fig. 1). According to the results, the modified PG electrodes can be used for determination of DA because they provide simple, rapid, sensitive and inexpensive analysis.

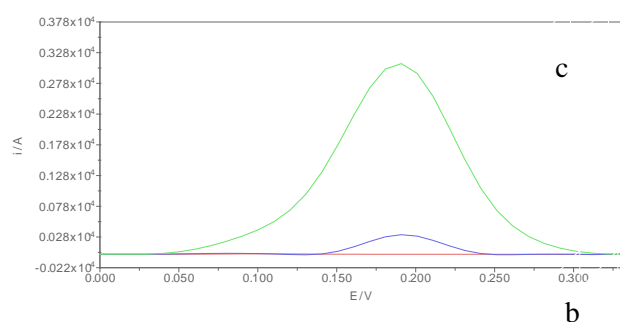


Fig. 1. DPV for (a) modified PG electrode in PBS medium at pH 7.4 (b) modified electrode after addition 1 μ M DA (c) modified electrode after addition 10 μ M DA.

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Determination of Rimsulfuron by Square Wave Voltammetry Using Static Mercury Drop Electrode

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Sulfonylurea herbicides were first introduced in 1982 by DuPont and they are unstable and weakly acidic compounds. This class of herbicide provides good crop selectivity. It is commercialized for use in wheat, barley, rice, corns, soybeans and oilseed rape. Rimsulfuron is a member of the sulfonylurea family herbicide. It is applied at a large scale against species of annual and perennial broadleaf weeds and grass in the cultivation of corn, potatoes and tomatoes[1]. Sulfonylureas are present at very low concentrations in environmental sample since low dose using and chemical stability. Various analytical methods have been applied to the analysis of rimsulfuron and most of them are based on chromatographic techniques [1]. However, only a small number of methods are available for the voltammetric determination of sulfonylurea pesticides[2] and, as far as is known, no publications dealing with the voltammetric determination of rimsulfuron appeared so far. The determination of rimsulfuron was investigated on static mercury drop electrode (SMDE) using square wave voltammetric technique and the optimum conditions were : a frequency of 150Hz, an amplitude of 175 mV, a step potential of 8 mV, a deposition time of 80 s and an accumulation potential of -100 mV in pH 3.0 B-R buffer solution. The recommended method was successfully applied to natural samples such as lake water, agrochemical herbicide formulation and tomatoes juice (Figure 1). Recoveries calculated for tomatoes juice spiked with rimsulfuron (0.05 mg/L) were 99.47 ± 1.65 (n=3).

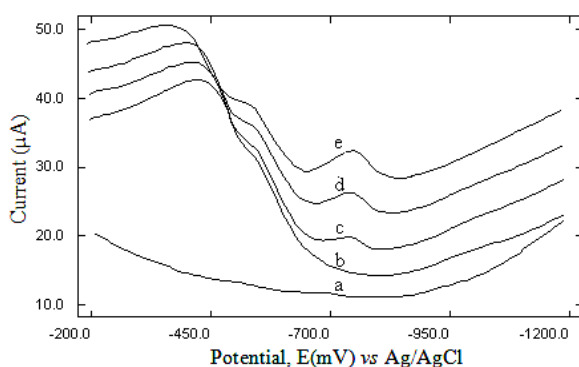


Figure. 1. Determination of rimsulfuron by square wave voltammetric method a) pH=3.0 BR buffer b) herbicide free tomatoes juice c) 0.05 mg/L rimsulfuron spiked tomatoes juice d) 0.05 mg/L standard addition of rimsulfuron e) 0.10 mg/L standard addition of rimsulfuron.

KEYWORDS: Rimsulfuron, determination, square wave voltammetry, static mercury drop electrode.

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Determination of Methacetin [N-(4-Methoxyphenyl)Acetamide] by Square Wave Voltammetry Using Multiwalled Carbon Nanotube Electrode

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Anilide herbicides are encouraging weed control agricultural chemicals for a wide variety of crops, including potatoes, cotton, rice and corn. Methacetin is a systemic anilide grup of herbicides which is widely used in agriculture for pre- and post-harvest protection of crops [1]. Herbicides are directly introduced to soils or sprayed over crop fields and toxicity therefore remains in the environment for a long time and finally enters the food chain and natural water [2]. Because of their extensive use and suspected carcinogenic activity, reliable analytical procedures are vital for their accurate determination.

A literature survey showed that no approach has been found on the voltammetric behavior of methacetin. The oxidation behavior of methacetin was studied on the newly prepared multi wall carbon nano tube paste electrode (MWCNTPE) using cyclic voltammetry (CV) and square wave voltammetry (SWV) in the pH range of 1.0–10.0. A calibration curve was constructed by obtaining the SW voltammograms of methacetin (Fig. 5) in the range of 0.47 and 22.3 mgL⁻¹ with a detection limit of 0.47 mg L⁻¹.

4.71 ± 0.02 µg mL⁻¹ of Methacetin was detected in the 5.0 µg mL⁻¹ of methacetin spiked lake water sample with the relative standard deviations of 0.21%.

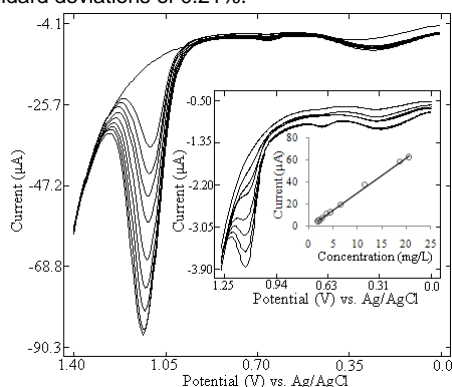


Figure. 1. Calibration curve for methacetin by using square wave voltammetry.

KEYWORDS: Voltammetry, determination, methacetin, multi wall carbon nano tube paste electrode

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The Determination of the Stability Constant of the Finasteride Complexes with Cadmium(II) And Copper(II) By Potentiometric Method

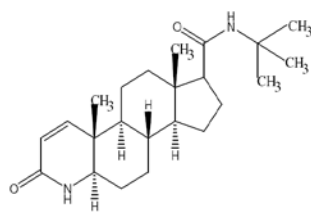
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Finasteride, chemical name is N-(1,1-dimethylethyl)-3-oxo-(5 α ,17 β)-4-azaandrost-1-ene-17-carboxamide, is a synthetic 4-azasteroid compound [1]. It inhibits the type II 5 α -reductase enzyme that converts testosterone to dihydrotestosterone (DHT) in prostatic epithelial cells. Blocking of DHT production, finasteride reduces androgenic activity in the scalp, treating hair loss at its hormonal source. In the prostate, inhibition of 5 α -reductase leads to a reduction of prostate volume, which improves the symptoms of benign prostatic hyperplasia (BPH) and reduces the risk of prostate cancer [2,3].



Finasteride

In this study, the stability constants of finasterid complexes with cobalt(II) and zinc(II) were determined potentiometrically by using Irving-Rossotti and Calvin-Bjerrum procedures [4,5,6]. In addition, the conditional formation constants were calculated depending on pH values. The evaluated protonation constant of finasteride was found as $\log K = 2,21$. The values of stability constants of metal-ligand complexes at 25°C ($I = 0,10$) are as follows:

$\log K = 3,04$ for cadmium(II)-finasteride

$\log K = 2,85$ for zinc(II)-finasteride

KEYWORDS: Finasteride, stability constant, potentiometry

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A Novel Conductometric Biosensor for the Detection of Diazinon Using *Candida Rugosa* Lipase Enzyme

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Organophosphate pesticides (OP) have come into widespread use in agriculture because of their high insecticidal activity and relatively low environmental persistence [1]. However, over use of these pesticides results a pesticide residues in food, water, environment and leads to a severe threat to human health due to their toxicity to acetyl cholinesterase (AChE) which is the essential for the functioning of the central nervous system in humans [2]. Diazinon is one of the most commonly used OP in the world which was used as insecticide although it is toxic to mammals [3]. Micro quantities of organophosphorus compounds had measured using analytical methods such as spectrophotometer, gas liquid chromatography and thin-layer chromatography[4], but, these analytical methods are having certain limitation such as require specialized laboratory personnel, expensive equipment, complicated pretreatment, certified standards of each known pesticides for evaluation and cannot be applied for online monitoring. In order to simplify procedure and decrease cost, enzyme based biosensor could be a reliable and promising alternative to classical methods because of their simple fabrication, easy operation, high sensitivity and selectivity [5].

In this work, a novel enzymatic Conductometric biosensor for highly specific, sensitive and rapid quantitative detection of Diazinon in water was developed based on immobilized lipase *Candida Rugosa* on gold interdigitated electrodes with the using of gold nanoparticles. Lipase which is characterized by its ability and specificity to hydrolyze the ester functions was immobilized by cross-linking and it was able to effect the hydrolysis of Diazinon to produce DETP and IMHP (2-iso propyl-4-methyl-6-hydroxypyrimidine). The sensor signal and response time were optimized with respect to buffer PH, enzyme loading, temperature and immobilization time. The best sensitivity and response time were obtained using a sensor with 5 mg enzyme incubated for 20 min in glutaraldehyde and operating in PH 5.2, 20mM phosphate buffer. Using optimum conditions, the biosensor had a large linear range of response up to 40 μM with a detection limit of 2 μM . Moreover, the biosensor was stable for 3 weeks when stored at 5°C and had excellent reproducibility and rapid quantitative determination of Diazinon; it is a promising new tool for pesticide analysis.

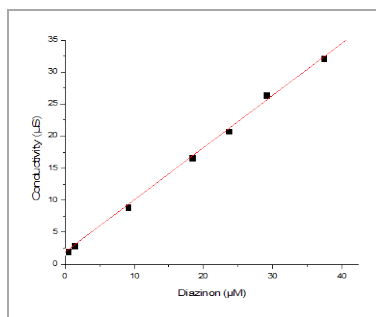
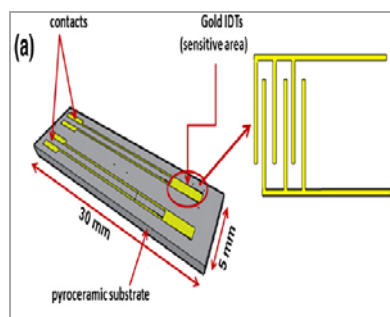


Fig1: Scheme of microelectrodes with gold IDTs

Fig2: Calibration curve for Diazinon conductometric biosensor

KEYWORDS: biosensor, conductometric, Diazinon, lipase, interdigitated electrode, gold nanoparticles.

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Chemical/Ecological Status of Surface Waters from The Region, Situated Close to Abandoned Copper Mine in Bulgaria

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The European Water Framework Directive establishes a framework for the protection of groundwater, inland surface waters, estuarine waters, and coastal waters. This legislation has several well defined objectives: (i) to prevent further deterioration, to protect and to enhance the status of water resources; (ii) to promote sustainable water use; (iii) to enhance protection and improvement of the aquatic environment, through specific measures for the reduction of discharges; (iv) to ensure the progressive reduction of pollution of groundwater and prevent its further pollution; and (v) to contribute to mitigating the effects of floods and droughts. The result will be a healthy water environment achieved by taking due account of environmental, economic and social considerations. The objective of the Drinking Water Directive is to protect the health of the consumers in the European Union and to make sure the water is wholesome and clean. Water status is assessed through chemical and ecological parameters with defined environmental quality standards.

Mining sites, along with associated facilities for the preparation and processing of ores and disposal of tailings, are potential environmental polluters. In the past, upon cessation of mining, mines have often been abandoned with no prior environmental protection measures in place. When mining ceases and the mines are no longer drained, nature begins to re-establish baseline groundwater and surface water regimes and the mines become flooded. This process of "reverting" to natural groundwater levels in abandoned deep mines, flooding open-cast mines and creating pools at lower elevations leads to the degradation of mine water quality. Due to uncontrolled discharges of mine waters, abandoned mines can act as pollution sources even decades after they were shut down. Mine waters resulting from acid mine drainage contribute to elevated concentrations of toxic elements, well in excess of maximum allowable concentrations in surface water, groundwater and river sediments.

The aim of present study is assessment of chemical and ecological status of river and underground waters from the region close to abandoned copper mines. Main physicochemical and chemical parameters, including more than 25 chemical elements were measured at about 15 sampling points with final aim evaluation of mining water impact on drinking and surface water quality and necessity of measures for further environmental protection actions.

KEYWORDS: surface water quality, abandoned mine, pollution, toxic elements

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Determination of Surface Acidic Properties of Humic Acid and Thermodynamic Properties of Proton Binding

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Humic substances are macromolecular compounds emerging from degradation of plants in soil or surface water. They can be classified under the "natural organic matter (NOM)" category. Humic acids are chemically heterogeneous compounds having different functional groups such as hydroxyl, carboxyl, phenolic-OH or amine existing at different percentages [1]. The acid-base properties of humic substances have an important role on proton uptake/dissociation equilibrium of soils and natural waters, in addition to their effect on heavy metal mobilization in environmental systems. Because carboxylic groups of humic acids are dominantly responsible for acidic properties, the acidity constants of different humic acids are variable depending on their carboxyl content [2]. Carboxylic and phenolic ingredients of humic acids form stable complexes with heavy metal cations via their donor O atoms. Explaining the acidic properties of humic acid is necessary for understanding heavy metal-humic acid complexation.

Humic acids are described as polymers forming colloidal, polydispersed and weakly acidic polyelectrolytes in aquatic media, containing carboxylic and phenolic groups giving hydrophilic character and aliphatic and aromatic groups giving hydrophobic character. Due to these functional groups, humic acids specify physical and chemical properties of soils such as aggregate stability, sorption/desorption transport of organic compounds, and complexation, mobilization and bioavailability of heavy metal cations. Additionally, the proton binding/release ability of these acidic groups cause a buffering effect of humic acid, which is explicit in a pH scale between 5.5 and 8.0 with a maximum buffer capacity at pH = 6.0 [3, 4].

The complexity of the structure leads to uncertainty in understanding proton binding behaviour of humic acid, for which the NICA (Non-ideal Competitive Adsorption)-Donnan Model has been mainly used in addition to other models. This model assumes that humic substances can form an electrically neutral gel-like phase having uniform electrostatic potential and consisting of more than one binding sites. This model also discriminates between chemical and electrostatic interactions and takes into account ionic strength effects. By fitting the NICA-Donnan Model to potentiometric data obtained at different ionic strengths, acid-base properties of humic substances including site density, heterogeneity and proton affinity can be clearly explained [4].

Acidimetric and alkalimetric titrations were carried out in the presence and absence of an inert electrolyte at different temperatures to explain the buffering capacity and isoelectric point of humic acid and the thermodynamics of proton binding. Further experiments are underway to characterize three humic acid samples collected from different sources using diverse instrumental methods.

KEYWORDS: humic substances, acid-base properties, thermodynamic properties, proton binding

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Accumulation Levels of Some Heavy Metals in Different Tissues of Horse Mackerel (*Trachurus mediterraneus*) Caught in Southeastern Black Sea

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The aim of this study was to assess the relationship between the levels of metal concentrations in gonads, gills, and muscle tissues of both genders of horse mackerel. The condition factor (CF) and gonadosomatic index (GSI) were calculated for assessing the differences in elemental bioaccumulation according to age, size, gender and spawning status of each specimen. For this purpose, concentrations of metals were measured in the muscle, gill and gonads of the pelagic fish of horse mackerel (*Trachurus mediterraneus*) that is important both commercially and for the ecosystems in the Black Sea. The varied sizes of horse mackerel were collected by the purse seine during 2011 from the Southeastern area of the Black Sea. Size, weight and length of the fish samples were measured and then classified as male and female. Composite samples from dorsal muscle, gonad and gills of tissues were taken and weighed from each fish. Frozen muscle, gonad and gill samples were dried with freeze dryer under vacuum until constant mass weight and homogenized. A temperature controlled microwave heating was used for digestion of the dried fish tissues. Sample preparation was carried out according to the procedure described by literature [1]. Approximately 0.5 g of homogenized samples were taken and placed into digestion flasks. Ultra-pure concentrated HNO₃ and H₂O₂ (7:1 v/v) were added to the samples and heated to 200 °C for approximately 15 minutes until dissolution was complete. The analyses As, Cd, Co, Cr, Cu, Mn, Ni, Pb and Zn were determined using ICP-MS (inductively coupled plasma mass spectrometry) [2]. The Collision Reaction Interface (CRI) was used during the determination of As. Both Sc and In (Scip Science, Canada) (50 ppb) were added to all standards, blanks and samples and acted as internal standards. Accuracy and reproducibility of the sample preparation were tested by the analysis of the certified reference material DORM-3 (National Research Council, Canada) and blanks along with each set of samples.

The highest concentrations of Zn were found in muscle tissue, whereas the lowest concentration of Pb was found in muscle tissue. Results showed that average metal concentrations in the tissues of *Trachurus mediterraneus* decreased in the order gill > gonad > muscle respectively. When metal concentrations of fish tissues were compared between fish gender, there were only statistical differences in the gonads of the studied fish species ($p < 0.05$). The present study demonstrated that the metals have different correlation with CF and GSI of the fish species. Chromium and gonadosomatic index showed statistically important positive correlation in male whereas As showed negative correlation in female. Condition factor and Cd showed statistically important positive correlation and also Co showed negative correlation in male of *Trachurus mediterraneus*. Cadmium concentrations in the muscle tissues of the horse mackerel were below the maximum acceptable concentration set by FAO (Food and Agricultural Organization) and above the maximum acceptable concentration set by TFC (Turkish Food Codex) and EC (European Commission) for human consumption.

KEYWORDS: horse mackerel, metal, gender, condition factor, gonadosomatic index

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The Determination of Heavy Metal Contents in Turkish Wines

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Analyses of the accumulation of heavy metals in foods frequently are seen in the literature since the early 1970s [1]. In reported studies about alcoholic beverages commonly wine samples were used at last ten years [2-5]. However, although Turkey is a manufacturer of grape and wine, only two studies reported in the literature that has been made in Turkey [6,7].

In this study, heavy metal concentration have been determined the manufactured 43 wine samples from grapes that were grown in various locations in where there are many thermal power plants by GFAAS. Therefore, the results of this study, especially Cd and Pb amounts, may be also useful in showing the effects of thermal power plants. 37 of these were red and the other 6 were white wine samples. All these are manufactures of the four largest companies in Turkey. Firstly, wine samples were treated with hot HNO₃ – H₂O₂ for decomposition of organic matrices after that determined the Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd and Pb elements with GFAAS method. Following general conclusions can be made from the data;

Fe content of red wines is higher than of white wines.

Zn and Ni content of white wines are higher than of red wines.

If relative abundances of essential elements in red wines are compared, the ranking is as follows;

Fe>Mn>Zn>Cu>Ni>Cr

If relative abundances of essential elements in white wines are compared, the ranking is as follows;

Zn>Fe>Ni>Cu>Mn>Cr

All data from analyses are in agreement with literature values [8].

Cd and Pb contents were determined to be below the permitted limit and concluded that the effect of thermal power plants are not too much.

All studied elements were tested with standard addition method for 10 randomly selected samples. Recovery values were found in between 96% and 107%.

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Trace Elements and Organochlorine Pesticides in the Epiphytic Moss *Hypnum cupressiforme* from Eastern Romania

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Concentrations of trace elements and organochlorine pesticides (OCPs) were determined in moss samples collected from Eastern Romania (Moldavia province). Samples of the epiphytic moss *Hypnum cupressiforme* were collected in 2005 at a total of 15 sampling sites in forest locations. Cu, Zn, Cd and Pb were determined by atomic absorption spectrometry and Na, Mg, Al, Cl, K, Sc, Ca, Ti, Cr, V, Mn, Ni, Fe, Co, Ga, Se, As, Br, Sr, Rb, Mo, Sb, I, Ba, Cs, La, Ce, Nd, Sm, Eu, Tb, Dy, Tm, Yb, Hf, Ta, W, Au, Th, and U were determined by epithermal instrumental neutron activation analysis. Hexachlorocyclohexane isomers (α -, β -, γ and δ -HCH), DDT and metabolites (o,p'-DDE; p,p'-DDE; o,p'-DDD; o,p'-DDT; p,p'-DDD; p,p'-DDT), hexachlorobenzene (HCB), oxychlordane (OxC), trans-nonachlor (TN), trans-chlordane (TC) and cis-chlordane (CC) were extracted using accelerated solvent extraction (ASE) and determined by gas chromatography – mass spectrometry (GC-MS). Statistical analysis of the data was carried out using non-parametric tests. DDTs and HCHs were the principal organic pollutants found in the analysed samples. Principal component analysis was used to identify possible sources of trace elements and organic pollutants in moss. The main factors represent: long-range atmospheric transport and agricultural activities for trace elements and OCPs; local emissions from industrial sources and road traffic for trace elements. The mean concentration of organic pesticides was lower than for trace metals. Organic pollutants and trace elements distribution showed differences as regards emission sources and atmospheric transport pathways.

KEYWORDS: trace elements, organochlorine pesticides, epiphytic moss

Chemical Composition of a Permanent Grassland of *Nardus stricta* L. and *Festuca rubra* L. Under Influence of Organic Fertilization

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For a long-term period no elementary management measures were applied on permanent meadows in Romania, estimating that they could get efficient yields without technological inputs. Currently agricultural practices recommend reducing the use of chemical fertilizers and promote other sources of fertilizer. In this respect, organic fertilizers can be an alternative, but their effect on the nutritional value of feed is not yet well known [1]. Fertilization with organic fertilizers is one of the main means by which we can increase the yield of permanent grasslands and have a strong influence on forage quality by modifications in floristic composition, chemical structure, consumption and digestibility with implications on nutritive and energetic values [2]. The first aim of this study was to assess the effect of organic fertilization on the chemical composition of forages from a permanent grassland of *Nardus stricta* L. and *Festuca rubra* L. located in Dorna Depression (north-eastern Romania). The second aim of the study was to establish the best dose of fertilization in order to improve the quality of forages on the permanent grassland. The study was carried out on a *Nardus stricta* L. and *Festuca rubra* L. permanent grassland situated at an altitude of 940 m and slope of 10 degrees in the Saru Dornei Depression, Moldavia province (north-eastern Romania). For studying the influence of fertilization on forages' quality the experiments were set up, in 2006, as a random block system in three replications. In this experience was evaluated the influence of 5 different organic fertilizing variants: V_1 - unfertilized control, V_2 - 20 t ha⁻¹ manure applied every year, V_3 - 30 t ha⁻¹ manure every year, V_4 - 30 t ha⁻¹ every two years and V_5 - 50+0+40+0 t ha⁻¹ manure on the quality of forages harvested from such areas. Triplicate samples were analyzed for the dry matter (DM), crude protein (CP), ether extract (EE), ash content (CA), neutral detergent fibre (NDF), acid detergent fibre (ADF), sulphuric lignin content (ADL), total phosphorus and calcium content. The analyses performed allowed the calculation of parameters for assessing the quality of the feed, such as the Digestible Dry Matter (DDM), Digestible Dry Matter Intake (DMI), Total Digestible Nutrients (TDN), net energy of lactation (NEL) and relative nutritional value (RFV). Selective results (mean of three years) obtained in accordance with fertilization variants are presented in table 1.

Table 1 Effect of organic fertilization on chemical composition (% per dry matter) of forages obtained from a permanent grassland from Romania

Variants	Ntotal	CP	CA	EE	ADF	NDF	ADL	P
V1	1.44	9.02	7.99	2.57	50.03	59.51	9.58	0.13
V2	1.57	9.81	7.61	2.31	42.99	58.08	9.84	0.20
V3	1.72	10.74	8.03	2.30	45.47	54.14	11.37	0.22
V4	1.63	10.22	7.99	1.91	44.05	53.90	9.87	0.21
V5	1.49	9.33	8.48	2.50	42.97	53.55	9.55	0.23

The use of organic fertilizers improves the quality of forages produced on mountain permanent grassland, as evidenced by the values of chemical components and a set of characteristic parameters of forages. Thus, there was a significant increase in dry matter, crude protein and total phosphorus, and a decrease in content of insoluble fibre and acid detergent fibre and of the lignin, respectively.

The results for the relative nutritional value indicate average quality forages produced on the fertilized variants. Information obtained in this study could be useful in understanding the nutritional potential of the forages, representing basic information in ruminant nutrition.

KEYWORDS: organic fertilization, permanent grassland, forages quality

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Atmospheric Organic Pollutants in Eastern Romania Monitored by Passive Air Sampling

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The passive sampling technique using PUF filters was applied to determine the levels of POPs in the atmosphere. The temporal and spatial trends of POPs concentrations in ambient air in Romania were evaluated and compared with concentrations of POPs in the countries of Central and Eastern Europe, and with those from around the world. In order to have a complete overview of the investigated area PUF based passive samplers were employed at 5 sampling sites for 5 consecutive periods of 28 days between March and August 2006. Three sampling sites were located in suburban area (RO-03, RO-05, RO-07), 4 sites in urban area (the most industrialised cities from eastern part of Romania: RO-01, RO-02, RO-04, RO-06) and a background site (RO-08). The samples were extracted with dichloromethane in a Büchi System automatic extractor and PCBs: PCB 28, PCB 52, PCB 101, PCB 118, PCB 153, PCB 138, PCB 180, and OCPs: α -hexachlorocyclohexane (HCH), β -HCH, γ -HCH, δ -HCH, 1,1-dichloro-2,2-bis (p-chlorofenyl) ethylene (p,p' -DDE), 1,1-dichloro-2,2-bis (p-chlorofenyl) ethan (p,p' -DDD), 1,1,1-trichloro-2,2-bis (p-chlorofenyl) ethan (p,p' -DDT) were determined by GC-ECD. 16 US EPA polycyclic aromatic hydrocarbons were determined in all samples using GC-MS. Discriminant function analysis was performed to determine whether OCPs levels differ among the sampling sites (background, urban and rural). A good separation was observed between the two most industrialised (RO-01 and RO-06) and the other sampling sites (Fig.1). PCBs and PAHs concentrations in Romania are higher with 1-2 order of magnitude compared with other Central and South-eastern European countries. Among PAHs, phenantren, fluoranthene and naphthalene are the most abundant compounds in the atmosphere.

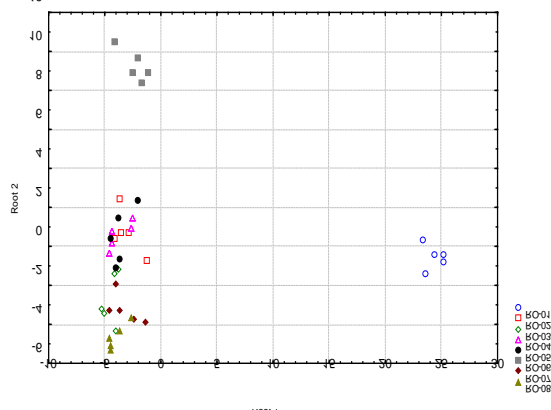


Fig. 1 Sampling points discrimination on the basis of principal component analysis performed on data recorded on OCPs levels

KEYWORDS: passive air sampling, Romania, Persistent Organic Pollutants

Enrichment of Iron Ions from Water Samples with Trensai

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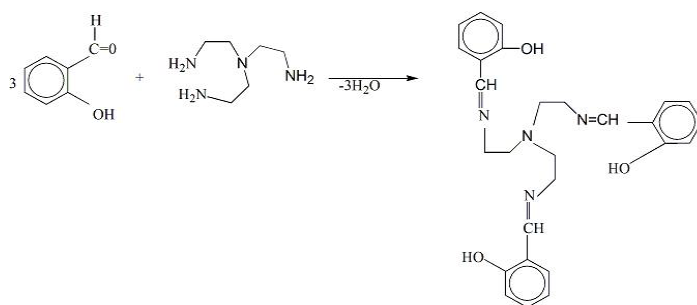
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Tris[N,N'N''(salicylidene)aminoethyl]amine (Trensai) is a O₃N₃ type Schiff base which prepared from tris(2-aminoethyl) amine and salicylaldehyde and it has been known since 1969 [1]. This Schiff base forms complex with three charged ions like Fe(III) and Co(III) however does not form complex with two charged transition metals [2-5]. In addition, if there are ions like Fe(II) or Co(II) in the medium, this Schiff base oxidize these ions to Fe(III) or Co(III) and forms complexes [3]. In this study, this characteristic was used. Firstly, Fe(II) ions were converted to Fe(III) ions and formed complexes with using Trensai then, these Fe (III) complexes were extracted with CHCl₃. Fe(III) ions which transferred to the aqueous phase using with HNO₃, were analyzed by FAAS.

10-100 ppb Fe(II) and Co(II) standard solutions were prepared and complexes were formed with Trensai in pH= 3-9 while there is acetate and phosphate buffer solutions in the medium. These complexes were extracted with CHCl₃. Fe atoms were determined and recovery % was calculated after stripping of Fe with HNO₃. Optimum conditions were determined as pH=5 and concentration of Schiff base= 2.0 10⁻³ M for formation complexes. In these conditions, recovery % was found 96%. Increasing concentration of Schiff base during agitation with CHCl₃ causes precipitation of the Schiff base and complex. Although Co (II) ions formed complexes under these conditions have been reported in the literature [2], in this study, neither complex extraction nor enrichment were observed with Co(II).



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Separation and Preconcentration of Au(III) Ions in Natural Waters and Environmental Samples by Carrier Element Free Coprecipitation Method

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Coprecipitation is one of the efficient methods for separation and preconcentration of trace amount of heavy metal ions in various environmental samples [1]. In the present study a simple, rapid, sensitive and environmentally friendly separation and preconcentration procedure, based on the carrier element free coprecipitation (CEFC) of Au(III) ions by using an organic coprecipitant, N-Benzyl-2-([3-methyl-4-(2-morpholine-4-ylethyl)-5-oxo-4,5-dihydro-1H-1,2,4-triazole-1-yl] acetyl)hydrazinecarboxamide[2].

The Au(III) ions level was determined by flame atomic absorption spectrometric (FAAS) method. The optimum conditions for the coprecipitation process were investigated on several commonly tested experimental parameters such as pH of the solution, amount of coprecipitant, sample volume, standing time, centrifugation rate and time, etc. From the results, the optimum conditions were determined as follows: pH; 3.5, coprecipitant amount; 6.0 mg (2 mL, 0.3%(w/v)), standing time; 30 min, centrifugation rate; 2500 rpm, and centrifugation time; 5 min. The preconcentration factor was found to be 375. The influences of some anions, cations and transition metals on the recoveries of Au(III) ions were also investigated, and no considerable interference was observed. The method was validated by analyzing certified reference materials and spike tests. The procedure was successfully applied to sea water and stream water as liquid samples and soil and anodic slime as solid samples.

KEYWORDS: Gold(III), Carrier element-free coprecipitation (CEFC), 1,2,4-Triazole derivative, Preconcentration, Flame atomic absorption spectrometry

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Doping polypyrrole particles by removing of Cd^{2+} , Co^{2+} from aqueous solutions

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The development of simple methods for removing heavy metals from aqueous samples is a relevant field of research. For this, various techniques are used such as chemical sedimentation [1], surface absorption [2, 3] ions-exchanger [4, 5] and reverse osmosis [6].

In the same aims, the objective of this study is to investigate the removal of Cd^{2+} and Co^{2+} ions, from aerated aqueous solutions by complexing them with polypyrrole particles. A mass of polypyrrole powder was immersed in solutions of metallic salts (CoSO_4 , CdSO_4), with concentration of 10^{-2} M for 48 h, at room temperature, then the mixture was filtered and dried. The obtained complexes were characterized by analytical methods: FTIR spectroscopy, cyclic voltammetry, X-ray diffraction, atomic force microscopy. Conductivity measurements of the polypyrrole and complexes were made using the four-points method.

The results show that the FTIR confirmed the metal coordination with azomethine nitrogen of polypyrrole [M-N] and the complexes present an amorphous structure which was determined by XRD. The voltammetric response of PPy modified with metallic microparticles showed higher current and a shift in the peaks potentials compared to unmodified polymer electrode. the conductivity of complexes are very important in presence of metallic cations, particularly in the case of Co.

From economic view, the new composites open us many application in different fields as catalysis, batteries, fuel cells or microelectronics.

KEYWORDS: heavy metals, polypyrrole, complexes, doping, conductivity

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Preparation and Characterization of Polyaniline Fiber for Headspace Determination of Chlorpyrifos and Bromopropylate Pesticides Used in Vineyards

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Pesticides are common source of soil and water pollution and many of them are considered as carcinogenic or endocrine disrupting chemicals [1]. Their analytical control is mandatory in different water samples within the EU including drinking [2] and surface waters [3]. Turkey is the sixth country in the world from the view point of the area planted grapevines which was estimated at about 640.000 hectares [4]. A wide range of insecticides, fungicides, acaricides and herbicides are used in vineyards [5]. *The possibility exists that residues of these pesticide products can be transmitted from soil and later to water with the resulting risk to human health. Chlorpyrifos (CP) and Bromopropylate (BRP) are endocrine disruptor pesticides [1] were the most used types in grape pest control in Turkey.*

Legislation in EU set the limits in water at sub ppb level for total pesticide residue [2]. These levels require very sensitive methods for pesticide determination in water samples. Solid phase micro extraction (SPME) method was applied for pesticide analysis efficiently for attaining very low limit of detection. In this method, the extracting phase is a thin polymer film coated fiber and the analyte preconcentrated on the fiber is, then, rapidly delivered to a GC column. SPME can also be combined with headspace technique (HS-SPME) for the determination of volatile organic compounds eliminating the interferences from complex matrices [6] and the life time of fiber is increased.

Present study describes a preparation of an in house solid-phase micro extraction (SPME) surface for the headspace (HS)-SPME determination of pesticides, namely, Chlorpyrifos and Bromopropylate in well waters collected from different areas of vineyards in Manisa city. Aniline monomer was electrochemically polymerized on a stainless steel wire in laboratory conditions from an acetonitrile containing 0.5 M H₂SO₄ pyrrole and 4.8 M Aniline by using cyclic voltammetry. The electropolymerization procedure was initiated by cycling the potential in a range of -0.2–1.0 V with a scan rate of 30 mV s⁻¹. Electrochemical coating procedure was completed after 30 cycles of the potential. The surface of the fibers were characterized by using scanning electron microscopy (SEM) and thermo gravimetric analysis (TGA) technique was also applied for evaluating thermal stability of the fibers.

Operational parameters effecting the extraction, mainly, pH, sample volume, adsorption temperature and time, desorption temperature, stirring rate and salt amount were optimized. The regression coefficients of two pesticides relating to linearity were at least 0.99.

In virtue of diminishing the cost and enhancing the analyte retention on its surface to exert better selectivity and hence the developed polymerized surface could offer to analyst to exploit it as a fiber in headspace SPME analysis.

KEYWORDS: Polyaniline, SPME fiber, Pesticide, Gas Chromatography

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Heavy Metals Concentrations in the Mussel *Mytilus Galloprovincialis* Followed During Five Seasons in Southeastern Adriatic Sea

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This work represents a summary of the level of heavy metals, correlation coefficient (r) and bioconcentration factor (BCF) determined for mussels (*Mytilus galloprovincialis*) sampled in Boka Kotor Bay, Southern Adriatic sea, Montenegro, from the Fall 2007 to the Spring 2009. As a result of this work, *Mytilus galloprovincialis* have found a new application as sea water pollution indicators.

Next microelements: Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Cd, Hg and Pb were investigated in all samples of the mussels *Mytilus galloprovincialis*. Mussels were sampled from seven different locations in Boka Kotor Bay: Krašići, Kukuljina, Tivat, Opatovo, Sv. Stasija, Perast i Herceg Novi. The highest concentrations were detected for Fe and Zn. Concentrations of Pb and Hg in investigated mussels were higher than MDC, indicating on the pollution of marine environment of the Bay. By analyzing the correlation coefficient of the investigated elements in the mussel it can be concluded that there were synergistic and antagonistic relationship between some metal pairs. Analysis of BCF provides conclusion that the mussel *Mytilus galloprovincialis* could be good bioindicator of sea water pollution.

KEYWORDS: heavy metals, mussel, bioindicator, pollution, Montenegro

The Main Issues in Assessing the Accumulation of Metals in Fish Ontogenesis

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Composition of metals in fish is one of the links of biological monitoring of metals and assessment of trends of substance and energy circuit in aquatic ecosystems. Researching the phenomenon of accumulation of metals in fish has both ecological and hygienic importance.

In terms of increasing anthropogenic influence on aquatic ecosystems, the issues of accumulation of metals, particularly of heavy metals, are of major importance. These data are of high value, because metals, of course, in optimal amounts, are always necessary for human beings, but in the case of abnormal concentrations they can cause the balance disorders, endemic diseases and even intoxication.

The complicated nature of the metal accumulation processes into representatives of ichthyofauna, determined by the diversity of physiological and environmental factors that influence these processes, underlines the necessity, scientific and practical importance of carrying out the monitoring of metal accumulation dynamics in fish tissues and organs.

We have come to the conclusion that in the case of research and assessment of metal accumulation processes in fish three main directions shall be highlighted: 1-processes of accumulation of metals in fish eggs and larvae; 2- accumulation of metals in fish fry and immature fish; 3- accumulation of metals in organs and tissues of sexually matured individuals.

In early ontogenesis surplus or shortage of at least one trace element can lead to the fish perishment, thus the knowledge on the accumulation of metals in fish eggs, larvae and fry are particularly valuable both for assessing the ecological status of aquatic ecosystems, and creating the optimal conditions for the fish development in the case of fish artificial reproduction. The numerous aquarium experiences have shown the presence of synergism and antagonism in the accumulation of metals in the fish early ontogenesis, which are quite difficult and uneven phenomenon. Therefore, in such complicated environment as natural water is the mutual influence of chemical elements in their accumulation process cannot be univocal. Probably, namely by water are determined contradictory conclusions, when, for example, some authors consider the copper and zinc as antagonist elements and others, opposite, as synergist ones.

Already at the stage of fry for fish is characteristic a clear expression of homeostasis and redistribution of metals among different organs and tissues, depending on the peculiarities of fish physiological age and the period of year. At the same time, the total content of metals in fry, in general, is a reflection of the environment.

As result of multiannual investigations the modification of content of metals during the fish vital cycle has been established, for example, accumulation of iron, copper, zinc and manganese in liver in the period of intense feeding, increase of concentrations of iron, zinc, manganese, cobalt, copper, and molybdenum in the gonads - directly before spawning, this process being accompanied by lowering their content in muscles.

Thus, apart from the influence of external factors, for fish is characteristic the metal distribution between different organs depending on the biological need in one or another chemical element and physiological status of fish, including age, gender, type of nutrition.

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KEYWORDS: metals, aquatic ecosystems, fish ontogenesis, accumulation, biological monitoring

Heavy Metal Contents of Total Suspended Solids in Oxic/Anoxic Interface Layer of the Black Sea

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The Black Sea is a semi-enclosed inland sea and 83% of its total mass is anoxic water. Oxygen transportation is limited due to the density difference. Depending on the specific location, waters below 100 meter depth contain toxic H₂S (hydrogen sulphide) gas [1, 2, 3]. Metals can be precipitated with sulphide as metal sulfides which are low solubility in anoxic environment [4]. The Black Sea is a natural laboratory for studying involving redox reaction due to presence of both oxic and anoxic conditions [2].

This study aims to investigate the heavy metal changes of the suspended matter at different depths of both oxic and anoxic environments of the Black Sea. For this purpose, the total of 12 samples were taken from different depths of a station which is offshore Kızılırmak river (Samsun-Bafra). Sampling station is 10 nautical miles from the shore and coordinates is of 41°54.195'N - 35°58.205' E. The samples were filtered with 0.45 micron pore diameter membrane filters. The filters were digested with acid in the temperature control microwave heating device (Milestone Ethosplus, Italy). Metals (Al, Cr, Mn, Co, Ni, Cu, Zn, As, Se, Mo, Cd, Sb ve Pb) were determined by ICP- MS (Inductively coupled plasma mass spectrometry) (820-MS Varian, Australia).

Samplings were carried out with intervals of 5 meters in the oxic / anoxic interface layer and at the same time, physicochemical parameters (temperature, salinity, electrical conductivity, sigma-t, pH, ORP), dissolved oxygen and hydrogen sulfide concentrations were measured of the water column in the station. Dissolved oxygen reached to depths of 175 meters and H₂S was found to be present in waters deeper than 160 meters. Light transmission minimum was observed at a depth of 150 meters, which indicates an excess of the suspended particulate matter. A small but significant increase was observed at the pH value in the same depth. Mn, Ni, Zn, As, Co, Mo and Sb maximas were detected over the depth of the initial H₂S onset while maximum concentration of Cu, Pb, Cd, Cr, Se and Ag were determined in the anoxic layer (Figure 1).

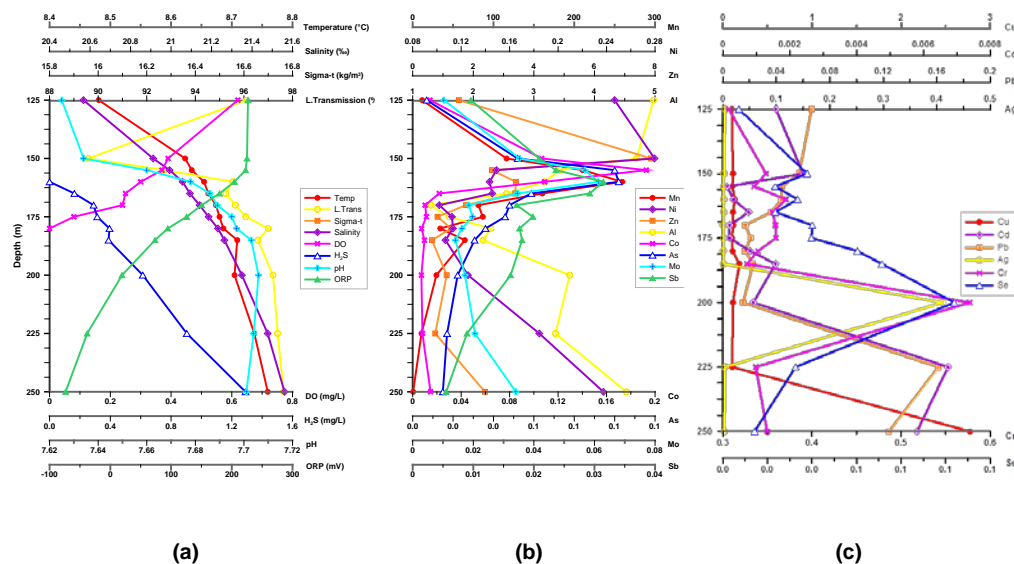


Fig 1. Black Sea water column profiles of physical parameter (a), and metal concentrations of suspended solids (b, c)

Also depths which maximum metal concentration were observed were associated with water density. Maximum metal values were found for Ni and Zn at $16.50 \sigma_t$ (sigma-t) value (150 m), for Mn, Co, As, Mo and Sb at $16.25 \sigma_t$ (155-160 m), for Cr and Se at $16.50 \sigma_t$ (200 m), for Pb and for Cd at $16.60 \sigma_t$ (225 m).

KEYWORDS: Black sea, total suspended solid, heavy metal, hydrogen sulphide

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Determination of Phenolic Pollutants in Water Samples by Capillary Electrophoresis with a UV-Detector

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Phenolic compounds are widely distributed in natural waters because of their wide range of applications in household products and industrial synthesis. They are used as disinfectants in household cleaners, lotions, salves, ointments and in mouth wash. The compounds of phenols are widely used in many industrial processes such as the manufacture of plastics, dyes, drugs, pesticides, antioxidants, paper and wood and petroleum products. They exist extensively in environmental waters and soils. They possess high toxicity even at low concentrations. Phenolic compounds are subject to regulation as water pollutants due to their toxicity. Several phenols have been designated as priority pollutants by the United States Environmental Protection Agency (US EPA) and the European Union (EU). According to EPA regulations, the maximum contaminant levels of these compounds in drinking water is 0.5 µg/L.

In this study, a method for the determination and separation of phenol and substituted phenols was developed; an organic modifier was used to improve the separation. The effects on selectivity of buffer pH and the concentrations of organic modifiers were investigated. Reproducibilities of migration times, linear ranges and limits of detection using UV detector were also determined. The developed method was then applied to measure concentrations of phenolic pollutants in water samples.

KEYWORDS: Capillary electrophoresis, phenolic pollutants, buffer composition, organic modifier

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**Development of a Cloud Point Extraction and Preconcentration
Method for Determination of Lead Water Samples**

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Cloud point extraction (CPE) a newly developed liquid-liquid extraction protocol for the separation and preconcentration of analyte of interest from bulk matrix. The small volume of the surfactant-rich phase obtained with this methodology permits the design of extraction schemes that are simple, highly efficient, rapid and environmentally benign, compared with conventional liquid extraction using organic solvents [1,2].

Cloud point extraction has been used for the preconcentration of lead, after the formation of complex with 2,7-naphthalenedisulfonic (SPADNS), and later analysis by atomic absorption spectrometry using octylphenoxypolyethoxyethanol (TritonX-114) as surfactant. The main factors affecting CPE efficient, such as pH of sample solution, concentration of SPADNS and TritonX-114, equilibration temperature and time were investigated in detail. After optimization of extraction conditions, preconcentration factor and the limit of detection were determined. The proposed method was applied to the determination of lead in water samples.

KEYWORDS: Preconcentration, CPE, lead, Atomic Absorption Spectroscopy

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Removal of Reactive Black 5 from Aqueous Solutions by TiO₂ Immobilized Onto Activated Carbon

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Adsorption onto activated carbon (AC) and oxidation using photocatalyst are widely used techniques to remove dyes from waste water. The aim of this work is to enhance the removal capacity of activated carbon by combining AC and titanium dioxide (TiO₂) in a Photocatalytically Regenerative Activated Carbon.

Anatase titania were deposited on powder activated carbon made from grape seeds (AGS) by impregnation/mixing method and then the composite photocatalyst was employed for the removal of reactive black 5 from aqueous solution. The TiO₂/AGS was characterized by BET, MEB, XRD and optical absorption spectroscopy. The BET surface area and the pore structure of composite photocatalyst (TiO₂/AGS) and activated grape seeds (AGS) were evaluated from nitrogen adsorption data at 77 K in relation to process conditions. Our results indicate that the photocatalytic activity of TiO₂/AGS was much higher than single phase titania. The adsorption equilibrium of reactive black 5 from aqueous solutions on the examined materials was investigated. Langmuir, Freundlich, and Redlich–Petersen models are in good agreement with the experimental equilibrium data. The degradation kinetics fitted well to the Langmuir-Hinselwood pseudo first order rate law. The photocatalytic activity of TiO₂/AGS was much higher than virgin TiO₂. COD removal was measured at regular intervals to quantify the mineralization of the dye. Above 96% mineralization was observed. These results suggest that UV-irradiated TiO₂ immobilized onto activated carbon may be considered as an adequate process for the treatment of diluted colored textile waste water.

Analysis of Trace Elements in Various Matrix by Coprecipitation Method Using a Triazole Derivative Ligand

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Determination of metals in environmental samples is an important part of analytical chemistry. Nowadays, the pollution by metals is a major interest owing to their potential toxic effects on living organisms [1]. There has been an increasing interest in studying the toxicity and effect of elements on human health and environment. Hence, the development of sensitive methods is important for the determination of the elements in water and food samples. Lately, a new coprecipitation method, carrier element-free coprecipitation (CEFC), has been developed. The CEFC method has many benefits for separation and preconcentration of metals due to the lack of contamination and adsorption risks for metal ions from a carrier element [2]. In this study, the usage of ligand, in selective and simultaneous separation and preconcentration of some trace metal ions such as Cu(II) and Co(II) by using carrier element free coprecipitation (CEFC), which was brought into the literature as a new method in recent years, has been evaluated. From the obtained results, it was seen that, the 2-(3-(4-methylbenzyl)-4-[2-(1H-indol-3-yl)ethyl]-5-oxo-4,5-dihydro-1H-1,2,4-triazol-1-yl)-N'-(2-hydroxyphenyl methylidene) acetohydrazide ligand can be used in CEFC method for selective separation and preconcentration of Cu(III) and Co(III) ions at pH 7.0 (figure 1). For optimization of the developed methods, the effects of some experimental parameters such as pH, ligand amount, sample volume, standing time, centrifugation rate and time were evaluated. The interference effects of some anions and cations, which may present in the environmental samples together with the analyte ions, were investigated. In order to evaluate the analytical performance of the methods, the values of limit of detection (LOD) is $0.79\text{--}1.16\text{ }\mu\text{g L}^{-1}$, limit of quantification (LOQ) is $2.38\text{--}3.48\text{ }\mu\text{g L}^{-1}$ and relative standard deviations (RSD) is 3-3.7%, were calculated. After determined the optimum conditions of the methods, for checking the accuracy of them, spike tests were performed and the certified reference materials were used. The developed method were applied to environmental solid and liquid samples and food samples. The analyte ions were determined by using atomic absorption spectrophotometric method.

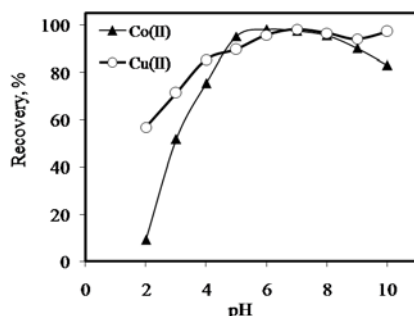


Figure 1.

KEYWORDS: trace element, separation and preconcentration, coprecipitation, carrier element free coprecipitation

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Carrier Element-free Coprecipitation with 3-(4-*Tert*-Butylphenyl)-5-Phenyl-4-(2-Hydroxy-4-Methoxybenzylamino)-4H-1,2,4-Triazole for Separation/Preconcentration of Pb(II) and Cd(II) from Various Matrix

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The detection of heavy metal ions in environmental sources such as natural water and food is a great concern in analytical chemistry due to their toxicity for living organism [1]. For these reasons, the determination of elements in water and food samples are very significant. The precise determination of heavy elements is needed improved analytical techniques. Recently, the carrier element free coprecipitation (CEFC) method has been developed for separation and preconcentration of metal ions. The CEFC method has many advantages for preconcentration of trace metals such that in this method the contamination and adsorption risks for the interested analyte ions from a carrier element can be eliminated [2]. In this work, a simple, rapid and sensitive separation/pre-concentration method for Pb(II) and Cd(II) in environmental samples has been developed. The present procedure is based on a combination of carrier element-free coprecipitation (CEFC) and flame atomic absorption spectrometric (FAAS) determination of trace metals ions. An organic coprecipitant, 3-(4-*tert*-butylphenyl)-5-phenyl-4-(2-hydroxy-4-methoxybenzylamino)-4H-1,2,4-triazole was used without adding any carrier element for coprecipitation of metal ions. The optimum conditions for the coprecipitation process were investigated on several commonly tested experimental parameters, such as pH of the solution, amount of ligand, sample volume, standing time, centrifugation rate and time. The influences of some anions, cations and transition metals on the recoveries of analyte ions were also investigated, and no considerable interference was observed. The pre-concentration factor was found to be 50 and the detection limits corresponding to three times the standard deviation of the blank ($N = 10$) for Pb(II), Cd(II), ions were found as 2,0 and 0,2 $\mu\text{g L}^{-1}$, respectively. The relative standard deviations were found to be lower than % 6,0 for both analyte ions. The present procedure was successfully applied for separation and pre-concentration of investigated ions in sea water and stream water as liquid samples and tobacco, black tea as solid samples. In order to support the accuracy of the method, the certified reference materials (CRM-SA-C Sandy Soil C) were analyzed. The experimental results are in good agreement with the certified values.

KEYWORDS: separation and preconcentration, FAAS, coprecipitation, carrier element free coprecipitation

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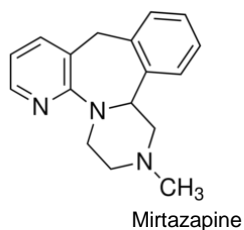
Spectrophotometric Determination of Mirtazapine in Pure and Tablets

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Simple and sensitive extractive spectrophotometric method was developed for the determination of mirtazapine in pure and tablets. Proposed method is based on the formation of yellow ion-pair complex between the basic nitrogen of the drug and methyl orange. The ion pair complex was extracted with dichloromethane. Spectrophotometrically, under the optimum condition, the ion pair complex showed an absorption maximum at nm. Beer's law is obeyed in the concentration ranges µg/mL. The proposed method is successfully applied to the determination of mirtazapine in pure and tablet.



KEY WORDS: Mirtazapine, Methyl orange, Ion pair, Spectrophotometry

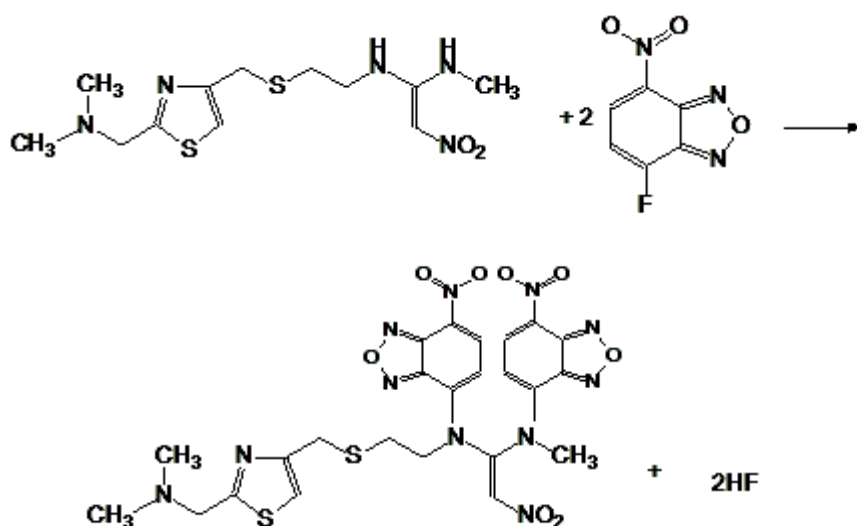
HPLC Fluorescence Method for the Determination of Nizatidine in Human Plasma and its Application to Pharmacokinetic Study

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A sensitive high performance liquid chromatographic method was developed for the determination of nizatidine in human plasma. Nizatidine was derivatized by 4-fluoro-7-nitrobenzofurazan. Chromatographic separation was performed on a Inertsil C₁₈ column (150 mm×4.6 mm, 5 µm) using isocratic elution by a mobile phase consisting of methanol – water (55:45) at a flow rate of 1.2 mL/min. Amlodipine was used as the internal standard (IS). Fluorescence detector was used operated at 461 nm (excitation) and 517 nm (emission), respectively. This method was successfully applied to a pharmacokinetic study after oral administration of a dose (150 mg) nizatidine.



The reaction between nizatidine and NBD-F

KEYWORDS: nizatidine.derivatization. pharmacokinetics. fluorescence detector

Impact of Soluble Endothelial Protein C Receptor and Interleukin 6 on Induced Hypercoagulability and Inflammation in HCV Infected Patients

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The aim of the present study was to estimate plasma levels of soluble endothelial protein C receptor (sEPCR) and interleukin 6 (IL-6) in HCV infected patients and to evaluate their role in hypercoagulability and inflammation.

Patients and methods: It included 40 patients newly diagnosed as HCV positive with and without history of schistosomal infestation and 40 healthy individuals, matched for age and sex, were taken as a control group. Thorough history, clinical examination and laboratory investigations were done.

Results : Both sEPCR and IL-6 levels were found to be significantly elevated in HCV infected patients than in the control group ($p < 0.001$), reflecting a state of hypercoagulability and inflammation in those patients. The elevated plasma level of sEPCR was positively correlated with elevated IL-6 plasma level in HCV infected patients group which supported the state of hypercoagulability and inflammation mostly encountered in HCV infected patients and emphasized the close relation between inflammation and hypercoagulability.

Conclusion: The previous results indicated that there was an increased plasma level of sEPCR in HCV infected patients and that HCV infected patients may be at a greater risk of thrombotic events. In addition, plasma level of sEPCR may serve as a prognostic marker of hypercoagulability where most of the basic laboratory tests don't truly represent the balance of coagulation in vivo.

KEYWORDS: sEPCR – HCV – IL-6 - Hypercoagulability.

Possible Association of Interleukin-1beta (-511c/T) and Interleukin-6 (-174g/C) Gene Polymorphisms with Atherosclerosis in End Stage Renal Disease Egyptian Patients on Maintenance Haemodialysis

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In end stage renal disease, inflammation is considered a critical regulator of atherosclerotic plaque formation and progression, to which many dialysis and non-dialysis- related factors may contribute .Since circulating inflammatory cytokine levels vary inter-individually, one may speculate that genetic factors, such as polymorphisms in genes encoding them, may be involved in determining the individual inflammatory reaction in response to a given insult. AIM: The present work aimed to study interleukin-1B (-511C/T), and interleukin- 6 (-174G/C) gene polymorphisms and their possible association with atherosclerosis in Egyptian patients with end stage renal disease on maintenance haemodialysis. Subjects and methods: The present study was conducted on one hundred Egyptian subjects, the control group (n=30) and the patients group (n=70) with end stage renal disease on maintenance haemodialysis which were further subdivided into two subgroups with (n=33) and without atherosclerosis (n=37) as evidenced by CIMT, ECG ischemic changes, cerebrovascular insufficiency (CVI), and peripheral vascular insufficiency (PVI). All studied subjects were subjected to detailed history taking, routine laboratory investigations and molecular studies including detection of IL-1B (-511C/T) and IL-6 (-174G/C) gene polymorphisms using Polymerase chain reaction / Restriction fragment length polymorphism (PCR / RFLP) technique. Results: The genotype distribution and alleles frequency of IL-1B (-511C/T) and IL-6 (-174 G/C) showed no statistical significant difference among the studied groups. Conclusion: The development of atherosclerosis among Egyptian patients on maintenance haemodialysis cannot be attributed to these two gene polymorphisms.

The Effect of CaNa₂-EDTA On Zinc, Carbohydrate Metabolism and Glutamic Oxalic, Glutamic Pyruvic Aminotransferases (GOT, GPT) and Alkaline Phosphatase Activities in Experimental Diabetes

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To investigate the effect of CaNa₂-EDTA and experimental diabetes (IDDM) on zinc and carbohydrate metabolism and the activities of GOT, GPT and alkaline phosphates. Forty male weaning normal albino (Wistar) rats of 8 weeks of age were fed with a basal diet. Twenty rats (n = 20) were then intraperitoneally injected with alloxan to induce diabetes. Then after one week ten rats from each group (n = 20) were administrated intraperitoneally with CaNa₂-EDTA for further three weeks. Body weight gain and food intake were recorded regularly. On day 21 after an over night fasting, animals were killed and blood glucose, serum zinc, femur and pancreatic zinc concentrations, liver glycogen contents, serum glutamic oxalic transaminase (GOT), serum glutamic pyruvic transaminase (GPT) and serum alkaline phosphatase were determined. Diabetic rats given CaNa₂-EDTA or not had a low body weight gain, high total food intake (hyperphagia), low liver glycogen contents and low serum and pancreatic zinc concentrations compared to normal ones. The administration of CaNa₂-EDTA significantly altered the body weight gain, food intake and serum zinc concentration of either diabetic or non-diabetic animals. Both diabetic and non-diabetic rats given CaNa₂-EDTA had higher blood glucose than their control counterparts. Liver glycogen was also found to be higher in CaNa₂-EDTA non-diabetic rats than their controls. In alloxan diabetes, serum GOT and GPT were significantly increased compared to normal rats, while the level of serum alkaline phosphatase was decreased. The administration of CaNa₂-EDTA led to increasing of GOT and GPT, and decreasing serum alkaline phosphatase. To conclude, the present study demonstrates that CaNa₂-EDTA had an effect on body weight gain, glucose utilization and serum zinc. In addition CaNa₂-EDTA has affected the activities of GOT, GPT and alkaline phosphatase. Therefore it was appeared that CaNa₂-EDTA resulted in the development of severe diabetes.

KEYWORDS: diabetic rats, non-diabetic rats, alloxan, CaNa₂-EDTA, GOT, GPT, alkaline phosphatase, Glycogen.

Estimation of Lipid Components and Fatty Acid Composition of Human Serum in Fatty Liver Patients

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The study was designed to estimate the effect of fatty liver disease on the level of some biochemical parameters, percentage of fatty acids in serum lipids .the study includes (25) fatty liver patients as verified by ultrasonography of the liver ,the age ranged between (50-70) year and (25) apparently healthy subjects of matched age group .The some biochemical parameters were measured as well as analysis and measurement of Percentage and level of fatty acids in serum lipids, lipids extraction from serum and separation of serum lipids (Cholesterol ester ,Triglyceride, Phospholipids) by TLC, and then esterification of fatty acids and measurement of percentage of fatty acids by Capillary Gas Chromatography (CGC).the result showed that there was large effect of fatty liver disease on the biochemical parameters and the percentage of fatty acids comparison with control group.

Design and Optimization of a New Kinetic Spectrophotometric Method for the Determination of Losartan Potassium in Pharmaceutical Products

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Losartan potassium (LP) is chemically described as 2-butyl-4-chloro-1-[p-(o-1H tetrazol-5-ylphenyl)benzyl]imidazole-5-methanol monopotassium salt) and it is a nonpeptide angiotensin II receptor antagonist used for the treatment of hypertension[1,2]. In this study we aimed to assess losartan potassium in pharmaceutical products via a new UV-Visible spectrophotometric method based on the oxidation reaction between iodide and iodate in the presence of carboxylic acid form of LP.

Carboxylic acid form of losartan (LS) was derived by oxidation of methyl group in butyl chain of LP (converted to Losartan) with iodate. In the presence of carboxylic acid molecule; oxidation of iodide with iodate produced yellow triiodide ion and defined at 286 nm in the UV-Visible spectrophotometry. LC/MS method, kinetic studies and central composite design method was used for formation reactions, equilibration and determination of stability duration and experimental conditions, respectively. Developed spectrophotometric method was validated. The equilibration period was calculated as 10 minutes. KIO_3 and KI amount was calculated as 1.961 mL and 1.953 mL respectively; and temperature was measured as 32.3 °C. It was revealed that the method was linear between 4-30 $\mu\text{g/mL}$ with correlation coefficient of 0.9996. LOD and LOQ parameters were calculated as 0.61 and 1.85 $\mu\text{g/mL}$ respectively. Pharmaceutical preparations named Cozaar, Eklips, Loxibin, Sarilen and Sarvas were analyzed by the developed kinetic spectrophotometric method and the results ranged between 94.9 % and 100.9 %.

This new kinetic UV-Visible spectrophotometric method for assessment of LP in pharmaceutical products was resulted as successful. The method can be used in routine analysis.

KEYWORDS: Losartan potassium , UV-visible spectrophotometry, central composite design

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Indirect Spectrophotometric Determination of Ketoconazole in Pharmaceutical Products

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A simple method has been developed for the determination of antifungal Ketoconazole in pure and pharmaceutical formulations. The method is based on oxidation of KZ with excess amount of cerium (IV) in sulfuric acid solution, then the residual oxidant reacted with Indigo carmine dye then the amount of the drug is determined indirectly by monitoring the increase of the absorbance of the remaining dye at 610 nm. The factors affecting the results of the reaction were studied and optimized this include oxidant, dye and pH. Statistical analysis was performed to investigate the sensitivity and accuracy of the method which showed that the results are comparable with reference methods.

KEYWORDS: Spectrophotometric, Ketoconazole, Determination, pharmaceutical

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Comparison of Liquid Chromatographic, Capillary Electrophoretic and UV Spectrophotometric Methods for Determination of Leflunomide

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Leflunomide is a disease-modifying drug that is used in the treatment of rheumatoid arthritis. It reduces inflammation in the joints that is responsible the destruction of joints by suppressing the activity of immune cells [1]. Leflunomide suppresses by inhibiting dihydroorotate dehydrogenase, an enzyme that is necessary for the production of DNA and RNA [2].

This study presents an comparison of three different analytical methods for leflunomide quantification in pharmaceutical preparations in terms of validation parameters (linearity, sensitivity, selectivity, accuracy, precision, robustness and ruggedness), costs, analysis time. The methods compared are high performance liquid chromatography, micellar electrokinetic capillary chromatography and UV spectrophotometry.

The liquid chromatographic analyses were performed with a reversed-phase column (Nucleosil C₁₈ 250 x 4.6 mm, 5µm i.d.) with a mobile phase containing acetonitril-water (50:50 v/v) at a flow-rate of 1.0 mL min⁻¹ and UV detection was performed at 260 nm.

The electrophoretic analyses were performed at micellar electrokinetic chromatography (MEKC) mode. MEKC method was performed by using a fused silica capillary (i.d. 75.0 µm, total length 48.5 cm and effective length 40.0 cm). The optimal separation was carried out at 30 C° and 20 kV, using 25 mM borate buffer and 70 mM sodium dodecyl sulphate adjusted to pH 9.5. Detection was performed by using a diode array detector at 205 nm.

The spectrophotometric analyses were performed in methanol. The measuring of UV absorbans was done at 260 nm.

The obtained data of the three methods were evaluated. These methods were applied for the analysis of leflunomide in pharmaceutical preparations and compared the results for being applicable of them to routine analysis of leflunomide in the quality control laboratories.

KEYWORDS: Leflunomide, chromatography, spectrophotometry, capillary electrophoresis, validation, pharmaceutical preparation.

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Electrochemical Aptasensor Design For Clinical Analysis

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Aptamers are short single-stranded DNA or RNA sequences which have high specific affinity in binding protein targets [1]. Aptamer based studies represent a novel modern and a strategic approach in bioanalytical analysis for specific protein detection [2-3]. Due to their high stability, chemical simplicity, and easy applicability, they can be used as alternative captures to antibodies. Thereby, aptamer applications hold a great promise for biosensing of proteins, genes, and cells for developing clinical detection arrays [4].

In recent years, there has been a great interest in developing aptamer sensors, thereby different strategies have been developed for aptamer based protein and cell screening. Affinity biosensors have a great promise in aptamer sensing analysis due to their, high sensitivity, selectivity, simple instrumentation, portable and cost effectiveness. Thus a lot of aptamer based sensing interfaces have been developed including optical, piezoelectrical transduction, fluorescence, atomic force microscopy [5-7].

Herein we describe a label free detection of aptamer / protein and aptamer / cancer cell interactions based on electrochemical impedance spectrometry (EIS) technique. The 5' chemically modified aptamer sequence was immobilized onto disposable graphite electrode (DGE) surfaces. The binding of target protein and / or cancer cell onto aptamer sequence were monitored by EIS transduction of the R_{ct} in the presence of 5mM $[\text{Fe}(\text{CN})_6]^{3-/4-}$. This study gives a new approach and an overview of alternative electrochemical biosensors for clinical analysis.

KEYWORDS: aptamers, biosensor, protein, cancer cell, electrochemical impedance spectrometry

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Biochemical and Histological Studies on the Effect of the Patulinmycotoxin on Male Rats' Liver and Treatment by Crude Venom Extracted from Jelly Fish

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Patulinmycotoxin on some biochemical parameters and histological changes on male rats' liver and effect of crude venom extracted from jelly fish *Cassiopea Andromeda* as a treatment. 50 Inbreeding weanling white male wistarlewis rats were divided randomly into 5 groups. Control group was gavage fed daily with distilled water; three treated groups were gavage fed daily dose with Patulin (0.2 mg/kg b.w.) for one, two and three weeks respectively. The last group was treated by Patulin for one week then injected intraperitoneally with single dose of crude venom (1.78 mg/20 g b.w.) for 24 hours according to LD50. Level of (AST) and (GGT) were increased significantly in serum of all treated groups compared with control group but level of (ALT) was increased significantly in treated group after one week only. Although the concentration of (TNF- α) was increased significantly and gradually in all treated groups, the concentration of ferritin was decreased significantly in treated three after three weeks only. Histopathological changes of rat liver coincided with biochemical changes. In conclusion, oral exposures of Patulin indicate that hepatic alteration was produced in manner related to dose duration and crude venom may used as new therapeutic approach to detoxify hepatocytes from Patulin. [Nagwa M. El-Sawi, Hanaa M. Gashlan, Sabry H. H. Younes, Rehab F. Al-Massabi and S. Shaker. Biochemical and histological studies on the effect of the Patulinmycotoxin on male rats' liver and treatment by crude venom extracted from jelly fish. *Life Sci J* 2012;9(4):1143-1153]. (ISSN: 1097-8135). <http://www.lifesciencesite.com>. 171

KEYWORDS: mycotoxin, patulin, liver, rat, Jelly fish crude venom.

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Simultaneous Determination and Validation of a Hplc Method for Some Active Ingredients in Cough and Cold Pharmaceuticals

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Cough and cold pharmaceutical preparations are one of the most extended formulations in the world and have got many pharmaceutical forms: syrup, suspension, sachets, capsules and tablets [1]. These preparations represent complex formulations containing several active ingredients and a broad spectrum of excipients such as flavoring agents, saccharose, acidulants, natural or artificial coloring and flavoring agents, dyes, sweeteners and preservatives. The majority of these ingredients are present as a mixture of basic nitrogenous amino compounds and their separation in pharmaceutical forms is quite complicated due to similarities of their physical and chemical properties. Several methods describing the simultaneous determination of a wide variety of active compounds in various cough–cold formulations have been reported. These parathion and determination of these products in dosage forms are complicated due to their similarities in some physical and chemical properties. Ultraviolet (UV–Vis) spectroscopy [2,3], high performance liquid chromatography (HPLC) [4,5], gas chromatography(GC) [6] and multivariate spectrophotometric methods [7–9] have been used to determine these compounds in preparations.

A new simple and sensitive liquid chromatographic method has been developed and validated for the simultaneous determination of pseudoephedrine HCl, pheniramine maleate, acetaminophen, guaifenesin, pyrilamine maleate, chlorpheniramine maleate, triprolidine HCl, dextromethorphan HBr, diphenhydramine HCl in cough and cold pharmaceuticals. 2,4,6-trimethoxybenzaldehyde was used as an internal standard (ISTD). These separation of these compounds was achieved within 37.9 min on a Nucleodurgravity C18 column (250 x 4.0 mm, 5µm) using an isocratic elution. The mobile phase was a mixture of 38% methanol, 62% of 80 mM KH_2PO_4 aqueous solution adjusted to pH 3.0, to which was added 10% (v/v) orthophosphoric acid. The chromatographic separation of these compounds performed at room temperature, with flow rate of 0.75 mL/min. An ultraviolet absorption at 210 nm was monitored.

The selectivity, linearity of calibration, accuracy, intraday and interday precision, recovery and forced degradation studies were examined as parts of the method validation. Stress testing was carried out under different stress conditions. Intentional degradation was attempted to stress condition of acid (0.1 N HCl at 80 °C/2 h and 80 °C/8 h), base (0.1 N NaOH at 80 °C/2 h and 80 °C/8 h), oxidation (10.0% H_2O_2 at 24(±2) °C/2 h and 8 h, 30.0 % H_2O_2 at 24(±2) °C/2 h and 8 h), and photolytic (under the UV light 35 h) to evaluate stability of active ingredients. The proposed liquid chromatographic method was successfully applied for the routine analysis of these compounds in different cough and cold pharmaceutical preparations such as syrups and tablets.

KEYWORDS: Reversed-phase liquid chromatography, simultaneous determination, cough syrup, validation, cold formulations, forced degradation

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Application of Derivative Spectrophotometric Method for the Analysis of a Ternary Mixture Containing Erythrosine, Quinoline Yellow and Indigotine in Tablets

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A simple, rapid, accurate, precise, reliable and economical spectrophotometric method has been proposed for simultaneous determination of Erythrosine (E127, E), Quinoline Yellow (E104, QY) and Indigotine (E132, I) in laboratory prepared mixtures and commercial tablets without any prior separation and purification. In this proposed method the E and I contents were determined from the first derivative spectrum by measuring the signals at 537 and 544 nm ($^1D_{537}$, $^1D_{544}$) (Zero-crossing point for QY and I) and the signals at 638 and 670 nm ($^1D_{638}$, $^1D_{670}$) (Zero-crossing point for E and QY) and by using appropriate calibration graph. The QY content was determined in the same way by measuring the signals at 420 and 423 nm ($^2D_{420}$, $^2D_{423}$) (Zero-crossing point for E and I) at the second derivative spectra. Calibration graphs were obtained between 2-10 $\mu\text{g.mL}^{-1}$ for each colorant. The values of limit of detection (LOD) were 0.6 $\mu\text{g.mL}^{-1}$, 0.6 $\mu\text{g.mL}^{-1}$ and 0.3 $\mu\text{g.mL}^{-1}$ and the LOQ values were 2 $\mu\text{g.mL}^{-1}$, 2 $\mu\text{g.mL}^{-1}$ and 1 $\mu\text{g.mL}^{-1}$ for E, QY and I, respectively. The precision values were less than 10% RSD. The developed spectrophotometric method was applied to the laboratory mixtures and two pharmaceutical preparations. The recoveries at the tested concentrations for all colorants were in the range of 92-108% with relative standard deviations < 10% regardless of the type of sample matrix and spiking level. The high recoveries and low coefficients of variation confirm the suitability of this method for analysis of the above colorants. The obtained results were statistically compared with derivative ratio spectrophotometric method and very similar values were found by both methods.

KEYWORDS: derivative spectrophotometry, Erythrosine, Quinoline Yellow, Indigotine, pharmaceuticals.

Simultaneous Spectrophotometric Determination of Three Food Colorants in Tablets by Using Derivative-Differential Spectrophotometry

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An analytical procedure has been developed for the determination of three food colorants Erythrosine (E127, E), Quinoline Yellow (E104, QY) and Indigotine (E132, I) in tablet formulations. The derivative-differential spectrophotometry, comprised of measurement of the difference absorptivities derivatized in the first order of a tablet extract in 0,1N NaOH relative to that of an equimolar solution in 0,1N HCl at wavelengths of 525, 390 and 637 nm for E, QY and I, respectively. Zero-crossing point technique was used to estimate the amount of each colorant. To confirm the analytical method is suitable for its intended use, several validation parameters, such as linearity, limit of detection and quantification, trueness and repeatability were evaluated. Calibration curves were linear within a studied range of concentrations ($r^2 \leq 0,999$) for three investigated colorants (E, QY, I). The method detection limits (corresponding to signal-to-noise (S/N) ratio of 3) were below $0.6 \mu\text{g.mL}^{-1}$ whereas the method quantitation limits (corresponding to signal-to-noise (S/N) ratio of 10) were below $2 \mu\text{g.mL}^{-1}$. The recoveries at the tested concentrations for all colorants were in the range of 93-108% with the relative standard deviations $< 2\%$ regardless of sample matrix and the spiking level. The method was applied to the laboratory prepared mixtures and commercial tablets. The results were statistically compared with those obtained by derivative spectrophotometry by means of Students t-test and the variance ratio F-test. It was concluded that the developed method was accurate, sensitive, and precise. The proposed method could be applied to determine E, QY and I in the pharmaceutical products.

KEYWORDS: derivative-differential spectrophotometry, food colorants, Erythrosine, Quinoline Yellow, Indigotine.

Application of Derivative-Differential Spectrophotometry for Determination of Synthetic Colorants in Tablets

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A method is presented for the direct determination of Sunset Yellow (E110, SY), Ponceau 4R (E124, P) and Quinoline Yellow (E104, QY) in synthetic mixtures and in tablets without prior separation. Derivative-differential spectrophotometry, comprised of measurement of the difference absorptivities derivatized in the first order (Δ^1D) of a tablet extract in 0,1N NaOH relative to that of an equimolar solution in 0,1N HCl at wavelengths of 589, 546 and 390 nm for SY, P and QY, respectively. Zero-crossing point technique was used to estimate the amount of each colorant in tablets. The linearity ranges were found to be 2-10 $\mu\text{g.mL}^{-1}$ for each colorant. The relative standard deviation of the proposed method was in the range of 0.9-2% and percent recoveries were less than 109%. The method detection limits (corresponding to signal-to-noise (S/N) ratio of 3) were below 0.6 $\mu\text{g.mL}^{-1}$, whereas the method quantitation limits (corresponding to S/N ratio of 10) were below 2 $\mu\text{g.mL}^{-1}$. The high recoveries and low coefficients of variation confirm the suitability of this method for analysis of the above colorants. The proposed method has been successfully applied to the determination of the three colorants in tablet formulations. The results were compared with those obtained by derivative spectrophotometry and very similar values were found by both methods. The procedure described here is simple, accurate and precise and is suitable for routine quality control analysis of tablets.

KEYWORDS: derivative-differential spectrophotometry, synthetic colorants, tablets, Sunset Yellow, Quinoline Yellow, Ponceau

Validated Derivative Spectrophotometric Determination of Food Colorants in Pharmaceutical Products

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Multicomponent analysis has become one of the most appealing topics for analytical chemists in the last few years. In recent years Partial Least Squares multivariate spectrophotometric calibration (PLS1, PLS2 and PCR) [1,2] and derivative spectrophotometry have been widely used for the resolution of binary and ternary mixtures and satisfactory results were reported [3,4]. A simple, rapid, accurate, precise, reliable and economical spectrophotometric method has been proposed for the simultaneous determination of Sunset Yellow (E110, SY), Ponceau 4R (E124, P) and Quinoline Yellow (E104, QY) in laboratory prepared mixtures and in commercial tablets without any prior separation and purification. In this method the SY content was determined from the first derivative spectrum by measuring the signals at 506 and 538 nm ($^1D_{506}$, $^1D_{538}$) (Zero-crossing points for P and QY) and by using appropriate calibration graph. The P and QY content were determined in the same way by measuring the signals at 525 and 570 nm ($^1D_{525}$, $^1D_{570}$) (Zero-crossing point for SY and QY) and the signals at 406 and 420 nm ($^1D_{406}$, $^1D_{420}$) (Zero-crossing point for SY and P). Calibration graphs were obtained between 2-10 $\mu\text{g.mL}^{-1}$ for each colorant. The values of limit of detection (LOD) were 0.3 $\mu\text{g.mL}^{-1}$, 0.6 $\mu\text{g.mL}^{-1}$ and 0.6 $\mu\text{g.mL}^{-1}$ and the LOQ values were 1 $\mu\text{g.mL}^{-1}$, 2 $\mu\text{g.mL}^{-1}$ and 2 $\mu\text{g.mL}^{-1}$ for SY, P and QY, respectively. The precision values were less than 10% RSD. The developed spectrophotometric method were applied to the laboratory prepared mixtures and two pharmaceutical preparations. The recoveries at the tested concentrations for all colorants were in the range of 100-110% with relative standard deviations < 10% regardless of the type of sample matrix and spiking level. The high recoveries and low coefficients of variation confirm the suitability of this method for analysis of the above colorants. The obtained results were statistically compared with derivative ratio spectrophotometric method and very similar values were found by both methods.

KEYWORDS: derivative spectrophotometry, pharmaceuticals, Sunset Yellow, Quinoline Yellow, Ponceau 4R.

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Resolution of Ternary Mixtures of Sunset Yellow, Ponceau 4r and Quinoline Yellow by the Derivative Double Divisor-Ratio Spectra and Derivative Ratio Spectra-Zero Crossing Methods in Pharmaceutical Tablets

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Synthetic food colorants such as Sunset Yellow, Ponceau 4R, and Quinoline Yellow normally contain azo and aromatic rings and are often used for dyeing foods, drinks, medicine and cosmetics. During the fifties, it was found that these dyes are somewhat harmful to people's health. In most countries their uses are strictly limited and, it is important to detect and to analyze them in different products. Generally, spectrophotometry is used for assay of these colorants and due to serious spectral overlapping a prior separation is usually needed. Two very simple spectrophotometric methods are described for resolving ternary mixtures of the food colorants Sunset Yellow (E110, SY), Ponceau 4R (E124, P) and Quinoline Yellow (E104, QY) by using the first derivative of the ratio spectra with measurements at zero crossing wavelengths and the first derivative double divisor-ratio spectra. The proposed methods were applied to the analysis of synthetic laboratory mixtures and pharmaceutical tablets containing the title compounds without using a chemical separation procedure. In the use of both methods, the calibration graphs were linear in the range of 2-10 $\mu\text{g.mL}^{-1}$ for SY and P, and 3-15 $\mu\text{g.mL}^{-1}$ for QY. These methods were satisfactorily used for determining synthetic mixtures of these dyes in different ratios (from 4:1:1 to 1:3:3; K:P:S or even higher) with recoveries in 100%-108% range and the methods were successfully applied over two commercial products containing the three dyes and they did not require any separation step. The recovery values range from 100%-108% for QY, 100% to 108% for SY and 101% to 108% for P, respectively. The high recoveries and low coefficients of variation confirm the suitability of these methods for analysis. The precision values were less than 2% RSD for the two methods. The standard deviation of the results of analyses does not exceed 1%. The common excipients and additives did not interfere in their determinations. The results obtained by the proposed methods have been statistically compared by means of Student t-test and by the variance ratio F-test.

KEYWORDS: spectrophotometric method, synthetic dyes, Quinoline Yellow, Sunset Yellow, Ponceau 4R derivative double divisor method, ratio-spectra derivative method, ratio spectra-zero crossing method.

Simultaneous Determination of Synthetic Dyes in Tablets with the Use of Double Divisor-Ratio Spectra Derivative and Ratio Spectra-Zero Crossing Methods

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Synthetic food dyes, mostly petroleum derived, are U.S approved for use in foods under the foods, drugs and cosmetics Act of 1938. Water insoluble dyes called lakes are made by combining dyes with salts to make insoluble compounds and they tint by dispersion. Lakes are not oil soluble but are oil dispersible. Lakes are most stable than dyes and are ideal for coloring products containing fats and oils or items lacking sufficient moisture to dissolve dyes. Typical utilization include coated tablets, cake and doughnut mixes, hard candies and chewing gums, lipsticks, soaps, shampoos, talc etc [1]. Food dyes can cause serious disorders and diseases like nausea, headache, ulceration, lung cancer, hyperactivity, anemia [2], and also have effect on eye, skin, mucous membrane etc. That's why there is a necessity to control the content of these dyes in food, and pharmaceutical products. For that purpose many analytical methods have been developed like: Derivative spectrophotometry [3], H-point standard addition method [4] and Cloud point extraction [5]. Two simple, rapid, accurate, precise, reliable and economical spectrophotometric methods have been proposed for the simultaneous determination of Erythrosine (E127, E), Quinoline Yellow (E104, QY) and Indigotine (E132, I) in pure and commercial formulations without any prior separation or purification. They were derivative ratio spectra zero-crossing method and double divisor ratio spectra derivative method. The ranges for E, QY and I found to be 2-10 $\mu\text{g.mL}^{-1}$, 2-10 $\mu\text{g.mL}^{-1}$ and 1-5 $\mu\text{g.mL}^{-1}$, respectively. For method 1, the values of limit of detection (LOD) were 0,6 $\mu\text{g.mL}^{-1}$, 0,6 $\mu\text{g.mL}^{-1}$ and 0,3 $\mu\text{g.mL}^{-1}$ and the limit of quantitation (LOQ) were 2 $\mu\text{g.mL}^{-1}$, 2 $\mu\text{g.mL}^{-1}$ and 1 $\mu\text{g.mL}^{-1}$ for E, QY and I, respectively. For method 2, the values of limit of detection (LOD) were 0,6 $\mu\text{g.mL}^{-1}$, 0,6 $\mu\text{g.mL}^{-1}$ and 0,3 $\mu\text{g.mL}^{-1}$ and the limit of quantitation (LOQ) were 2 $\mu\text{g.mL}^{-1}$, 2 $\mu\text{g.mL}^{-1}$ and 1 $\mu\text{g.mL}^{-1}$ for E, QY and I, respectively. The precision values were less than 2% RSD for two methods. These methods were satisfactorily used for determining synthetic mixtures of these colorants in different ratios (from 1:2:2 to 1:10:10, I:E:QY, or even higher) with recoveries in 94-108% range. The methods were successfully applied over two commercial products containing the three dyes and they did not require any separation step. The recovery values range from 99% to 107% for E, 93% to 107% for QY and 94% to 98% for I, respectively. The results were compared with those obtained by derivative spectrophotometry. There was no significant difference between the proposed methods and the derivative method regarding both accuracy and precision.

KEYWORDS: spectrophotometric method, synthetic dyes, Quinoline Yellow, Indigotine, Erythrosine

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Spectrophotometric Determination of Clopidogrel in Bulk Drug and Pharmaceutical Preparation

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Clopidogrel is a derivatized form of ticlopidine whose IUPAC name is methyl 2-(2-chlorophenyl)-2-(6,7-dihydrothieno [3,2-c]pyridin-5(4H)-yl)acetate. Clopidogrel is an oral, thienopyridine class antiplatelet agent used to inhibit blood clots in coronary artery disease, peripheral vascular disease, and cerebrovascular disease [1]. It is aimed to develop and validate a spectrophotometric method for determination of clopidogrel and apply these methods on pharmaceutical formulations that includes clopidogrel.

In order to develop and validate a novel spectroscopic method for clopidogrel standards and pharmaceutical preparations, the spectrum of clopidogrel was taken in different solvent mixtures and optimum absorbance values were obtained, where it detected at 202 nm, in methanol-acetonitrile (50:50, v/v) mixture. After the optimization of spectrophotometric method, validation tests were made including recovery, linearity, accuracy, intra and inter day precision. It was noticed that methods was linear for spectrophotometric method in concentration range 1.25-25 µg/mL. The accuracy and precision values of proposed method were lower than 4.40% and 4.38%, respectively. Limit of quantification (LOQ) value was described as the concentration whose %RSD lower than 8% and similarly limit of detection (LOD) was calculated to be the point whose %RSD value was lower than 20%. So, LOQ and LOD of the method were measured to be 1.25 and 0.4 µg/mL, respectively. Developed and validated spectrophotometric method was applied to pharmaceutical formulations including clopidogrel which were named as Karum, Plavix and Atervix. According to the data, analytical recovery values were averagely in between % 99-102. It indicated that method can be used in routine quality control studies.

KEYWORDS: clopidogrel, UV spectrophotometric method, pharmaceutical preparation

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Spectrophotometric, Chromatographic and Electrophoretic Techniques to Quantify of Varenicline in Quality Control

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It is well known that quality control is an important task in the pharmaceutical industry. The term quality control refers to the sum of all procedures undertaken to ensure the identity and purity of a particular pharmaceutical. It not only protects the manufacturer against compensation claims, but also guarantees the patient a safe and effective product. Quality control measurements include stability testing of the drug formulation, dissolution testing and analysis of active pharmaceutical ingredients in pharmaceuticals. A pharmaceutical company usually has to measure a large number of quality control samples. High-performance liquid chromatography (HPLC) is used in the pharmaceutical industry for a wide variety of samples. It is the method of choice for checking the purity of pharmaceuticals, in-process testing for developing new formulations, and quality control/assurance of final drug products [1]. Capillary electrophoresis (CE) is a powerful analytical technique that is widely used in research and development and in quality control of pharmaceuticals. Many reports of highly efficient separations and methods have been published over the past 15 years. CE offers several advantages over HPLC. These include simplicity, rapid analysis, ruggedness, different mechanisms for selectivity, and low cost [2]. UV spectrophotometry can be used for the quantitative determination of compounds that absorb UV radiation. Therefore, it could be easily used for the analysis of active pharmaceutical ingredients in pharmaceutical dosage forms. It is well known that smoking causes cancer and varenicline is used along with education and counseling to help people stop smoking. It is in a class of medications called smoking cessation aids. It works by blocking the pleasant effects of nicotine (from smoking) on the brain. The nicotinic acetylcholine receptor plays an important role in nicotine dependence, alcohol consumption and induced cocaine craving[3]. In this study, it is compared the developed and reported analytical techniques for determination of the varenicline tartrate in tablet dosage forms. Thus, the advantages and disadvantages of UV spectrophotometry [4], HPLC [5] and CE[6] were discussed by evaluating the methodology and the analysis results for the tablet assays. The developed methods were validated by evaluating validation parameters such as precision, accuracy, robustness and ruggedness respect to the ICH guidelines. In conclusion, the reported methods were compared each other and they were proposed for the quality control in pharmaceutical industry.

KEYWORDS: Varenicline tartrate, UV-Visible spectroscopy, HPLC, Capillary electrophoresis, Validation.

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Determination of Zn Levels in Patients Who Have Undergone Coronary Artery Bypass Surgery

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Macronutrients are micronutrients chemical elements essential to life in large quantities. They are essential, must be derived from external sources, and are integral components of enzymes or coenzymes involved in chemical reactions. Reduced circulating levels of such micronutrients as Zn²⁺ and Se²⁺, together with macronutrients, expressed as ionized hypocalcaemia and hypomagnesaemia, are found in patients with either hypertension or congestive heart failure (CHF), irrespective of race, ethnicity, or the aetiological origins of the failing heart. Hence, a deficiency of multiple macro- and micronutrients is an important accompaniment of hypertension and CHF. Each has the potential to adversely influence the structure of the failing myocardium. Both hypertension and CHF represent progressive systemic illnesses whose major features include: (i) the presence of oxidative stress that overwhelms antioxidant defenses provided by Cu/Zn-SOD and Se-glutathione peroxidase, in diverse tissues including the heart; Zinc is an essential micronutrient integral to the activity of various metalloenzymes that include angiotensin-converting enzyme and matrix metalloproteinases(1).

Clinical use of antioxidant vitamin supplementation may help to prevent coronary heart disease (CHD). Epidemiologic studies find lower CHD morbidity and mortality in persons who consume larger quantities of antioxidants in foods or supplements(2).

The aims of this study is to determine serum Zn level in patients who have undergone coronary artery bypass surgery. Blood samples from patients and controls were drawn in sterile syringes containing of sodium citrate anticoagulant, transferred into tubes. Serum was obtained by immediately centrifugation at 5000 rpm for 10 minutes and stored at -70°C until assayed. Serum concentration of Zn, was determined by Atomic Adsorption spectrophotometer. Patients who have undergone coronary artery bypass surgery had lower serum zinc concentrations than the controls. The serum zinc levels in the normal healthy controls were found in the range of 132.28±6,48 µg/L, in patients of prior the bypass surgery 116,35±13,18 µg/L and after the bypass surgery 83,35±14,87 µg/L. The difference serum zinc values statistically significant (p<0,001) as compared to normal healthy controls.

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Use of Ceric Ammonium Sulphate and Two Dyes, Methyl Orange and Indigo Carmine, in the Determination of Mefenamic Acid in Pharmaceuticals

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Two spectrophotometric methods are proposed for assay of mefenamic acid (MF) IN Bulk drug and dosages by using ceric ammonium sulphate (CAS) and two dyes, methyl orange and indigo carmine, as reagent. The methods involve addition of a known excess of (CAS) to mefenamic acid in aqueous medium followed determination of residual (CAS) by reacting with a fixed amount of either methyl orange measuring the absorbance at 520 nm (method A) or indigo carmine measuring the absorbance at 610 nm (method B). In both methods, the amount of (CAS) reacted corresponds to the amount of (MF) and the measure absorbance was found increase linearly with the concentration of (MF), which corresponds to the amount of (MF) which is corroborated by the correlation coefficient of 0.9994 and 0.9997 for method A and B respectively. The systems obey Beer's law for 0.5—8 $\mu\text{g ml}^{-1}$ and 0.5—10 $\mu\text{g ml}^{-1}$ respectively. The molar absorptivities were 61048 and 42082 $\text{l.mol}^{-1}\text{.cm}^{-1}$ for method A and B respectively. The limits of detection (LOD) and quantification (LOQ) were 0.015, 0.049 and 0.026, 0.087 $\mu\text{g ml}^{-1}$ respectively. Both methods were comparable accuracy (er. < 2.7%), also both methods were equally precise as shown by relative value < 1.6%. The methods were successfully applied to the assay of (MF) in pharmaceutical preparation and the results agree favorably with British pharmacopeia method.

KEYWORD: mefenamic acid, methyl orange, ceric ammonium sulphate

Method for A New Spectrophotometric Determination of Promethazine Hydrochloride in Pharmaceutical Preparations

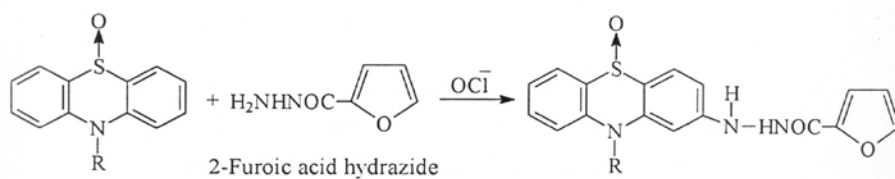
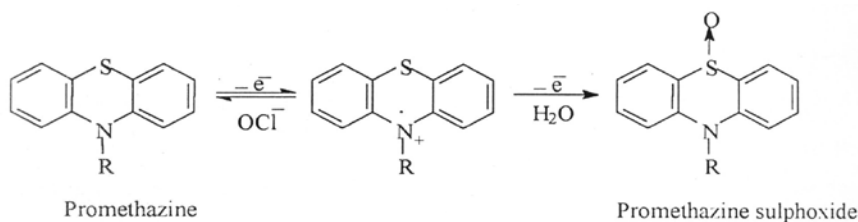
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A new, simple, sensitive and selective spectrophotometric method has been described for the determination of promethazine hydrochloride in bulk and pharmaceutical preparations. The method depends on the reaction of drug compound with 2-furoic acid hydrazide in the presence of calcium hypochlorite in acidic medium to form violet colour product that has a maximum absorption at 550 nm with molar absorptivity $6569 \text{ l.mol}^{-1}\text{cm}^{-1}$. Microgram amounts can be estimated (0.8-40 $\mu\text{g/ml}$) with LOD and LOQ 0.18 $\mu\text{g/ml}$ and 0.59 $\mu\text{g/ml}$ respectively. The accuracy (average recovery) is 98.70% and precision (RSD) is less than 4.0%. The method is successfully employed for the determination of promethazine. HCl in pharmaceutical preparations (tablets and injections) and the results agree favourably with British pharmacopoeia method and also with certified values.

Proposed reaction sequence :



where R : $\text{CH}_2-\underset{\text{CH}_3}{\text{CH}}-\text{N}(\text{CH}_3)_2$

Multi-Wavelength Spectrophotometric Determination of Acid Dissociation Constants of Fenopropfen and Indomethacin in Acetonitrile-Water Binary Mixtures

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Non-steroidal anti-inflammatory drugs (NSAIDs) are useful analgesic adjuncts that can improve pain relief. Given as single doses or in short-term therapy NSAIDs can relieve mild to moderate pain. However, it may take up to 3 weeks of use before their anti-inflammatory effects become evident. They are used in musculoskeletal and joint disorders such as ankylosing spondylitis, osteoarthritis, and rheumatoid arthritis, in soft-tissue disorders such as sprains and strains, for postoperative pain, and in mild to moderate pain including dysmenorrhoea and migraine. Also some NSAIDs are used in the management of dental or postoperative pain. The mechanism of action of the NSAIDs, is not completely understood but may be related to prostaglandin synthetase inhibition. Fenopropfen propionic acid derivative, is the members of NSAIDs. Indomethacin the members of indole acetic acid and phenylacetic acid derivatives of NSAIDs, respectively [1-3].

The pK values of the studied these compounds were determined by means of the data obtained from spectrophotometric titrations in 0.40, 0.45, 0.50, and 0.55 volume fraction acetonitrile+water mixtures at (25.0(±0.1) °C and in 0.1 mol.L⁻¹ KCl. The spectrophotometric multiple-wavelength pH titration was carried out. During spectrophotometric titrations, the test solution was pumped to a spectrophotometric flow cell by means of a peristaltic pump. After each addition of titrant, and after waiting for the emf reading to be stable, the spectra were recorded with 1 nm resolution over the (190 to 350) nm interval to obtain different spectra around the maximum λ for each studied compound. The solutions of individual compounds were prepared at a concentration of approximately 1.10⁻⁴ mol.L⁻¹ for spectrophotometric titration. The spectral data obtained at different pH values were treated using the program STAR and LNREG.

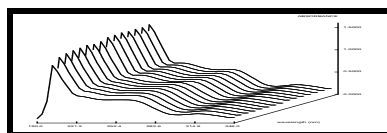


Figure 1. Plot of experimental absorbance values of indomethacin versus λ as a function of pH in ACN-water mixtures with 45% (v/v) of ACN.

KEYWORDS: NSAID, propionic acid, indole acetic, phenylacetic acid

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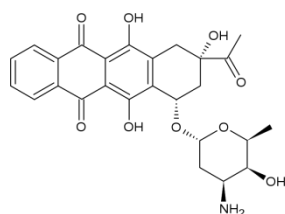
In-Situ Evaluation of Idarubicin-DNA Interaction Using Spectroscopic Techniques

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Idarubicin, 4-demethoxydaunorubicin, is an anthracycline antileukemic drug. It belongs to the family of drugs called antitumor antibiotics. It is an analog of daunorubicin, but the absence of a methoxy group increases its fat solubility and cellular uptake. It inserts into DNA and prevents DNA from unwinding by interfering with the enzyme topoisomerase II.



The interaction of idarubicin with DNA was investigated by UV-VIS, spectrofluorimetric, and surface enhanced Raman spectroscopic techniques. In these methods, titration has been carried out. Considerable decreases in analytical signals were observed when adding ds-DNA to the solution of the idarubicin. Furthermore, there were slight red shifts at the maximum wavelengths of the simulated spectra. The results indicate that quenching mechanism of idarubicin by ds-DNA is a combined dynamic and static quenching and interaction mode is intercalation.

Development and validation of UFLC-MS/MS method for determination of bosentan in rat plasma: Application to a rat real samples

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Bosentan is a potent nonpeptide dual endothelin receptor antagonist with affinity for both endothelin A and endothelin B receptors. It decreases both pulmonary and systemic vascular resistance, thereby increasing cardiac output without increasing the heart rate [1,2].

Shimadzu UFLC-XR-MS/MS system which includes an 8030 LC-MS/MS system, a CBM-20ALite system controller, two LC-20ADXR pumps with a micro gradient mixer and DGU-20A3R degasser, one SIL-20ACXR autosampler with cooling function, one CTO-20AC column oven (Shimadzu Co., Kyoto/JAPAN). Mass spectrometric detection was performed using ESI ion source in the positive ionization mode; the nebulizing gas, and drying gas flow rates and the ESI voltage are; 3L/min, 15L/min and 4500V, respectively. MRM using the precursor ion at m/z 551.9 to the product ion at m/z 201.9 was used for quantification for bosentan. Similarly, for the IS the precursor ion at m/z 288.2 to the product ion m/z 172.0 was used for quantification purposes. Intersil ODS-4 column (3µm, 2.1 mm x 50 mm; GL science, Japan) was employed for the separation at 40°C. The mobile phase consisted of 0.1 % acetic acid with 5 mM ammonium acetate in water for solvent A and 5 mM ammonium acetate in acetonitrile-methanol (50:50, v/v) for solvent B. Stock solutions of bosentan and IS were prepared separately in mobile phase (20:80, V/V) at concentrations of 100 µg/mL. Working solutions of bosentan were prepared by serial dilution of the stock solution in mobile phase (20:80, V/V). Calibration standards were prepared by spiking 20 µL of the appropriate standard solutions to 250 µL of blank rat plasma giving concentrations of 0.5, 5, 25, 100, 500, 1000 and 2000 ng/mL. An aliquot of 250 µL plasma sample was transferred to a polypropylene tube, 20 µL of IS solution (10 µg/mL) was added and vortex mixed for 30 s. 100 µL of methanol and 500 µL of 1 M HCl was added to the mixture, respectively. The mixture was vortexed for 30 s and extracted with 5 mL of diethyl ether–chloroform (4:1, v/v) by vortexing for another 60 s. After centrifugation at 3500 rpm for 8 min, the upper organic layer was then transferred into another clean glass tube and evaporated to dryness at 40°C under a gentle stream of nitrogen. The residue was reconstituted with mobile phase (20:80, V/V), and transferred into an autosampler vial. Samples were analyzed at a flow rate of 0.3 mL/min and the injection volume of 1 µL. The proposed method for determination of bosentan in rat plasma has highly sensitive and selectivity. The method offers significant advantages; lower sample requirements (250 µL), simplicity of liquid phase extraction procedure and short analysis time. The linear range established was adequate to measure the plasma concentration of bosentan in rat plasma. The analytical method is successfully applied to five healthy male rat following oral administration of bosentan (50 mg/kg and 100 mg/kg). This method can be adapted to pharmacokinetic studies and routine clinical estimation of bosentan.

KEYWORDS: bosentan, UFLC-MS-MS, rat, plasma

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Spectrophotometric Assay of some Nitrogen Containing Drugs in Pharmaceutical Formulations using p-Chloranilic Acid Reagent

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A spectrophotometric method is developed for the determination of some drugs containing amino groups (sulfacetamide sodium, lidocaine and terbutaline sulfate) based on their reaction with p-chloranilic acid reagent in an organic medium forming colored charge transfer complexes. The absorbances are measured at 530 and 527 nm for sulfacetamide sodium and lidocaine respectively, terbutaline sulfate gives two peaks measured at 529 and 319 nm. Beers law is obeyed over the concentration range of 10-60 $\mu\text{g.ml}^{-1}$ for sulfacetamide sodium and lidocaine and 5-70 $\mu\text{g.ml}^{-1}$ for terbutaline sulphate. The molar absorptivity values are 940.7, 913.8 $\text{L.mol}^{-1}.\text{cm}^{-1}$ for sulfacetamide sodium and lidocaine respectively while terbutaline sulphate gives 987.7 $\text{L.mol}^{-1}.\text{cm}^{-1}$ at 529 nm and 7407.5 $\text{L.mol}^{-1}.\text{cm}^{-1}$ at 319 nm with accuracy range between 100.20% and 101.42% and RSD better than 3.15%. The method is applied successfully for determination of these drugs in pharmaceutical formulations and compared favorably with British Pharmacopeia standard methods. F and t tests are less than the tabulated values at 95% confidence level.

Keywords: Spectrophotometric, p-Chloranilic acid, Charge transfer complex, Sulfacetamide sodium, lidocaine and Terbutaline sulfate.

Validation of a Method for Determination of Phthalates in Common Use Objects (Toys and Child Care Articles) by Gas Chromatography Mass Spectrometry (Gcms)

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Phthalates or phthalate esters are esters of phthalic acid, and are mainly used as plasticizers (substances added to plastics to increase their flexibility, transparency, durability and longevity). Their primary role is to soften polyvinyl chlorid (PVC), and there fore their use is widespread in production of common use object. The need for determination of phthalates in toys and childcare articles is related to the fact that they are potential cancerous. According to directive 2005/84/EC, phthalates (bis(2-ethylhexyl) phthalte, dibutyl phthalate and benzyl buthyl phthalate) must not be used as substances or as constituents of preparation at concentration greater than 0,1 % by mass of the plastic material in toys and childcare articles. The same conditions are applicable for diisononyl phthalate, diisodecyl phthalte and di-n-octyl phthalate in toys and childcare articles which can be placed in mouth by children.

Method for determination of phthalates in toys and childcare articles is based on extraction of sample (1g), with dichloromethane on Soxtherm, followed by gas chromatography mass spectrometry analyses of resultig extracts. Method is validated according to Norm HRN EN 14372:2004, with some improvements of extraction time (4h instead 6h) and sample quantity (1g instead 2g). During validation of method following values have been achived: recovery (83%-107%), limit of detection (0,05% and 0,01%), limit of quantification (0,01% and 0,02%), linearity range (0,015-0,15%).

Obtained results satisfy given criteria of acceptability. Method is accredited in flexible area, and can be used for determination of phthalates in common use objects.

KEYWORDS:phalates, gcms, common use objects

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Application of Mesogenic Materials with Alkoxy Lateral Chains as Stationary Phases for the Separation of Derivatives Phenolic Compounds

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Two liquid crystals containing alkoxy lateral chains has been synthetised and used as stationary phases in capillary gas chromatography. The fuse silica capillary column of 30 meters and 0.25 millimeter of internal diameter have been impregnated of each of the liquid crystals according to dynamic method (mercury index). The determination of transition temperatures is realised by differential scanning calorimetry. Some analytical properties behaviour of these mesogenics compounds are determinated by capillary gas chromatography. The results show that the analytical performance of the mesogenic materials allow an excellent resolution in the separation of derivatives phenolic compounds.

KEYWORDS: liquid crystals, capillary gas chromatography, derivatives phenolic compounds, analytical properties

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Application of Schiff Bases Liquid Crystals as Stationary Phases for the Separation of Positional Isomers Compounds

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The synthesis of several nematics schiff bases liquid crystals was carried out. Several fused silica capillary columns were then prepared according static method using the schiff bases liquid crystals as stationary phases. These columns were tested in gas chromatography for the separation of positional isomers compounds. The results show that the analytical properties of the mesogenic materials allow an excellent resolution in the separation isomers compounds.

KEYWORDS: Liquid Crystals Schiff Bases, Capillary Gas Chromatography, Positional Isomers Compounds, Separation

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Effect of Temperature on Terpenic Compounds Retention in Capillary Gas Chromatography

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The use of capillary gas chromatography as a powerful separation technique in the analysis of complex mixtures such as natural products, both from a qualitative and quantitative standpoint, has proved to be unvaluable. However, in spite of the high resolution capability of fused silica capillary columns, the analysis of essential oils often shows coelution of some terpenic compounds which share certain similarities, regardless of their structural diversity.

This work describes the retention behaviour on two fused silica capillary columns of two series of common monoterpenic components, the first one including fourteen aliphatic and cyclic hydrocarbons and the second fifteen oxygenated terpenoids. Retention indices of the studied solutes were calculated using a numerical interpolation method in isothermal conditions in the range 60°-120°C for the first series and 90°-160°C for the second one. Most solutes show regular slightly increasing curves with different slopes, which means that the elution order depends on the experimental temperature programme. On the other hand, retention indices greatly depend on the molecular structure as they increase in the order tricyclic, bicyclic, monocyclic and aliphatic skeleton, but also on the position of unsaturated bonds.

In the case of oxygenated compounds, a similar correlation is observed between retention index increments and molecular structure, the influence of functional groups being less important. For all the studied solutes, retention indices are higher on the polar column which allowed a better separation. Nevertheless, for some interesting couples, a higher resolution is obtained on the non-polar column over all the studied temperature range. The elution order of the studied terpenic components was compared to that observed for some essential oils separated in programmed temperature conditions.

KEYWORDS: retention indices capillary column , monoterpenic hydrocarbons ,oxygenated terpenic compounds, iterative method

Preparation Procedures and Chromatographic Determination of Organic Pollutants in Airport Runoff Waters

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One of the most important problems in this respect are the runoff waters (stormwater) that form when precipitation or atmospheric deposits flush the airport surface during operation: aircraft and ground vehicle washing, cleaning, fuelling operations, fuel combustion, de/anti-icing operations. This runoff gets into the soil, surface waters, and even ground water. Airport runoff can contain high concentrations of various pollutants, in particular polycyclic aromatic hydrocarbons (PAHs), benzotriazoles, glycols and polychlorinated biphenyls (PCBs), the environmental levels of which have to be monitored.

The subject of this research are sample preparation and chromatographic procedures of determination of PAHs, benzotriazoles, glycols found in airport runoff waters from four international airports in Poland and United Kingdom. The aromatic fractions were separated by liquid-liquid extraction (LLE), solid phase extraction (SPE) and analysed by gas chromatography with mass spectrometry (GC-MS). Target analytes concentrations are discussed in terms of sampling location, seasonal variation, origin. The results obtained during the implementation of this research programme will constitute a source of information essential for assessing the extent of the threat to surface and ground waters. They can also be used to draw up new standards of airport infrastructure administration, the aim of which would be to minimize the effects of airport operations on animate and inanimate nature.

KEYWORDS: airport runoff water, PAHs, benzotriazols, glycols, SPE, LLE, GC-MS

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Analysis of Xenobiotics in Runoff Waters Collected from Airport

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Increases in aviation developments have serious consequences on the surrounding air, soil and water bodies like lakes, rivers and ground water. The management of local water and air quality is a significant environmental issue for many airports [1,2]. One of the more important problems in this respect are the runoff waters (stormwaters) that form when precipitation or atmospheric deposits flush the airport surface during its operation. A variety of chemical agents get into the environment with airport runoff waters. During winter, conditions require the use of greater quantities of deicing salts, detergents and other compounds than at other times of the year. Therefore most airport water quality problems caused by pollution occur during winter [3,4].

The present work deals with the determination of total organic carbon (TOC), heavy metals, detergents, formaldehyde, total phenols, PAHs, PCBs, as well as cations and anions found in airport runoff waters from four international airports in Poland and UK. The data presented here provide a useful baseline for airports—a source of information essential for assessing the hazard to surface and ground waters in their vicinity. It is therefore crucial that samples of runoff waters from airports should be monitored and analysed for the largest possible number of contaminants. Only monitoring of this kind can supply data that can be used to assess the intensity of the effects of airport operations on the biotic and abiotic environment. They can also be used in the development of new norms for managing airport infrastructure, the aim of which should be to reduce the impact of airport operations on the biotic and abiotic environment.

KEYWORDS: airport runoff water, stormwater, metals, detergents, cations, anions, PAHs, PCBs, ICP-MS, GC-MS, IC

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Experimental Design of Reversed-Phase High Performance Liquid Chromatographic Conditions for Simultane Determination of Ascorbic Acid, Potassium Sorbate and Sodium Benzoate

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Box-Behnken design for three factors and three levels was applied to optimize the chromatographic conditions of the RP-HPLC separation of ascorbic acid, potassium sorbate and sodium benzoate. Using the C18 reversed phase column, the influence of pH, flow rate and solvent ratio of mobile phase were investigated. To study of effects of selected three factors fifteen runs are used. The resolution was chosen as analytical response. The optimum conditions for this determination were found to be pH 6, flow rate 1.0 mL^{-1} , solvent ratio 10:90 acetonitril/ buffer . As a result the separation is accomplished in a short analysis time with a good resolution for all components peaks of interest. The optimized method was successfully applied to the determination of ascorbic acid, potassium sorbate and sodium benzoate in food.

KEYWORDS: experimental design,HPLC, ascorbic acid, potassium sorbate and sodium benzoate

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Analysis of Organic Nitrogen Compounds in House Dust Samples using GCxGC-NCD

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A novel, highly selective method for the determination of Organic nitrogen (ON) compounds in indoor dust samples is presented in this study. ON compounds are a group of contaminants of special concern because of their known carcinogenic activity and their adverse environmental effects. Although the presence of ON compounds in atmospheric samples has been largely demonstrated [1], there is little information regarding the composition of ON in indoor dust.

The aim of this study is the determination of ON compounds in indoor dust samples. The high complexity of this matrix requires the use of highly selective extraction and high resolution techniques. The analytical method used here was based on in-cell clean up pressurized liquid extraction (PLE) of the dust samples followed by comprehensive two dimensional gas chromatography with nitrogen chemiluminescence detection (GCxGC-NCD) [2]. The GCxGC-NCD method showed high selectivity, sensitivity and equimolarity in its response to individual ON compounds.

The method has been used for determining the ON content of indoor dust samples from smoking and non-smoking homes from Spain and the UK. Several ON compounds have been detected in the samples including nitriles, alkyl nitrocompounds, amides, nitro-PAHs, nitrosamines, nicotine and tobacco-specific nitrosamines. The presence of these compounds in the different kinds of samples and their health concern is also discussed.

KEYWORDS: Organic nitrogen compounds, house dust, pressurized liquid extraction, GCxGC-NCD

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Quantitative Determination of Ibuprofen and Famotidine in Their Combined Dosage Form by Thin Layer Chromatography- Densitometry and High Performance Liquid Chromatography

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Two simple validated chromatographic methods for the simultaneous determination of ibuprofen and famotidine in the presence of ibuprofen impurity (4-isobutylacetophenone) and or famotidine degradates were described. The first method was a simple high performance thin layer chromatographic (HPTLC) method where separation was performed on precoated plates silica gel 60 F₂₅₄ as stationary phase using ethyl acetate: methanol: ammonia (9:2:1, by volume) as the mobile phase. This method allowed the separation of ibuprofen and famotidine in the presence of ibuprofen impurity, famotidine acid and basic degradation products. Densitometric quantification of the two drugs was carried by the reflectance mode at 265 nm. R_f values were found to be 0.40, 0.94, 0.66, 0.27, 0.83 for ibuprofen, 4-isobutylacetophenone, famotidine, famotidine acid and base degradation products, respectively. A linear relationship was obtained in the concentration range 5-30 mg/ml and 0.3-1.3 mg/ml for ibuprofen and famotidine respectively. The second method depends on the separation of the two drugs in presence of ibuprofen impurity by HPLC method on C18 column with UV detection at 265 nm using methanol: phosphate buffer pH 3 (80:20) as a mobile phase pumped at a rate of 1 ml/min. Retention time was found to be 2.2, 9.9, and 8.6 for famotidine, ibuprofen, and 4-isobutylacetophenone, respectively. A linear relationship was obtained in the concentration range 0.48-1.12 mg/ml and 0.015- 0.037 mg/ml for ibuprofen and famotidine, respectively. Both methods were validated according to the ICH guidelines and successfully applied for the determination of ibuprofen and famotidine in pure powder and in combined dosage form without interference from the excipients.

KEYWORDS: ibuprofen, famotidine, high performance liquid chromatography, thin layer chromatography, densitometry.

Application of Novel Core-shell Type Polysaccharide-based Chiral Stationary Phases for Separation of Enantiomers in Nano Liquid Chromatography and Capillary Electrochromatography

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Capillary electrochromatography (CEC) is a relatively new separation technique governed by both chromatographic separation principles and electrokinetic migration of analytes. If properly operated, CEC provides higher separation efficiency compared to chromatographic separation techniques under otherwise similar experimental conditions. This has been systematically proven in achiral, as-well-as chiral separations using CEC. Faster intraparticle mass transfer due to flow through particles has been identified as one of the major contributions to the peak efficiency enhancement in CEC experiments compared with nano-liquid chromatographic (nano-LC) experiments performed on the same capillary column. The fact that intraparticle mass transfer in CEC experiments is faster compared to nano-LC is unquestionable as it has been clearly illustrated experimentally by a lower C-term in the van Deemter equation, as well as based on the effects of silica pore size, ionic strength of the background electrolyte and other factors on peak efficiency in CEC. Core-shell silica particles which became commercially available recently have a nonporous core potentially prohibiting (or at least impeding) flow through particles. Thus, a comparative evaluation of the performance of such materials in nano-LC and CEC should provide further direct experimental evidence of the important role played by intra-particle flow in enhancing peak performance in the latter technique. In addition, the current opinion is that core-shell particles do not perform as well in smaller bore (2.1 mm I.D.) columns as in standard columns of 4.6 mm i.d. The advantages of chiral stationary phases (CSP) based on core-shell silica in standard diameter HPLC columns have been recently demonstrated. It seems interesting to evaluate the performance of core-shell particle based chiral capillary columns as such columns should prove even less efficient given their even lower aspect ratio (i.e. column internal diameter to particle diameter ratio) compared to 2.1 mm i.d. columns. In order to answer the above questions, six polysaccharide-based CSPs (Fig 1.) were prepared by coating the same polysaccharide derivative on core-shell and totally porous silica particles. These materials were evaluated for the separation of enantiomers in nano-LC and in CEC.

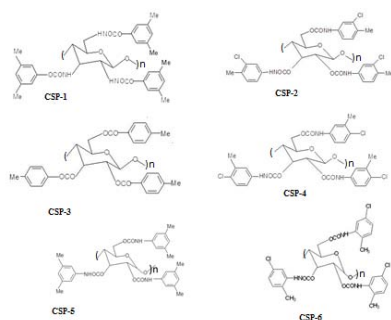


Fig.1 Structure of chiral selectors in novel core-shell chiral stationary phases

Three important conclusions can be drawn based on the results reported in this preliminary study:

- 1) core-shell materials which have been found to underperform in narrow bore columns may be quite useful under CEC conditions in spite of the much larger aspect ratio of capillary columns;
- 2) Flow through-particle (assumed to be affected by the presence of the core in core-shell particles) cannot be considered a major factor in producing lower HETP values for the same capillary column when operated in CEC mode versus nano-LC mode;
- 3) the subtle mechanisms leading to higher observed plate numbers in CEC compared to nano-HPLC on the same capillary column need further investigation, especially for columns made with core-shell materials.

KEYWORDS: core-shell, enantiomer, chiral, nano-LC, capillary electrochromatography

A New Spectrophotometric Method for Trace Mercury Determination

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Mercury is a very toxic heavy metal that causes serious environmental and health problems [1]. These characteristics of mercury element have intrigued intense research efforts in developing sensitive, accurate, and simple analytical techniques to monitor mercury in biological and environmental samples especially spectrophotometric methods including atomic absorption spectrometry (AAS) [2], atomic fluorescence spectrometry (AFS) [3], inductively coupled plasma optical emission spectrometry (ICP-OES) [4], inductively coupled plasma-mass spectrometry (ICP-MS) [5], and ultraviolet-visible (UV-vis) spectrophotometry [6]. Compared to the sophisticated techniques, UV-vis spectrophotometry has a special position due to the relatively inexpensive instrumentation and easy handling.

However, mercuric ions usually exist in the environment at trace levels, thus extraction and preconcentration procedures are often required before UV-vis measurement. Among the currently available extraction and preconcentration methods [7] miniaturized preconcentration methods based on single-drop microextraction (SDME) have recently aroused a great interest, due to the favorable characteristics of simplicity, cheapness, rapidity, minimized organic reagents consumption [8] A high enrichment factor can be obtained by this method because of the microliters volume of the liquid drop [9].

In the present work, an in-situ single-drop microextraction method was proposed for the spectrophotometric determination of mercury in real water samples. The method is based on the extraction of colored complex of mercury(II) with dithizone into the organic phase. In appropriate pH, Hg(II)-Dit complex in organic phase gives a absorption maxima at 490 nm. Variety of parameters affecting the signal such as pH, dithizone concentration, sample volume, extraction solvent volume, extraction time and temperature, salt effect were optimized. Under optimized conditions the linear range was found between 2×10^{-8} M - 5×10^{-7} M and the detection limit was calculated as 5 ng mL^{-1} . Validation of the proposed method was performed for determination of mercury in natural samples.

KEYWORDS: Single drop micro extraction, mercury determination, dithizone, spectroscopy

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Polymer/Clay Nanocomposites as a New Sorbent for Chromatographic Methods

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The extensive use of pesticides in modern agriculture raises a number of environmental and health concerns. For this reason their analytical control is mandatory in different water bodies within the EU including drinking waters [1]. Therefore, rapid, simple and sensitive analytical techniques are imperative for pesticide analysis especially in water samples. Liquid-liquid extraction and solid phase extraction (SPE) classical extraction methods were used widely for the sample preparation steps. However, they display some drawbacks such as large consumption of reagent, low enrichment factor, multistage operation [2]. In the past decades considerable attention has been paid to SPE which is expensive and time-consuming due to the limited rate of diffusion and mass transfer of analytes in the bulk sorbent phases packed in a cartridge. Furthermore, solid particles, which widely exist in the samples may cause a blockage of cartridges and lead to extraction failure. By increasing the interfacial area between the solid adsorbent and sample solution the problems can be overcome. To increase the area, micro or nano-scale sorbent were used in present years [3]. In recent years polymer-clay nanocomposites have attracted great interest, both in industry and academia, and represent radical alternative to conventional polymers [4]. Because of their nanometer size dispersion, the nanocomposites exhibit remarkable improvement in materials properties when compared with virgin polymer or conventional micro- and macrocomposites [5]. Polybicyclo[2.2.1]hepta-2,5-diene (PNBD) belongs to the class of cycloaliphatic polyolefins. In this study PNBD-clay nanocomposite were prepared and used as SPE sorbent for pesticide determination in water samples. PNBD -clay nanocomposites were prepared for the first time by in situ intercalative method via ring opening metathesis polymerization (ROMP) with using Ruthenium catalyst. Clay layers were dispersed in polymers matrix and polymer-clay nanocomposites are obtained. The structures of nanocomposites were characterized by X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM) and Transmission electron microscopy (TEM) methods. In this study, a novel and fast procedure, sonication-assisted emulsification microextraction combined with vortex assisted micro-solid phase extraction (m-SPE) was developed by using this firstly prepared nanocomposite SPE material for the determination of pesticides in water samples. In the present work, 5.0 mg of Polybicyclo[2.2.1]hepta-2,5-diene-clay nanocomposite was weighed and placed in a centrifuge tube. 5.0 mL of water was added and the extraction was started by sonication for two min and vortexing for 2 min. After centrifugation and removing process of water sample, 50 mL of acetonitrile was used for extractant solvent. For extracting the analytes sonication was done for 5 min. At the end of the extraction, 30 mL of organic phase was placed in conical inserts and gas chromatographic analysis was started by using mass detector. Considering the number of parameters those can affect the signal, sorbent amount, extraction solvent type, extraction solvent volume, sonication and vortex time, sample volume and salt effect on pesticides extraction were optimized. As a result, PNBD-clay nanocomposite has given efficient extractions compared to unmodified montmorillonite. This new prepared material was demonstrated to be a good sorbent for pesticides in water samples and can be used a new column material in chromatographic applications.

KEYWORDS: Polymer/Clay Nanocomposites, SPE, Pesticides, Gas chromatography, Mass Dedector.

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Ionic Liquid-Modified Clay Materials as a New Sorbent for the Gas Chromatographic Determination of Pesticides: Part 3. Application of 1-Methyl-3-Octadecyl-Imidazolium Bromide Modified Montmorillonite

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Room temperature ionic liquid (IL) is a kind of green solvent, and has aroused increasing interest by its unique chemical and physical properties for their promising role as an alternative media in separation science [1]. It has a wide range of applications in sample preparation and analytical chemistry, such as, liquid-liquid extraction (LLE) [2], liquid phase microextraction (LPME) [3], solid phase extraction (SPE) [4] and solid phase microextraction (SPME) [5]. In recent years, studies were focused on modification of ILs on different supports to produce alternative surfaces for separation. Montmorillonite clay is the most important inexpensive alumino silicate smectite clay used in modification applications with important characteristic properties like cation exchange, swellability and intercalation properties [6]. Chemical modification of these clays by immobilization occurs by a simple ion exchange of organic and inorganic species with Na^+ cations. Since alkylimidazolium salts are one of the most important classes of ionic liquids; as such they have received much attention [7], 1-Methyl-3-Octadecyl-Imidazolium Bromide ($\text{C}_{18}\text{mimBr}$) was immobilized in the inter layers of clays in this study for improving the adsorption activity of pesticides. The structures of ($\text{C}_{18}\text{mimBr}$) modified clay material was characterized by X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM) and Transmission electron microscopy (TEM) methods. In this study, a fast procedure, sonication-assisted emulsification microextraction combined with vortex assisted micro-solid phase extraction (SE-SPME) was developed by using this prepared ($\text{C}_{18}\text{mimBr}$) modified clay material for the determination of pesticides in water samples. Considering the number of parameters those can affect the signal, pH, sorbent amount, extraction solvent type, extraction solvent volume, sonication and vortex time, sample volume and salt effect on pesticides extraction were optimized. The experiments were done with 5 mL of water sample (pH:3) containing 5.0 mg of ($\text{C}_{18}\text{mimBr}$) modified clay material. Sonication and vortex time was chosen as two min. After centrifugation procedure for 10 min at 4750 rpm, analyte was desorbed from the solid matrix by using 50 μL of acetonitrile. The method was validated for the determination of Chlorpyrifos pesticide in water samples. In virtue of diminishing the sample preparation time and enhancing the analyte retention on its surface to exert better selectivity and hence the developed ionic liquid modified surface offers to the analyst to exploit it as a sorbent in pesticide analysis. Treatment of layered silicates such as montmorillonite (MMT) with ILs may open new avenues for the preparation of new sorbents used in chromatographic applications for the reason that, this new sorbent has given efficient extractions compared to unmodified montmorillonite.

KEYWORDS: Ionic Liquids, 1-Methyl-3-Octadecyl-Imidazolium Bromide, Montmorillonite, Pesticide, Gas Chromatography

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Development of a Sequentially Applied Spectrophotometric and Voltammetric Methods for the Determination of Iodide in Salt Samples

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Iodine is an essential micronutrient for animals and human, mainly because it is a constituent of the thyroid hormones. Excessive or deficient iodine intake results in a variety of human thyroid dysfunction and disorder, as hyperthyroidism. Insufficient iodine intake can be responsible for the thyroid gland disease and fetus congenital anomalies [1,2]. The determination of iodine in biological, clinical and food samples has received considerable attention during the last few decades as it is considered as essential trace element which plays an important role in human metabolic processes. WHO recommendation for daily iodine intake is varies from 50 (for infants) to 170 μ g (for women during lactation). This led to universal salt iodination process, which was considered to be the most efficient way to improve iodine intake. Unfortunately, the process appears to be insufficient to cover the daily doses of iodine, as global consumption of salt decreases [3]. The objective of the presented study was to develop a method for the determination of iodide in salt samples. In this method sequentially applied analysis process can be applied for salt samples at the same time either by using spectroscopic and voltammetric technique. For this purpose, in the sample preparation step, 1.00 g of salt sample was dissolved in 25 mL water and taken into the beaker. Saturated bromine was added to sample solution and heated until the excessive bromine removed from the sample. Solution pH was adjusted to 2.0 by adding few amounts of sulphuric acid and 2 mL of 0.1 M KI solution was used to form iodine in the sample. This iodine was extracted to chloroform phase and spectrophotometric analysis was performed. After the extraction, the iodine in the chloroform phase can also be reversed to iodide by adding 2% of acetone to the separation funnel. Back extraction was performed to the water phase and the iodide content transferred to the water solution was analyzed by voltammetrically using a gold film electrode. Spectroscopic measurements were made at 510 nm. Voltammetric measurements were made by using gold film electrode prepared in 20.0 mL of electrolysis solution (1×10^{-5} M HAuCl_4 in 0.1 M HCl). by depositing the gold from Au(III) ions in the solution -0.5 V for 300 s. Iodide determination in the sample was performed in 0.1 M HClO_4 solution by applying the potential from 0.2V to 0.8V. Calibration curves were linear in a range of 0.75 - 5.0 mg/mL and 0.1 - 1.0 mg/mL for spectrophotometric and voltammetric method respectively. The limit of detection values were calculated as 0.09 mg/g and 0.01 mg/g. Recovery values were obtained in the range of 90.0-95.0% for two methods. The proposed methods were applied to salt samples and similar results were obtained. This method can easily be adopted by food quality control laboratories and does not necessitate expensive equipment like ICP-MS. In order to reduce effort and cost in food monitoring programs, the procedure used in this work can be applied to the sample before the analysis by spectrophotometric or voltammetrically. Hence by this way accuracy of the method can be compared by parallel approaches.

KEYWORDS: Iodide determination, Spectroscopy, Gold Film Electrode, Voltammetry, Liquid-liquid extraction

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Ionic Liquid-Modified Clay Materials as a New Sorbent for the Gas Chromatographic Determination of Pesticides: Part 2. Application of 1-Methyl-3-Undecyl-Imidazolium Bromide Modified Montmorillonite

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As a consequence of the widespread use of pesticides, the presence of their residues in both food and the environment has become an important issue in analytical science. Legislation upon drinking water in EU set the limits at sub ppb level for total pesticide residue [1]. These levels require very sensitive methods for pesticide determination in water samples. Chromatographic techniques are widely employed for sensitive determination of pesticides since they are powerful separation techniques but the difference of the sensitivity can be achieved by using different stationary phases in sample preparation methods.

In this study, a novel and fast procedure, sonication-assisted emulsification microextraction combined with vortex assisted micro solid phase extraction (SPE) was developed for the gas chromatography - mass spectrometric determination of pesticides from environmental water samples. Newly prepared ionic liquid modified clay adsorbents were used in the present study since ionic liquids (ILs), resulting from the combination of organic cations and various anions are gaining widespread recognition as potential environmentally compatible solvents. Good thermal stability, negligible vapor pressure, tunable viscosity and natural liquid nature at room temperature, merit the ILs as good candidates for stationary phase [2].

Chemical modification of Montmorillonite was done by immobilization by a simple ion exchange of 1-methyl-3-undecyl-imidazolium bromide with Na^+ cations. This new material was used for the separation and enrichment of Chlorpyrifos pesticide in SPE method. Considering the number of parameters those can affect the signal, pH, sorbent amount, extraction solvent type, extraction solvent volume, sonication and vortex time, sample volume and salt effect on pesticides extraction were optimized. The experiments were done with 5 mL of water sample (pH:3) containing 5.0 mg of ($\text{C}_{12}\text{mimBr}$) modified clay material. Sonication and vortex time was chosen as two min. After centrifugation procedure for 10 min at 4750 rpm, analyte was desorbed from the solid matrix by using 50 μL of acetonitrile.

The developed ionic liquid modified surface offers to analyst to exploit it as a sorbent in pesticide analysis. This micro extraction methods shares the advantages of the classical extraction methods such as excellent enrichment performance, easy operation and ability to employ a wide range of "green" extraction way.

KEYWORDS: Ionic Liquids, 1-methyl-3-undecyl-imidazolium bromide, Montmorillonite, Pesticide, Gas Chromatography

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Ionic Liquid-Modified Clay Materials as a New Sorbent for the Gas Chromatographic Determination of Pesticides: Part 1. Application of 1-Methyl-3-Octyl-Imidazolium Bromide Modified Montmorillonite

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Evaluation of the relationship between the molecular interactions and the selectivity of stationary phases can provide the basis for predicting and understanding the chromatographic performance of both stationary phases and analytes. In recent years many different types of stationary phases were prepared for the improvement of chromatographic signal of the analyte. Especially these newly prepared solid stationary phases were applied before the analysis by Solid phase extraction (SPE) method that uses a solid phase and a liquid phase to isolate one type of analyte from a solution. In recent years, materials science has propelled to the research forefront for SPE materials. Ionic liquids (ILs) with unique and fascinating properties have also left their footprints to the developments of materials science during the last years. ILs were especially immobilized in silica materials by covalent bonding and easily attached onto polymer surfaces. Although the liquid state of ILs is lost when they are immobilized on silica surface or polymerized, the other unique properties, such as polarity and low volatility associated to non polar and ionic interactions, are maintained [1]. Montmorillonite (Mont) clay is the most important inexpensive aluminosilicate smectite clay used in material science with important characteristic properties like cation exchange, swellability and intercalation properties [2]. Chemical modification of these clays by immobilization occurs by a simple ion exchange of organic and inorganic species with Na^+ cations. These new materials can be used as per industrial requirements and are being considered as potentially cost effective and environmentally friendly nano-materials. In this study the Mont clay was modified by a cation exchange method, which is a reaction between the sodium cations of Mont clay and 1-Methyl-3-Octyl-Imidazolium Bromide (C_8mimBr) ions of ionic liquids as the intercalating agent. This modified surface was used as a stationary phase for SPE application for the determination of Chlorpyrifos pesticide in water samples. Present study also describes, a novel and fast procedure, sonication-assisted emulsification microextraction combined with vortex assisted micro solid phase extraction methodology for the gas chromatography-mass spectrometric determination of pesticides. The surface of the C_8mimBr modified clay material was characterized by X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM) and Transmission electron microscopy (TEM) methods. Operational parameters effecting the extraction, mainly, pH, sorbent amount, extraction solvent type, extraction solvent volume, sonication and vortex time, sample volume and salt effect on pesticides extraction were optimized. The experiments were done with 5 mL of water sample (pH:3) containing 5.0 mg of ($\text{C}_{18}\text{mimBr}$) modified clay material. Sonication and vortex time was chosen as two min. After centrifugation procedure for 10 min at 4750 rpm, analyte was desorbed from the solid matrix by using 50 μL of acetonitrile. The method was validated for the determination of Chlorpyrifos pesticide in water samples.

In virtue of diminishing the cost and enhancing the analyte retention on its surface to exert better selectivity and hence the developed surface could offer to analyst to exploit it as a SPE stationary phase for chromatographic applications.

KEYWORDS: 1-methyl-3-octyl-imidazolium bromide, Ionic Liquid, SPE, Pesticide, Gas Chromatography

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Chromatographic Analysis of α -tocopherol in Deodorizer Distillate by Cyano Column

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Deodorizer distillate obtained from the deodorization process is a complex product consisting of many components including free fatty acids, tocopherols, sterols, squalene and neutral oil. The value of deodorizer distillate is essentially depends upon the content of tocopherols (vitamin E). Tocopherols are present in deodorizer distillate as α , β , γ , and δ . α -tocopherol is the main composition of natural vitamin E. Up to the present time these compounds have been analyzed by various high-performance liquid chromatography columns such as silica and diol (normal phase) as well as C18 and C8 (reverse phase). In recent years separation of tocopherols through Cyano column in normal-phase chromatography has emerged as a new technique. In the present study, separation of the tocopherols present in palm oil has been successfully performed using Reprosil-Pur 120 CN (250x4,6 ; 5 μ m) cyano column in normal-phase mode by fluorescence detector at 290-330 nm as wavelength of ex and em. Mixture of isopropanol-hexane used as a mobile phase.

KEYWORDS: α -tocopherol, Deodorizer Distillate, Vitamin E, Cyano column

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Selection of Optimum Condition For Simultaneous Determination of Three Carbapenem Drugs with Liquid Chromatography Method

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The carbapenems are β -lactam antibiotics, which inhibit the bacterial cell wall synthesis by binding to penicillin binding proteins. These parenteral antibiotics have similar broad spectrum activity against most of gram positive and gram negative bacteria. Moreover, these antibiotics are used in wide range of serious infections like intra-abdominal, urinary tract, lower respiratory tract or skin infections [1]. In this study, optimum condition were determined by using the dependence of the capacity factor on the pH of the mobile phase for three ionizable substances. The dependence of solute retention on the concentration of the organic component of the mobile phase in reversed phase liquid chromatography has received considerable attention in the optimization of separations [2]. A precise and accurate high-performance liquid chromatography method using UV detection has been developed and validated for simultaneous determination of carbapenem antibiotics. Ertapenem, meropenem and doripenem are parenteral carbapenems (Figure 1).

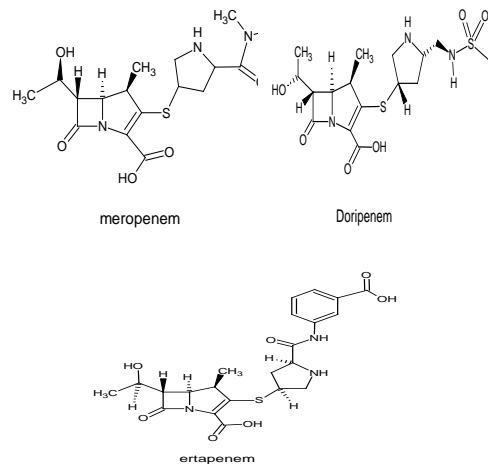


Figure 1. Chemical structure of ertapenem, meropenem and doripenem

A chromatographic separation was achieved on Luna C18 column (250 mmx4.6 mm I.D., 5 μ m) with a mobile phase consisting of a methanol : water binary mixture (18:82, v/v, pH 8.0). The method developed was linear over the concentration range of 15-50 μ g/mL for each antibiotic. The limit of detection of the procedure were found to be 2.362 μ g/mL for ertapenem, 1.137 μ g/mL for doripenem and 0.943 μ g/mL for meropenem. The method developed was applied for the determination of these compounds in human urine. Urine samples were spiked with the compounds and amoxicillin as internal standard and proteins were precipitated by methanol. Accuracy ranged from 98.47 to 99.58%.

KEYWORDS: Carbapenems RPLC, human urine, capacity factor

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Application of Experimental Design to Optimisation and Validation of a RPLC Method for the Estimation of Tricyclic Antidepressants in Urine

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Common structure of the antidepressants are composed of two aromatic rings connected with an allicyclic ring that contains seven atoms. Because desipramine, imipramine, nortriptyline, amoxapine, amitriptyline, trimipramine, and clomipramine have three ring molecular cores, they can be expressed as tricyclic antidepressants. Many of the antidepressants block the neuronal uptake of norepinephrine and serotonin in the brain. Imipramine, amitriptyline and other similar compounds were the first antidepressants. These drugs have been used for the treatment of the major depression since 1960's [1]. In order to select the optimum chromatographic conditions of drugs, generally, a trial and error approach is preferred. However, more systematic approaches should be chosen rather than this approach due to cost, time and labor intensive [2]. In this study, the development and validation of an isocratic reverse phase high performance liquid chromatography (RP-HPLC) method for the optimum separation of some tricyclic antidepressants are described by using experimental design and response surface design strategies. As a experimental design method, full central composite design was chosen and applied to obtain minimum analysis time and maximum resolution. The optimum separation has been achieved with a X-terra column (250 mm x 4.6 mm I.D., 5 μ m) at 215 nm detection wavelength and was carried out using an acetonitrile-water 55:45 (v/v). pH of mobile phase including 10 mM NH_4HCO_3 was 8.3. The temperature of the column and flow rate were set at 35 $^\circ\text{C} \pm 0.1$ $^\circ\text{C}$ and 1.0 mL min^{-1} respectively. The method was also performed successfully for determination of tricyclic antidepressants in human urine (Figure 1). The optimized assay condition was validated according to ICH guidelines to confirm specificity, linearity, accuracy and precision. Probable pK_a values of antidepressants in determined pH range were also predicted by using equations obtained CCD.

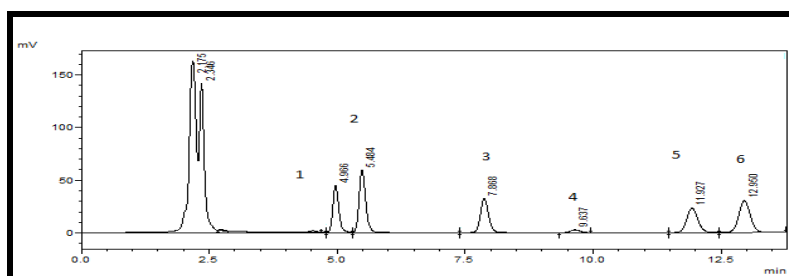


Figure 1. Chromatogram of urine spiked with (1) desipramine, (2) nortriptyline, (3) imipramine, (4) amoxapine, (5) amitriptyline, (6) trimipramine and (7) clomipramine

KEYWORDS: Antidepressants, experimental design, RPLC

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Determination of pKa Values of Methotrexate with Reversed Phase Liquid Chromatography Method in Different Acetonitrile-Water Binary Mixtures

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Methotrexate was developed to used for chemotherapy either alone or in combination with other agents. It is effective for the treatment of a number of cancers including: breast, head and neck, leukemia, lymphoma, lung, osteosarcoma, bladder, and trophoblastic neoplasms [1]. Although methotrexate was used as a chemotherapy drug (in high doses), in low doses methotrexate is a generally safe and well tolerated drug in the treatment of certain autoimmune diseases, including rheumatoid arthritis, Juvenile dermatomyositis, psoriasis, psoriatic arthritis, lupus, Crohn's disease, and many forms of vasculitis, to name a few [2].

The acid-base property of a drug molecule is important physical parameter for evaluation of biological activity in terms of quantitative structure-activity relationships. Reversed phase liquid chromatography is a high-precision technique for determining the pK_a values of compounds [3]. In this work, the pK_a values of methotrexate using reversed phase liquid chromatographic methods have been determined in acetonitrile- water binary mixtures. The mobile phases assayed were acetonitrile-water at 12%, 15% and 18% (v/v). At each composition, the pH of the mobile phase containing 30.10^{-3} mol/L phosphoric acid was adjusted between 2.4 and 8.0 by the addition of the sodium hydroxide. Chromatographic study was performed with Gemini NX C18 column (250 mmx4.6 mm, 5 μ m) at 30°C. In this study the retention factors were determined for each mobile phase composition and pH studied. The pK_a values of the methotrexate were calculated by NLREG program [4]. The examples of dependences of the retention factors on the pH value in the mobile phase (12% v/v) are given in Fig. 1.

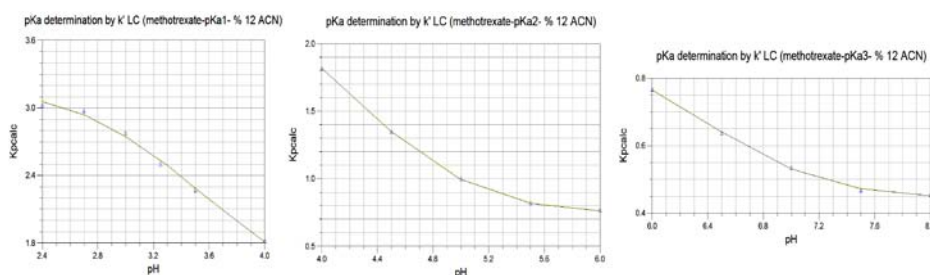


Figure 1. Plots of the retention factors versus the pH of the mobile phase for 12% v/v ACN

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Application of Optimum Condition for Determination of Sulfasalazine in Human Urine by using Reversed Phase Liquid Chromatography Method

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Sulfasalazine (4-hydroxy-40-(2-pyridylsulfamoyl) azobenzene-3-carboxylic acid) is a sulfa drug and is formed by combining sulfapyridine and salicylate with an azo bond. Sulfasalazine was developed in the 1950s specifically to treat rheumatoid arthritis believed at the time that bacterial infections were the cause of rheumatoid arthritis. Nowadays, sulfasalazine is commonly used for the treatment of chronic inflammatory bowel diseases, including Crohn's disease and ulcerative colitis [1]. In this study, the adequate separation condition for the chromatographic determination were chosen by evaluating relationship between the capacity factor and the pH of the mobile phase based on the different retention behaviors of sulfasalazine and donepezil (I.S.). A chromatographic separation was achieved on Gemini NX C18 column (250x4.6 mm I.D., 5 μ m) with a mobile phase consisting of a acetonitrile:water binary mixture (35:65, v/v, pH 8.0).

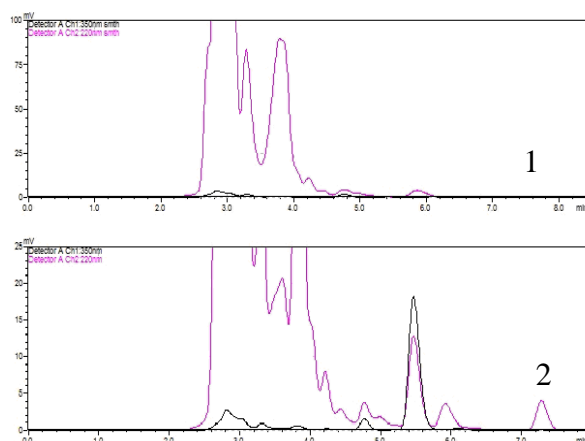


Figure 1. Chromatograms of sulfasalazine in human plasma. (A) Drug-free human urine; (B) human urine spiked with (1) sulfasalazine (4 ppm) and (2) donepezil (1 ppm)

The human urine assay was validated for parameters such as specificity, accuracy and recovery. The method developed was linear in the concentration range of 2-24 μ g/mL for sulfasalazine. The limit of detection (LOD) and limit of quantification (LOQ) of the procedure were calculated 0.086 μ g/mL, 0.261 μ g/mL for sulfasalazine, respectively. The method developed was applied for the determination of these compounds in human urine obtained from healthy volunteer. First of all, proteins in urine samples were precipitated by acetonitrile and then were spiked with the sulfasalazine and donepezil (I.S) (Figure 1). The proposed method is simple, selective and can be extended for routine analysis of sulfasalazine in biological matrices.

KEYWORDS: Sulfasalazine, urine, RPLC, method development

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Validation of RPLC Method for Assay of Azathioprine in Pharmaceutical Formulation

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Azathioprine is an immunosuppressive drug used in organ transplantation and autoimmune diseases and belongs to the chemical class of purine analogues. It is used to treat patients who have undergone kidney transplantation and for diseases in which activity of the immune system is important (psoriasis, severe cutaneous lupus erythema-tosus, rheumatoid arthritis, severe atopic dermatitis (ec-zema), cutaneous vasculitis etc.) [1]. In this study, the effect of eluent pH on chromatographic behavior of azathioprine was studied with reversed phase liquid chromatographic method. A simple, precise and accurate method to determine azathioprine in a pharmaceutical dosage form were developed and validated using reversed phase liquid chromatography (RPLC). Gemini NX C18 column (250x4.6 mm I.D., 5 µm) was used for LC separation. The chromatographic separation of azathioprine was carried out using acetonitrile-water binary mixture (15:85, v/v, pH 3.0), containing 30 mM phosphoric acid. Hydrochlorothiazide (HCT) was used as internal standard at a concentration of 1 µg/mL. Separation was achieved within 9 min. The adequate condition for the chromatographic determination of azathioprine and hydrochlorothiazide (I.S.) was established based on the different retention behaviors of the species.

The method was successfully applied for the determination of azathioprine in commercial pharmaceutical dosage form without any interference from common excipients. The proposed method was validated in tablet terms of reproducibility, precision and accuracy. The method developed was linear in the concentration range of 4-24 µg/mL for azathioprine. The limit of detection (LOD) and limit of quantification (LOQ) of the procedure were calculated 0.532 µg/mL, 1.610 µg/mL for azathioprine respectively. Results are satisfactory, and the method proved to be adequate for the determination of azathioprine in pharmaceutical formulations.

KEYWORDS: Azathioprine, RPLC, validation, pharmaceutical dosage form

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Experimental Design Approach for Determination of Some Tricyclic or Tetracyclic Antidepressants with LC Method and Application of the Solid-Phase Extraction in Urine

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Antidepressants have been widely prescribed in the treatment of psychiatric disorders such as depression, mainly endogenous major depression. These drugs have also been frequently encountered in emergency toxicology screening, drug abuse, and forensic medical examinations [1]. Because of having tricyclic or tetracyclic nuclei, they are called as tricyclic or tetracyclic antidepressants. Common structure of these compounds are composed of two aromatic rings connected with an allicyclic ring that contains seven atoms [2]. While desipramine, imipramine, amoxapine, amitriptyline, trimipramine, and clomipramine are tricyclic antidepressants, amoxapine and mianserin are tetracyclic antidepressants.

In order to understand the influence of the chromatographic factors on the separation of some antidepressants (mianserin, amoxapine, desipramine, imipramine, amoxapine, amitriptyline, trimipramine, clomipramine) and to obtain minimum analysis time and maximum resolution, central composite design (CCD). In this study, losartan was used as internal standard. Investigating chromatographic factors on the separation were chosen as a acetonitrile concentration of mobile phase (X_1), pH of mobile phase (X_2) and temperature of the column (X_3) (Table 1).

Table 1. The three-factor central composite design circumscribed used for the evaluation of the HPLC method

Factors	- α	-1	0	+1	+ α
Acetonitrile conc. (X_1)	26.591	30	35	40	43.410
pH (X_2)	3.160	3.5	4	4.5	4.841
Column temp. (X_3)	26.591	30	35	40	43.410

The optimum separation condition of this drugs was applied to urine. The solid-phase extraction (SPE) with Oasis HLB cartridges was preferred for sample preparation.

KEYWORDS: Antidepressants, central composite design, human urine, method validation

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**Effects of Chemical Substances on Pectin Lyase of Thermophilic
Aspergillus Niger Isolated from Natural Sources**

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Pectic substances consist α -1,4 linked D-galacturonic acid residues and their methylated derivatives [1]. Pectic substances are degraded by pectic enzymes. These enzymes are divided three main groups: pectin esterases, depolymerizing enzymes and protopectinase [2]. Pectin lyase is in depolymerizing enzymes group. It is very important due to their potential application in food and textile industry. In particular, lytic enzymes from fungi have been the subject of a vast number of studies due both to their advantages as models for enzyme production and their characteristics [3, 4].

In this study, pectin lyase was obtained from thermophilic *Aspergillus niger* in submerged culture. Enzyme was purified with ammonium sulphate fractionation, gel filtration and ion-exchange chromatography, respectively. Effects of several chemical substances like metal ions and amino acids on enzyme activity were tested. For this purpose, ammonium sulphate, ascorbic acid, FeCl₃, citric acid, ZnSO₄ and arginine were used. Their inhibitory and activator effects were evaluated.

KEYWORDS: pectin lyase, metal ions, gel filtration chromatography, ion-exchange chromatography.

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Production and Purification of Pectin Lyase Enzyme from Fruit Residues in Submerged Culture

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All over the world ,with increasing energy demand, renewable resources such as agricultural residues have great attention. The major components of these residues are pectin, starch, cellulose and xylan. These materials are alternative energy sources, since they are abundantly available. [1]

Pectic enzymes are produced by several microorganisms in submerged culture [2]. These enzymes degraded pectic substances which are major components of primary cell wall and middle lamella of higher plants. Pectic enzymes are very important due to their potential application in fruit juice, textile industry, coffee and tea fermentation [3].

In this study, several fruit residues were used for pectinase production in submerged culture. Crude enzyme partially purified with ammonium sulphate fractionation. Then, partially purified enzyme was applied to gel filtration and anion-exchange chromatography. So, the most purified enzyme was obtained with 3 step. Enzyme activity and protein determination analysis carried out every stage.

KEYWORDS: pectinase, fruit residues, submerged culture, gel filtration, anion-exchange chromatography.

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Characterization of Pectin Lyase from Thermophilic *Aspergillus Niger* Isolated from Natural Sources

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Pectic substances are the most complex class of plant polysaccharides [1]. Pectic substances are classified into protopectin, pectin, pectic acids and pectinic acids. Pectinases are the group of enzymes involved in depolymerisation of the pectic polymers [2]. These groups of enzymes consist of pectinesterases, polygalacturonases, pectate lyases and pectin lyases. Among them pectin lyase has biotechnological potential in fruit juice industries due to it degrades pectin without disturbing the ester group which is responsible for specific aroma of the fruit juice and it does not lead to methanol formation which is very toxic [3].

In this study, pectin lyase was obtained from thermophilic *Aspergillus niger* isolated from natural sources. Pectin lyase was produced by *Aspergillus niger* was purified to electrophoretic homogeneity using ammonium sulphate fractionation, anion exchange chromatography and gel filtration chromatography. Characterization studies were carried out for optimum pH and temperatures of purified enzyme.

KEYWORDS: pectin lyase, characterization, thermophilic *Aspergillus niger*, anion-exchange chromatography, gel filtration chromatography.

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Purification of Pectin Lyase with Chromatographic Techniques and Effects of Detergents on Enzyme Activity

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Pectin polysaccharides are complex, colloidal acid polysaccharides. They include 2 regions: smooth regions and hairy regions. These polysaccharides are found in plant primary cell wall. They provide rigid structure of plant cell wall. For degradation of these polysaccharides need complex enzyme systems [1].

Pectinolytic enzymes hydrolyse pectic substances with several mechanisms. Pectinases are the first enzyme groups to be used in homes in 1930 [1]. Nowadays, it has 25% share at global industry [2]. Polygalacturonases, pectin lyases, pectin esterases are widely used pectinolytic enzymes at industry. Such as textile and fruit juice industry, in poultry feed additives, and food industry [3].

In this study, pectin lyase was obtained from thermophilic *Aspergillus niger* in submerged culture. Enzyme was purified with ammonium sulphate fractionation, gel filtration and ion-exchange chromatography, respectively. Effects of detergents on enzyme activity were tested. For this purpose, Triton X-100, SDS were used, their effects were evaluated.

KEYWORDS: pectin lyase, gel filtration chromatography, SDS, TritonX-100.

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Central Composite Design for Investigating Chromatographic Behavior of Some Quinolones by Using Isocratic Reversed Phase Liquid Chromatographic Method

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Fluoroquinolones are an important class of quinolones family with antibacterial agent. They have a structure of a 1-substituted-1,4-dihydro-4-oxopyridine-3- carboxylic moiety combined with an aromatic or heteroaromatic ring adding a fluorine atom at position 6 of the quinolone aromatic ring system.

Reversed phase liquid chromatography (RPLC) has become an important tool for the analysis of single and various combinations of quinolones in biological fluids and pharmaceutical preparations using either UV or fluorescence as the detection method [1]. Since HPLC utilizes a wide selection of chromatographic factors, viz., the type and concentration of organic modifier, pH, buffer molarity, temperature, flow rate, etc., optimization of the experimental conditions is a complicated process. Therefore, a systematic approach such as experimental design to optimize chromatographic separations is more essential [2]. The best experimental design approach for the purpose of modeling and optimization of chromatographic separation are the response surface design. Central composite design (CCD) was effectively employed to investigate chromatographic behavior and to decide optimum conditions for the rapid separation of some fluoroquinolones (marbofloxacin, ciprofloxacin, sarafloxacin) using RPLC. Twenty experiments, taking the maximum resolution and minimum retention time of the last eluted peak as the responses with three important factors, mobile phase acetonitrile content, pH of mobile phase and column temperature, were used to design a mathematical model. The experimental responses were fitted into a second order polynomial and used to predict the optimum conditions for the effective separation of the studied compounds. pK_a values for marbofloxacin, ciprofloxacin, sarafloxacin were predicted using the relationship between the retention factor and mobile phase pH. The results are compared with the literature value [3].

KEYWORDS: RPLC, Experimental Design, Fluoroquinolones, marbofloxacin, ciprofloxacin, sarafloxacin

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Application of CCD to predict pKa values of Ofloxacin, Enrofloxacin, Danofloxacin

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Quinolones comprise a relatively large and constantly expanding group of antibiotics. These compounds are widely used in human as well as in veterinary medicine, for the treatment of pulmonary, urinary and digestive infections. The majority of quinolones in clinical use belong to the subset fluoroquinolones, which have a fluorine atom attached to the central ring system, typically at the 6-position or C-7 position [1]. This basic structure of fluoroquinolone molecules (pharmacophore) is represented in Fig. 1.

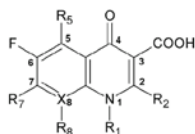


Figure 1. General structure of fluoroquinolones, using the accepted numbering scheme for positions on the molecule. The radicals R1, R2, R5, R7 and R8 indicate possible positions for structural modification; X usually corresponds to a C or N atom

In the study the effects of important factors (percentage of acetonitrile, pH of eluent and column temperature) for chromatographic behavior of ofloxacin, enrofloxacin, danofloxacin were investigated to predict pKa_i values of these compounds by using CCD. For three examined factors, this design requires fourteen different runs, plus central point replications (6 experiments) [2]. The upper and lower limits of the factors have been determined from the screening step. Logarithm of retention factor was chosen as response factor. Prediction of retention factors at different solvent composition / at different temperature was made by using the equations obtained. pK_a values for studied compounds were calculated by NLREG program[3]. Intrinsic capacity factors were also calculated. Yasuda-Shedlovsky equation was used in order to predict the aqueous pKa values of these compounds [4].

KEYWORDS: RPLC, CCD, Fluoroquinolones, Ofloxacin, Enrofloxacin, Danofloxacin

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Simultaneous Determination of Enalapril / Hydrochlorothiazide by HPLC Method

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Hypertension is a systematic disease that occurs with high arterial blood pressure and is defined as the rising of blood pressure above 140/90 mmHg and over [1]. Angiotensin-converting enzyme inhibitors (ACE inhibitors) are nowadays well-known group of compounds used especially in treatment of essential hypertension, congestive heart failure either alone or in conjunction with other drugs [2]. Enalapril maleate (EM) is a derivative of 2 amino acids, L-alanine and L-proline, and is an antihypertensive and a vasodilator in congestive heart failure. Hydrochlorothiazide (HCT), 6-chloro-3,4-dihydro-7-sulfamoyl-2H-1,2,4-benzothiazine-1,1-dioxide, is a thiazide diuretic which reduces the resorption of electrolytes and consequently of water [3]. The two drugs (Figure 1) are used in association in the treatment of hypertension [4].

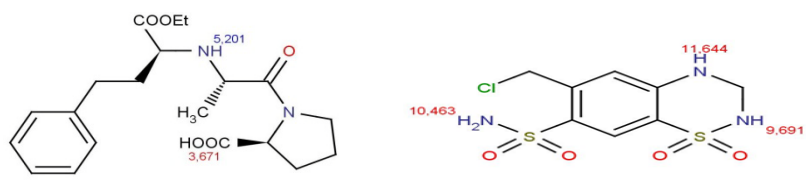


Figure 1. Chemical structures of enalapril and hydrochlorothiazide

These compounds are the compounds that have different chromatographic behavior due to their different characteristics, thus bringing about problems in separating. In this study, we aimed to simultaneously determine the required parameters for the analysis of the mixture of enalapril - hydrochlorothiazide by HPLC and did this analysis using the determined optimum conditions. Acetonitrile-water binary mixture was selected as hydroorganic solvent. The HPLC method was carried out on a X-Terra RP 18 (250mm, 4.6mm ID, S-5 μ m), maintained at different temperatures (30°C, 40°C, 60°C) to observe that effect of column temperature. CCD were employed to optimize the chromatographic separation. In the study, mobile phase pH was adjusted to $pK_a \pm 2$ range. The separation power and relationship between the parameters were analyzed by using MiniTab 16 software. The proposed HPLC method was successfully applied for the simultaneous quantitative analysis of hydrochlorothiazide and enalapril in tablet dosage forms. Validation parameters such as the specificity, linearity, precision, and accuracy were evaluated according to the ICH guidelines.

KEYWORDS: Experimental design, hydrochlorothiazide, enalapril, HPLC.

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Optimization and Validation of a HPLC Method for Simultaneous Determination of Chlorthalidone and Atenolol Using an Experimental Design

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Chlorthalidone, a monosulfonamyl diuretic, differs from other thiazide diuretics in that a double ring system is incorporated into its structure. Chlorthalidone has diuretic effect at maximal therapeutic doses. Chlorthalidone is used alone or with atenolol in the treatment of hypertension. The antihypertensive effects of these agents are additive, and studies have shown that there is no interference with bioavailability when these agents are given together in the single combination tablet. Atenolol is a water-soluble β 1-selective hydrophilic blocking agent. This compound was developed as a replacement for propranolol in the treatment of hypertension.

In the present study an isocratic reversed-phase high-performance liquid chromatographic method was investigated for the separation of atenolol, hydrochlorothiazide(I.S.) and chlorthalidone using central composite design(CCD). The key factors examined in the optimization phase were: the % concentration of acetonitrile in the mobile phase (A), the column temperature (B) and the chaotropic agent concentration(sodium perchlorate)(Table 1).

Table 1. The three-factor central composite design circumscribed used for the evaluation of the HPLC method

Factors	- α	-1	0	+1	+ α
Acetonitrile concentration (A)	9.9546	12	15	18	20.045
Column temperature (B)	30.955	33	36	39	41.045
Salt concentration (C)	8.1821	15	25	35	41.818

Chromatographic study was performed with ACE C18-PFP column (250 mm×4.6 mm, 5 μ m). At each condition, the pH of the mobile phase containing 10 mM phosphoric acid was adjusted to 6.5 by the addition of sodium hydroxide. The acetonitrile percentage of mobile phase is 15% and salt concentration of the eluent is 35 mM. Column temperature is 31°C at optimized condition. The proposed method was successfully applied for the estimation of atenolol and chlorthalidone in tablet dosage form(Tenoretic 100/25 mg).

KEYWORDS: RPLC, CCD, atenolol, chlorthalidone

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Application Of CCD To Optimisation Of RPLC Conditions For The Simultaneous Determination Of Amlodipine And Valsartan

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Having a structure of dihydropyridine, amlodipine is an important antihypertensive agent. Valsartan is also a dihydropyridine derivative with specific angiotensin II antagonist activity[1]. Amlodipine is in a group of drugs called calcium channel blockers. It is used alone or together with other medicines to treat angina, hypertension and other conditions caused by coronary artery disease. Hypertension may increase the risk of heart attacks. These problems may be less likely to occur if blood pressure is controlled. Amlodipine relaxes blood vessels and increases the supply of blood and oxygen to the heart while reducing its workload [1, 2]. Valsartan is a nonpeptide, orally active, and specific angiotensin II receptor blocker acting on the AT1 receptor subtype. It is indicated for the treatment of hypertension, to lower blood pressure. Lowering blood pressure reduces the risk of fatal and nonfatal cardiovascular events, primarily strokes and myocardial infarctions. These benefits have been seen in controlled trials of antihypertensive drugs from a wide variety of pharmacologic classes including the class to which valsartan principally belongs [1,2].

An isocratic reversed-phase high-performance liquid chromatography was investigated for the separation of amlodipine and valsartan using statistical experimental design. An optimization study including three factors (concentration of acetonitrile, column temperature, and mobile phase pH) was carried out in order to identify the optimum chromatographic conditions. For three examined factors, this design requires fourteen different runs, plus central point replications (6 experiments). The upper and lower limits of the factors have been determined from the preliminary experiments. Logarithm of retention factor and resolution factor were chosen the outputs of the experiments. The optimum conditions of separation were estimated by Derringer's desirability function. The acetonitrile percentage of mobile phase is 37.5% and pH of the eluent is 5.20 at this zone. The resolution values for each API and maprotiline (I.S.) are ≥ 3.0 at optimum condition. An isocratically separation was done for amlodipine and valsartan in less than 10 minute at this condition.

In this study, we also focused to predict retention factors of this compounds with the aid of overlay contour plots were in the following area: acetonitrile concentration from 36% to 44%, column temperature from 31 °C to 41 °C., eluent pH from 2.25 to 5.95. pK_a values for studied compounds. Were also predicted using the relationship between the retention factors and the mobile phase pH.

KEYWORDS: RPLC, CCD, amlodipine, valsartan

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Separation of Ketoprofen Racemate by TLC Plate with Different Chirals Selectors

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Separation of enantiomers has become a well-established technique in many fields of science; it is a matter of great importance in pharmaceutical, chemical and biotechnology. In fact, the biological and pharmacological activity of chiral compounds depends on their configuration; one of the enantiomers is pharmacologically active and even can be toxic [1]. It is thus desirable to have reagents and separation techniques to separate the enantiomers and analyze the enantiomeric purity. A variety of chromatographic methods have been developed for optical resolution recently [2]. Direct and simple separation of the enantiomers of ketoprofen is carried out on TLC plate used different chirals selectors in the mobile phase such as: quinidine, quinine carbamate, vancomycin and cyclodextrin. The success of enantioseparation of racemic ketoprofen is due to the difference in characteristics and selectivity of each selector.

Keywords: TLC, enantioseparation, chiral selector, ketoprofen.

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Effect of polyherbs on some blood serum lipid compositions of diabetic patients -Type II isolated by capillary gas chromatography

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This study include treatment of diabetic patients - type II with a polyherbs containing *Nigella sativa*, *Trigonell foenum graceum*, *Cyperus rotundus*, *Teucrium polium*

Finally, this study concluded that the long duration of diabetes mellitus lead to increase disorder in metabolism of lipids and deposition of it. Also disorders occurred in percentage of fatty acid in the first group compared with the second group of diabetic patients.

KEYWORDS: diabetic patients - type II, polyherbs, *Nigella sativa*, *Trigonell foenum graceum*, *Cyperus rotundus*, *Teucrium polium* divided into two groups, lipid component.

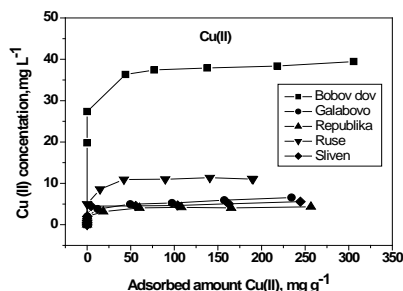
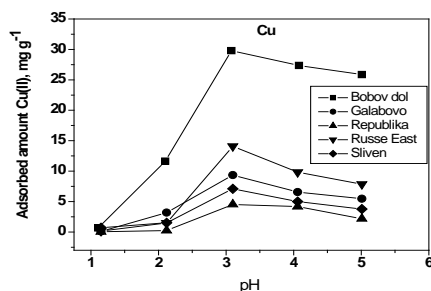
Fly Ashes from Bulgarian Power Plants as Potential Adsorbents for Cu(II) Removal

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divided into two groups, first group were taken from patients with chronic renal failure (dialysis) and the control group who used haemodialysis. These groups were compared with healthy persons as a control group. Separation of the lipid component containing ions of special concern because they are not biodegradable and therefore persistent. The effective removal of metal ions from wastewaters still remains to be a problem needing solution. There are many methods for removal of hazardous ions, such as diffusion, permeation, ion exchange, electrochemical precipitation, membrane separation and adsorption. The methods differ in technological design, in the used and costs. Among these technologies also such as primary gas chromatography (GC) and secondary GC are used. In this study was shown that for low concentrations of cations that there is a significant increase in the percentage of saturated and monounsaturated fatty acids (SFA, MUFA) before the treatment of the two groups compared to the healthy group and a significant decrease was observed in the percentage of polyunsaturated fatty acids (PUFA) in the two groups. The mixture of fatty acids is regarded as an essential metal at low concentrations, it becomes toxic for humans, animals and plants at higher concentrations. Studies on the utilization of industrial wastes as low cost adsorbents for removal of heavy metals from wastewaters are gaining attention. Fly ash is a solid by-product that is produced in power plants. In this study, patients in comparison with the control group and healthy people were a significant increase observed in (PUFA) percentage after the treatment. For high concentration in serum lipid the result of this study was shown that there is a significant increase in the percentage (SFA) and (PUFA) before treatment. In comparison with control group and after treatment for three months of the two groups of patients, a significant increase in the percentage of SFA and PUFA was observed in the two groups. The average pore radius, the adsorption properties with respect to Cu(II) ions in single component solutions were determined by means of the batch method. The effects of various parameters on Cu(II) removal, such as contact time, acidity of initial solutions and Cu(II) ion concentrations were studied. The sorption capacity increases with the increase in the acidity of initial solutions. The equilibrium is attained for results of the mechanism of adsorption is decreased the percentage of (SFA) before and after adsorption in (MUFA) after the treatment. In both groups compared with control and a decrease significantly in (PUFA) percentage was also shown for phospholipids part in the initial solutions. With the increase in pH the amount of adsorbed ions increases and the optimum pH range is found to be about 3. The amounts of adsorbed Cu(II) ions onto the investigated materials as a function of pH of initial solutions and experimental adsorption isotherms are presented below.



Equilibrium data were fitted to linear Langmuir, Freundlich and Dubinin-Radushkevich models and maximum adsorption capacities were calculated. Langmuir isotherm most adequately described the adsorption process. All materials showed good adsorption properties towards Cu(II) ions and could be used for their effective removal from aqueous solutions.

ACKNOWLEDGEMENTS to the National Science Fund of Bulgaria (Contract No DTK-02/5, 19 January 2010) for the financial support

KEYWORDS: fly ash, adsorption of cu ions, kinetics, adsorption equilibrium

Coal Fly Ash Characterization by the Combined Use of Analytical Techniques

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Fly ash represents the finest fraction of the non-combustible residue from coal burning, which is being collected in gas purification facilities. The total quantity of fly ash produced in Bulgaria is approximately 6 million tons per year. Less than 20% of it is utilized; the rest is being disposed in landfills creating serious risks of air, soil, ground- and surface water pollution. The elaboration of effective and low-cost methods and technologies for the utilization of fly ashes is of great practical interest. Although fly ashes generated in power plants worldwide have similar qualitative composition, their chemical and physical properties vary widely, depending on the kind of the coal fired, boiler type and burning regime, and collector system setup. Therefore, an individual investigation of fly ashes from different power plants is indispensable. Only a detailed study on the physical, chemical and morphological properties of a particular fly ash could gain an understanding of its potential environmental and health impact associated with its disposal and utilization. In the present study coal fly ashes from five Bulgarian power plants – “Bobov dol”, “Galabovo”, “Republika”, “Russe East” and “Sliven” were investigated. The materials were taken directly from the electrostatic gas cleaning systems in the plants. Moisture and ignition loss were measured by a standard thermogravimetric method. Granulometric analysis showed differences by several orders of magnitude within the particle size distribution for each sample. The measurements of slurry pH indicated that all fly ash samples displayed high pH values in the range between 8 and 11. The chemical crystallites of all fly ash samples were determined by XRD and they all showed similar XRD patterns. Chemical phases such as quartz, mullite, moissanite, albite, hematite and magnetite were identified. The elemental composition was established by combination of standard wet chemical analysis and atomic spectrometry. Spectral analytical pre-investigations were carried out on a grating spectrograph. Gravimetric chemical analysis was used for silica assessment. The elements Al, Fe, Ca and Mg were determined titrimetrically, and atomic absorption spectrometry was applied for micro- and trace element determination after dissolution using a mixture of acids. It was proved that Si, Al, Ca, Fe, K and Mg appear as major elements in all samples while Na, Cu, Mn, Ti, Zn, Pb, Cr, Ni, Mo, As, and Cd are present as minor elements or traces. The P, N, S and Cl contents were also determined. Some of the results obtained are presented in the table:

Fly Ash Parameter	“Bobov dol”	“Galabovo”	“Republika”	“Russe East”	“Sliven”
SiO ₂ [%]	49.9 ± 1.3	47.8 ± 1.2	57.9 ± 1.3	51.8 ± 1.3	59.8 ± 1.4
Al ₂ O ₃ [%]	21.8 ± 0.6	23.7 ± 0.6	24.9 ± 1.8	21.0 ± 0.6	17.7 ± 0.6
Fe ₂ O ₃ [%]	10.8 ± 0.3	9.4 ± 0.28	7.18 ± 0.16	8.47 ± 0.29	10.4 ± 0.3
CaO [%]	10.5 ± 0.2	8.09 ± 0.17	3.61 ± 0.11	2.73 ± 0.07	4.37 ± 0.14
MgO [%]	1.83 ± 0.6	1.06 ± 0.05	3.12 ± 0.14	2.41 ± 0.08	1.58 ± 0.06
Na ₂ O [%]	0.84 ± 0.02	1.02 ± 0.03	0.66 ± 0.02	0.98 ± 0.03	2.51 ± 0.07
K ₂ O [%]	2.45 ± 0.06	1.04 ± 0.03	2.33 ± 0.06	1.76 ± 0.05	2.42 ± 0.06
P ₂ O ₅ [%]	0.16 ± 0.03	0.05 ± 0.02	< 0.004	0.29 ± 0.06	0.03 ± 0.02
N [%]	< 0.005	0.029	0.027	0.007	0.026
N–NO ₃ [%]	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005
N–NH ₄ [%]	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005
Cl [–] [%]	0.04 ± 0.002	0.015 ± 0.002	0.014 ± 0.002	< 0.003	< 0.003
SO ₄ ^{2–} [%]	2.85 ± 0.08	2.34 ± 0.09	0.56 ± 0.05	0.55 ± 0.03	1.40 ± 0.05
As [μg g ^{–1}]	63 ± 4	18 ± 3	34 ± 4	11 ± 3	15 ± 3
LOI [%]	2.16	8.29	1.86	11.19	1.37
Moisture [%]	0.3	1.2	0.4	0.3	0.4
Conductivity	3.48 ± 0.11	1.75 ± 0.10	1.85 ± 0.10	4.05 ± 0.13	3.60 ± 0.12
Surface area [m ² g ^{–1}]	4.3	10.0	9.4	6.0	5.5
V [cm ³ g ^{–1}]	0.005	0.022	0.020	0.013	0.011
D [nm]	4.46	8.88	8.63	8.40	7.82
pH	11.4	8.0	8.1	10.4	8.0

The texture parameters of all studied fly ashes were determined by low-temperature adsorption of nitrogen. The data obtained for surface area and pore volume showed that all investigated materials could be used as low-cost adsorbents for different pollutants.

KEYWORDS: fly ash, XRD, atomic spectrometry, texture parameters

ACKNOWLEDGEMENTS to the National Science Fund of Bulgaria (Contract No DTK-02/5, 19 January 2010) for the financial sup

Argan and Almond Tree Walnuts Shells: Valuation and Application to the Adsorption of Methylene blue

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The increasing demand of adsorbents used in the processes of environmental protection rendered their cost more and more expensive, which requires research for new less expensive materials adsorbents especially from plant waste. The objective of our work is two fold: first, to contribute to on going search of a solution to this problem by elaborating adsorbents effective and less expensive than those conventional. Second, to value two materials of agricultural sources in this particular case of Argan tree walnuts Shells SAR and almond tree shells SAM (abundantly produced in the region). The efficiency of these materials is tested by the use of the Methylene blue MB: dye widely used in textile industry.

The experimental study which we led consists of three main parts:

Kinetic study.

The adsorption kinetics of the methylene blue on both adsorbents was followed by spectrophotométrie. It allowed the determination of the minimal time of contact allowing to reach equilibrium. The latter is reached from the first 5 minutes for both adsorbents. We conclude that the adsorption of methylene blue on the SAM and SAR passes by two stages: a fast stage and a slow and decisive stage.

Study of the parameters influencing the adsorption:

On one hand, it allows to determine the optimal mass of adsorbing, and on the other hand, the revealing of the temperature effect and the pH on the adsorption of MB.

Effect of the adsorbent mass.

This study consists in determining the adsorbing optimal mass to use during the work. The obtained results analysis shows that the efficiency on adsorption increases with the mass of adsorbent suspended in the solution. The stabilization is reached for a value close to 2g.

Effect of pH of the solution on the adsorption.

The influence of this parameter on the adsorption of the MB on the two adsorbents was studied. Several values pH were studied in both acid and basic domains. The obtained results show that, for area studied, acidic or basic a pH increase has a positive effect on the adsorption.

Effect of the initial concentration of the solution on the adsorption.

To study this effect, we used MB solutions of increasing concentrations while keeping the other parameters fixed. The analysis of the obtained results shows a strong increase of the quantity adsorbed by MB with the initial concentration for both adsorbents until the obtaining of a landing of saturation for the CAM, by against the CAR continues to adsorb MB.

Effect of the temperature on the adsorption.

In analyzing the obtained results we observe that in the field of temperatures studied, this parameter has a low influence on the adsorption.

Study of the adsorption isotherms and the modelling of the MB retention by SAM and SAR.

The isotherms of adsorption are obtained at first, by the graphic representation of $Q_e = f(C_e)$ where Q_e and C_e respectively the quantity of dye adsorbed by 1g of adsorbent and the equilibrium concentration of the dye. Henry isotherms, Freundlich and Langmuir are realized in identical operating conditions on our adsorbent. The obtained results show that: Henry's isotherms, Freundlich, and Langmuir are realized in identical operating conditions on our adsorbing. The obtained results show that: The Freundlich isotherm describes better the phenomenon of adsorption on them SAR. The Langmuir isotherm describes better the phenomenon of adsorption on the SAM.

KEYWORDS : material. Isotherms. Agro source. Adsorption. Environment. Methylene blue. Argan tree. Almond tree. Pollution. Water treatment.

Types of Adsorption In the Ion Exchange of Algerian Bentonite by Quaternary Ammonium Salts

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The work presented in this paper has the purpose of enhancing a clay deposit from the Algerian Boughrara Hammam. This clay has been primarily a sodification highlighted by several analytical methods.

The proprieties of clays, raw and sodic (swelling, cation exchange capacity) were studied and compared. The results showed that sodium bentonite contains more free water and presents a higher CEC. This tends to confirm its high swelling capacity and cation exchange. Therefore, we continued this work only with Na-bentonite.

The diffractograms of sodium bentonite exchanged hexadecyltrimethyl and dodecyltrimethyl ammonium bromide ((DDTMABr and HDTMABr) show an increase in the lattice spacing of 6 and 12 Å respectively. This increase is due to the substitution of inorganic ions by ion alkylammonium. The enhancement of the ray value (d001) shows better penetration of HDTMA⁺ in the lattice.

To obtain organophilic bentonites structure perfectly controlled, we have chosen for HDTMA⁺ since it causes greather spreading, thus a better ability to exchange in aqueous medium.

Analyzes carried out by XRD, TGA and DTA show successively starting free water followed by desorption is initially physisorbed ions and degradation of alkylammonium ions (chemisorbed) ionically bound to the surface of the leaves. Alkylammonium ion concentration in solution strongly influences the type of adsorption. As in the case of temperature increase at the higher concentrations, a displacement of the exchange equilibrium to deep galleries occurs at the expense of a simple physical adsorption.

KEYWORDS: adsorption, bentonite, organophilic clays, TGA / DTA.

Comparison of Removal Lead (II) from Aqueous Solution on Novel Inorganic-organic Hybrid Materials

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Nowadays, heavy metal adsorption processes are very attractive subject because of the heavy metal pollution is the most important environmental problem in the world. The problem has increased with the rapid development of industries, especially in developing countries [1]. There are many applications used in the removed of heavy metals from aqueous solution. Among of these methods, adsorption process is the most used one with easy, cheap and effective applied [2].

In the recent years, researchers have been examining the inorganic-organic hybrid materials as an adsorbent. Poly-GPTS was prepared by polymerization of 3-glycidyloxypropyltrimethoxysilane (GPTS) with potassium tert-butoxide (KOTBu) at 50 °C. After this stage, adsorbents poly-GPTS and poly-GPTS/Ti(O)/OH were prepared from hydrolysis of poly-GPTS and mixtures between poly-GPTS and titanium isopropoxide in 1:1 mol ratio [3]. The hydrolysis was carried out in 50 ml of isopropanol with 0.1 molar HCl.

These two adsorbents were used to remove lead (II) from aqueous solution. To investigate the maximum adsorption capacity, optimization studies of initial pH, adsorption time, amounts of adsorbent and initial metal concentrations were performed. The adsorption capacity of Si-Ti adsorbent was better than Si adsorbent. This is very reasonable because of each Ti atom containing four oxygen atoms which adsorb the metal ions.

KEYWORDS: Adsorption, heavy metal and hybrid materials.

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Removal of Cationic Surfactant from Aqueous Solutions by Using Clay Mineral

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Water pollution is indeed of great concern since it is a major carrier of both organic and inorganic contaminants [1]. Surfactants are one of the contaminants which produces from industrial application causes water pollution. Therefore, removing surfactants from wastewater has an important role for the environmental pollution. Adsorption is one of the major processes for the removal of the cationic surfactants from wastewater. Clay minerals are known to have excellent adsorption properties and therefore widely used to remove organics from water [2, 3]. Ion-exchange and hydrophobic bonding mechanisms can be occurred for the adsorption of the cationic surfactants [4]. When the amount of cationic surfactant is below of the critical misel concentration (CMC), ion-exchange mechanism occurs between the surfactant and positive ions on the clay surface. If the amount of cationic surfactant is equal to or above the CMC of the clay, both of the mechanisms can be observed.

In this study, hexadecyltrimethyl ammonium bromide (HDTMA) was used as the cationic surfactant and zeolite is used as the clay mineral. Zeolites are three-dimensional, microporous, crystalline solids with well-defined structures that contain aluminium, silicon, and oxygen. The silicon and aluminium atoms are tetrahedral coordinated with each other through shared oxygen atoms [5]. Therefore, natural zeolites have negative charges in their crystal structures, making them suitable surface modification using cationic surfactants [6]. Studies were performed in batch system to investigate the effect of initial solution concentration and equilibrium isotherms of batch system were also analyzed by Langmuir, Freundlich, Temkin and Dubinin-Redushkevich isotherm models. For zeolite initial HDTMA concentrations were changed from 0.1 to 1.7 mmol/L. The maximum HDTMA sorption percentage on zeolite surface was 96.5%. At low HDTMA concentrations which means HDTMA concentration is below CMC, HDTMA molecules were adsorbed on the clay surface by ion-exchange mechanism. In this case, clay surface was neutralized by the sorption of positively charged surfactant ions. When the amount of HDTMA molecules were above the CMC, hydrophobic interactions were occurred between hydrophobic sides of the HDTMA molecules and second layer was formed on the clay surface. The negative surface charge of the clays reversed to positive by sorption of cationic surfactant molecule. For zeolite, R^2 values for linear form of Langmuir, Freundlich, Temkin and Dubinin-Redushkevich isotherms are 0.99, 0.98, 0.93 and 0.95, respectively. According to R^2 values Langmuir isotherm model was fitted well for HDTMA sorption onto the zeolite clay. Theoretical q_e values were also calculated and found that they were fitted well with the experimental q_e values.

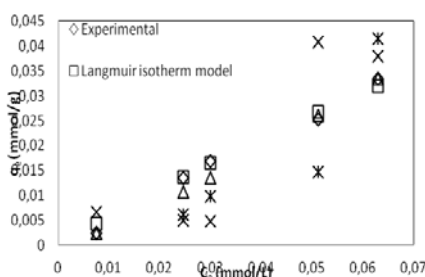


Figure 1. Adsorption isotherms for sorption of HDTMA on zeolite

KEYWORDS: sorption, isotherm, isotherm model, HDTMA, zeolite

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Removal Of Lead From Water Using Natural Zeolite And Granular Activated Carbon Adsorbents

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This paper presents the removal of Pb from drinking tap water dosed with lead using natural zeolite and granular activated carbon adsorbents. Sorption of Pb was investigated as a function of the solution temperature and contact time. Equilibrium data were analyzed by the Langmuir and Freundlich isotherm model. The microstructures of the activated carbon and natural zeolite before and after adsorption of lead were observed by scanning electron microscopy. Textural analysis was employed in order to determine the specific surface area and pores size distribution of the used activated carbon. The adsorbents were characterized by using Fourier transform infrared spectroscopy.

KEYWORDS: Lead, granular activated carbon, natural zeolite, drinking water

**Equilibrium and Thermodynamic Data for
Adsorption of Malachite Green, Sirius Blue and Congo Red onto
Bentonite**

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Colored dye wastewater arises as a direct result of the production of the dye and also as a consequence of its use in the textile and other industries. Dyes should remove from waste-waters before discharging to receiving environment for prevent their negative effect on environment. Adsorption of various dyes from aqueous solution has proven to be an excellent way to treat effluent also a cost effective technique.

In this study; Malachite Green, Sirius Blue and Congo Red dyes that can be used very commonly in textile wastewater, adsorption onto bentonite and modified bentonite were analyzed. In this study, concentration, pH, amount of adsorbent, stirring time, kinetic and temperature parameters were investigated and optimum conditions were determined. Equilibrium data were analyzed by two isotherms, namely the Freundlich isotherm and the Langmuir isotherm. The best fit to the data was obtained with the Langmuir isotherm.

According to the results, bentonite is a very suitable low cost adsorbent for removal of selected dyes.

KEYWORDS: ; Malachite Green, Sirius Blue, Congo Red, adsorption, bentonite

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Analysis of Metal Contents in Spinach, Lettuce, and Parsley Marketed in Marmara Region

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Green leafy vegetables are the most concentrated source of nutrition of any food. They are a rich source of minerals (iron, calcium, potassium, and magnesium), vitamins (K, C, E, and many of the B vitamins), and phytonutrients (beta-carotene, lutein, and zeaxanthin) which protect our cells from damage and age-related problems. They are also rich in fiber, extremely low in fat and carbohydrates and provide an excellent source of protein.

Pollution is caused by misuse of the soil; such as poor agricultural practices, mining and disposal of industrial and urban wastes. Furthermore, soil pollution is mainly a result of chemicals in herbicides defined as killers of harmful plants, and pesticides defined as poisons for insects [1]. As a result, the accumulation of heavy metals leads to contamination of the food chain, because vegetables absorb heavy metals from the soil and polluted air and water. In general, heavy metals are not biodegradable and therefore can accumulate in human vital organs.

The contamination of heavy metals constitutes a concern for human health for the capacity to enter in the food chain. Vegetables are vital for human's diet and in particular provide the wellknown heavy metals. To investigate the possible risks for the population due to the chronic exposure to heavy metal contamination of three different vegetables, this study has focused on the mineral and heavy metal contents in spinach, lettuce, and parsley. In January 2013; spinach, lettuce, and parsley samples were collected in Marmara Region for a total of 54 samples and sampling areas were represented by population.

Inductively coupled plasma-mass spectrometry (ICP-MS) measurements were made after microwave digestion and the metal contents (Na, Mg, Al, P, K, Ca, Fe, Cu, Zn, As, Se, Cd, Sn, Hg, Pb) of samples were determined. Each samples analyzed as two paralels and three replicates and the average values of these analysis were reported. Among the metal contents analysed by ICP-MS after microwave assisted digestion; the presence of heavy metals in general was in the order of Cu>Pb>Cd>As>Sn>Hg. The results showed that average values of Cu, Pb, Cd, As, and Sn concentrations were highest ($p<0.05$) in spinach samples. According to the analysis; the highest amounts of Cu, Pb, and Cd content were found in spinach samples collected from Tekirdağ (5.10 ± 0.3 mg/kg), Edirne (0.106 ± 0.007 mg/kg), and Tekirdağ (0.08 ± 0.004 mg/kg), respectively.

KEYWORDS: heavy metal, ICP-MS, microwave digestion, green leafy vegetables

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Study by FT-IR Spectroscopy of Adsorption onto Activated Carbon

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The adsorption of pollutants from aqueous solutions onto activated carbon prepared from vegetable waste was studied.

The surface characterization of activated carbon was performed using transmission -absorption FT-IR and ATR-FTIR spectroscopy. The use of biomaterials for the removal of colour from its aqueous solution will provide as a potential alternate to the conventional treatment methods.

In this work we use transmission -absorption FT-IR and ATR-FTIR spectroscopy to study spectral characteristics of surface changes and adsorption phenomena. The measured IR spectra of the activated carbon show that there is difference in the surface properties according to the nature of waste use to obtain activated carbon.

The spectra indicate the presence of highly reactive functional group which may explain the values of adsorption capacity of activated carbon.

KEYWORD: FT-IR spectroscopy, adsorption, activated carbon

**Comparison of Aluminum Alginate and Aluminum Alginate –
Montmorillonite Composite Beads on Defluoridation of Water**

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Alginate is a nontoxic biopolymer and extracted from seaweed. Alginate has the ability to form crosslinked structures with divalent and trivalent ions, resulting in stable hydrogels. Such gels have many uses in food packages, drug formulations, controlled release systems and many others.

Fluoride is a common pollutant in drinking water, and excess amounts of fluoride may cause health problems. Various studies are reported in literature, including ion-exchange resins, reverse osmosis systems and natural adsorbents. Among these, natural adsorbents are important, because they are cheap and non-toxic in general. A previous study by our group reported the defluoridation by aluminum alginate gel beads.

This study extends our previous work and investigates the effect of montmorillonite clay, a natural material with high surface area, on fluoride removal by batch adsorption. Beads were characterized by FT-IR, gravimetry, SEM. Effect of pH, initial fluoride concentration and bead dosage were investigated.

KEYWORDS: defluoridation, alginate, clay, aluminum, adsorption

Brilliant Yellow Adsorption onto Vinyl Imidazole Containing Microbeads

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Synthetic dyes are prevalently used in many fields of modern technology, e.g., in various branches of the textile industry, paper production, food technology, agricultural research, photoelectrochemical cells, and hair colorings. Moreover, synthetic dyes have been utilized for the control of the efficacy of sewage and wastewater treatment [1]. The main problem is the cleanup of wastewaters that contain visible concentrations of colored textile effluents. Dyes were usually adsorbed, activated carbon is the most commonly used adsorbent due to its high specific surface area and high adsorption capacity, which partly offset the high cost of running the adsorption process.

The brilliant yellow (BY) is an anionic azo dye, which is bivalent anion ($\text{Na}^+_2 \text{BY}^{2-}$) was used in this study [2]. In previous studies, it was showed that this dye can be used as optical sensor for pH, for ammonia and urea determination, as photometric indicator for magnesium, and also in electrochemical synthesis of polypyrrol films [3].

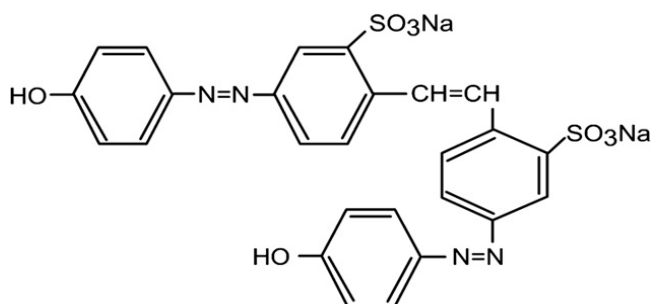


Fig. 1. Structure of BY.

In this study, poly(ethylene glycol dimethacrylate-*n*-vinyl imidazole) [poly(EGDMA-VIM)] containing microbeads were synthesized to remove BY dye from aqueous solutions and basic physicochemical properties of BY removal were investigated.

KEYWORDS: Dye adsorption, poly(ethylene glycol dimethacrylate-*n*-vinyl imidazole), synthetic dyes

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Acid Blue 9 Adsorption on Amino Acid Containing Magnetic Microbeads

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Acid Blue 9 (AB9) belongs to the triphenylmethane dye group. It has high solubility amount in alcohol (like ethanol or methanol) and in cold water. It can be found in a great many industrial applications such as textile dyeing for wool and silk, foodstuffs, pharmaceuticals, algaecides and herbicides [1]. AB9 has also been studied as film dopant to act as photosensitive chromophore for optics and laser technology application and ink jet technology [2]. Due to its widespread applications, adsorption of AB9 is widely important for many investigators. Among these, adsorption with polymeric materials is an alternative eco-friendly technology in relation to the existing costly water treatment technologies due to low initial cost, ease of operation, insensitivity to toxic substances, and complete removal of dyes from dilute solutions [3].

Magnetic polymers have been widely used in biotechnology, biomedical engineering, diagnosis and separation technology such as wastewater treatment, purification or immobilization of biomolecules. Magnetic separations are rapid, easy, needing a simple instruments and can combine with other chromatographic separation techniques. Separation of magnetic materials from the solution is easy due to its magnetic properties and can be applicabled large-scale operations [4,5,6]. In this study, amino acid containing cross-linked copolymer magnetic microbeads were prepared and adsorption parameters of AB9 with these magnetic microbeads were estimated. The characterization studies were also conducted for magnetic microbeads.

KEYWORDS: Dye adsorption, magnetic beads, synthetic dyes, acid blue 9.

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Removal of 17 β -estradiol with Microparticle-Embedded Cryogel System

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Endocrine disrupting chemicals (EDCs), either natural or synthetic, can cause environmental pollution and adverse health effects in an intact organism or its progeny, subsequent to endocrine function. EDCs have been defined as exogenous agents that interfere with the production, release, transport, metabolism, binding, action or elimination of the natural hormones in the body responsible for the maintenance of homeostasis and the regulation of developmental processes [1, 2].

The natural estrogen 17 β -estradiol (E2) is the most potent EDCs that have been entering water systems via human and animal waste products. In the aquatic life, up to 1 ng L⁻¹ concentrations of E2 can cause semen volume reduction on male rainbow trout [3], increase of vitellogenin production on male fishes. Due to that E2 must have been detected and removed from wastewater by some analytical/biochemical methods.

Membrane adsorbents, monoliths and cryogels have been used as new chromatographic components. Cryogels are a very good alternative bioseparation material because of its large pores, short diffusion path, low pressure drop, short residence time and low cost. In this study, microparticle embedded cryogel systems were prepared to remove E2. The material was characterized by X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM) and infrared spectroscopy (IR). The effect of operation pH, initial concentration and temperature of E2 adsorption were determined.

KEYWORDS: Endocrine disrupting chemicals (EDCs), 17 β -estradiol (E2), cryogels.

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Comparison of MLR And ANFIS Approaches For Biosorption Process

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Agricultural wastes could be assumed to be low-cost adsorbents since they are abundant in nature, inexpensive, require little processing and are effective materials [1]. Many agricultural waste materials have been used as adsorbents for the removal of copper from wastewater. In this study, date palm (*Phoenix dactylifera* L.) seeds as an agriculture waste, have a problem to the date industry, were used to remove Cu(II) ions from aqueous solutions by a batch sorption process.

Biosorption characteristics of Cu(II) onto date palm seeds were used as a raw, natural and abundantly materials in batch mode investigating the effect of the key process parameters. The biosorption process was optimized and compared by using both Multiple Linear Regression (MLR) [2] and Adaptive Neuro-Fuzzy Inference System (ANFIS) [3]. MLR and ANFIS models were compared in terms of their accuracy and predictive ability. Root Mean Squared Error (RMSE) and coefficient of determination (R^2) values were used for the evaluation of model performance. It was determined that ANFIS may be used as more effective than that for the MLR model to predict the sorption of Cu(II) onto date palm seeds [4]. In addition, it was proposed an alternative use of date palm seeds, as untreated sorbents for the removal of Cu(II) ions as an eco-friendly process.

KEYWORDS: ANFIS; biosorption; Cu(II) removal; date palm (*Phoenix dactylifera* L.) seeds; MLR

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Application of Response Surface Methodology for The Biosorption of Pb(II) Using Black Cumin

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Pb(II) salts and organic lead compounds are ecotoxicologically most harmful. Lead that have the most damaging effects on human health accumulate in organisms, sediments and sludge. Many conventional methods have been used to remove metal ions from aqueous solutions including oxidation, reduction, precipitation, membrane filtration, ion exchange and adsorption. Among these methods, the promising process in removing heavy metals from aqueous solutions is adsorption. In recent years, more attentions have been gained by the biomaterials. In the recent years, the multivariate statistical techniques have been preferred to identify the optimum combination of the factors and the interaction between factors, which is not possible in the univariate method [1,2].

A batch adsorption process was realized on *Nigella sativa* seeds (*black cumin*), a novel and natural biosorbent, to remove Pb(II) ions from aqueous solution [3]. Biosorption of *black cumin* was successfully utilized for the removal of Pb(II) ions from aqueous solution by using response surface methodology (RSM). The effect of process variables such as pH, biosorbent mass and temperature on the adsorbed amount of Pb(II) were investigated using two level three factor central composite design (CCD). Biosorbent mass was the most significant factors that affect the removal of Pb(II) under the studied conditions.

KEYWORDS: *biosorption, black cumin, Pb(II) removal, response surface methodology*

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Optimization of the Solid Phase Extraction Method by Using Box-Behnken Design

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The accurate and sensitive determination of metal ions at the trace level is an important search subject for analytical chemists. Due to the low concentration and matrix effects of metal ions, the direct determination of their presence in environmental samples by flame atomic absorption spectrometers (FAAS) is usually insufficient. Therefore, a sample pretreatment step prior to their analysis using FAAS or other techniques is necessary [1].

In this work, a preconcentration procedure is proposed that uses solid phase extraction for the determination of copper ions in different water samples and mussel samples by FAAS. The preconcentration steps were performed using a mini-column of MWCNTs-COOH. A three-level Box-Behnken design (BBD) [2] were used to evaluate the influence of various experimental parameters such as pH, amount of copper, and sample volume on the copper recovery without complexing agent or chemical modifier.

The proposed method was successfully applied to the determination of copper ions in tap water, drinking water, and bay water. The added copper ions can be quantitatively recovered from the water samples by the proposed procedure. The enrichment factor for the preconcentration procedure was obtained as 100 [3].

The accuracy of the proposed method was investigated by analyzing a *BCR-320R* standard reference material. A good agreement with the certified value was achieved.

KEYWORDS: *Box-Behnken design, solid-phase extraction, multi-walled carbon nanotube, copper*

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Comparison of Orange and Mandarin Juices In Terms Of Water Soluble Vitamins

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The importance of vitamins in nutrition was initially understood in the 1920s and 1930s. Because of their critical role in nutrition and their relative instability, qualitative and quantitative analyses are an important issue as well as a challenging task for food manufacturers [1]. Moreover, determination of vitamins in foods is often a challenging task due to their instability. Aging, storage conditions, and processing of foods cause vitamin loss, which varies widely depending on the type of food and a number of specific parameters (e.g., temperature, oxygen, light, moisture, pH) [2].

The main objective of this study was comparing the water soluble vitamins such as vitamin C, B₁ and B₃ in orange and mandarin juice. Orange and mandarin samples were taken from 10 different markets at Tunceli and squeezed. The obtained fruit juices were mixed firstly with 0.5 M HClO₄ and then water. The solutions were centrifuged. The clear solution filtered and analyzed with HPLC- DAD. Data were compared with independent samples T-test.

KEYWORDS: Orange juice, mandarin juice, water soluble vitamin, HPLC-DAD

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Teawaste as an Adsorbent for Copper Removal from Aqueous Solutions

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The metals of major environmental concern today are arsenic, cadmium, chromium, cobalt, copper, lead, manganese, mercury, nickel and zinc. A few familiar methods in practice for removal of these and other metals are chemical precipitation, ion exchange, solvent extraction, reverse osmosis, adsorption, etc. Adsorption has become one of the preferred methods for removal of toxic contaminants as it has been found to be very effective, economical, versatile and simple. Adsorption has the additional advantages of applicability at very low concentrations, suitability for using batch and continuous processes, ease of operation, little sludge generation, possibility of regeneration and reuse, and low capital cost [1].

In the past two decades, research has been carried out focused on using low-cost effective sorbents for heavy metal adsorption and the sorption behavior of several natural materials and waste products has been investigated [2]. The main objectives of this study has been to investigate the adsorption characteristics of teawaste.

In this study, for the removal of Cu ions from aqueous solutions using teawaste under different experimental conditions such as amount of adsorbent, stirrer time, final volume and pH was investigated to find out optimum operating conditions. Adsorption of Cu²⁺ on teawaste was carried out by batch process at room temperature. Residual metal concentration in the supernatant liquid was then determined by Atomic Absorption Spectrophotometer (AAnalyst 800). Because determination of Cu²⁺ and other metals, among atomic spectrometry techniques, flame atomic absorption spectrometry presents desirable characteristics, such as low costs, operational facilities, high analytical frequency and good selectivity. The effect of time on the adsorption of Cu was determined by analyzing the residual metal ions in the liquid after contact periods of 10, 30, 45, 60, 90, 120 and 180 minutes. Effect of adsorbent dose was studied by varying adsorbent amount from 0.1 g to 1.0 g. The effect of pH on the adsorption of Cu was studied and optimum pH was obtained.

KEYWORDS: Teawaste, Copper, Adsorption, AAS

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Use of Carrot Peel to Remove Heavy Metals from Aqueous Solution

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The removal of heavy metals from industrial wastes is important for public health because heavy metals in waste water are toxic and provide a major environmental hazard [1]. As a result, there have been several studies on the removal of heavy metals from wastewater. In recent years, the use of low-cost and environmental friendly adsorbent as a replacement for the current expensive methods of removing heavy metals from wastewater has gained importance [2].

In this study, the ability of carrot peel to remove heavy metals from aqueous water was studied. For this purpose, the effects of solution pH, contact time, metal ion concentrations, and sorbent dosage were studied in batch experiments. Metal ion concentrations were determined using flame atomic absorption spectrometry. The heavy metal removal efficiencies were over 90% for copper and 80% for lead. Results showed that the carrot peel could be an effective and environmentally friendly adsorbent to remove the metal ions from aqueous solutions.

KEYWORDS: heavy metals, adsorption, carrot peel, removal

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Various Approaches for The Estimation of Thermodynamic Functions of Adsorption for a Number of Azo Dyes on Activated Carbon

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This study is concerned with testing the adsorption efficiency of a new type of activated carbon for removal of azo dyes from their aqueous solutions. Three azo dyes are synthesized from the reaction of para substituted anilines with β -naphthol via diazonium salts are used as adsorbate for achieving this study.

The optimal conditions of the considered adsorption systems are determined by studying factors affecting adsorption efficiency such as adsorbent dose, contact time, initial concentration of dye, pH of the adsorption medium and temperature.

The amount of adsorbed dye is estimated spectrophotometrically by constructing a calibration curve for each dye at its maximum wave length (λ_{max}). The adsorption processes are carried out as batch methods and by employing single component systems.

Three models of adsorption isotherms namely; Freundlich, Langmuir, and Tempkin are applied to fit the experimental data of adsorption at equilibrium at certain range of concentrations (1×10^{-4} – 9×10^{-4} M) and at various temperatures. The results indicated that, the Freundlich isotherm is better fitted to the experimental data of the studied systems, although, the other isotherms exhibited good fit.

For sets of thermodynamic functions of adsorption (ΔH , ΔG° , and ΔS°) are estimated depending on the values of the equilibrium constants of adsorption which are represented by four different ways; First, the distribution coefficient calculated from the ratio between the concentrations of the adsorbed and free dye in solution at equilibrium. Its then represented by Freundlich constant (K_F), Langmuir constant (K_L), and finally is described by Tempkin constant (T_K). The results obtained showed good consistency among the four set of functions in terms of their values and physical meaning.

KEYWORDS : Adsorption, Azo dyes, Activated carbon, Thermodynamic functions

Adsorption of Cu(II) from Aqueous Solution using Drinking Water Treatment Sludge

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The objective of this study was to investigate the potential usage of drinking water treatment sludge (DWTS) as adsorbents in removal of Cu(II) from aqueous solutions. For that purpose; the characterization of DWTS was carried out by X-Ray diffraction (XRD), scanning electron microscope (SEM) and inductively coupled plasma-atomic emission spectroscopy (ICP-AES) methods [1]. The adsorption experiments were carried out by batch technique and the influences of several analytical parameters including pH (Figure 1), contact time, initial Cu(II) concentration, amount of adsorbent and temperature on the adsorption process were evaluated. From the results, adsorption process was dependent on solution pH and optimum pH was specified as 5.0 and contact time was determined as 4.0 hour. The sorption data followed the Langmuir and Freundlich isotherms. The results of this study demonstrated that DWTS can be used as a suitable adsorbent for removal of Cu(II) from aqueous solutions.

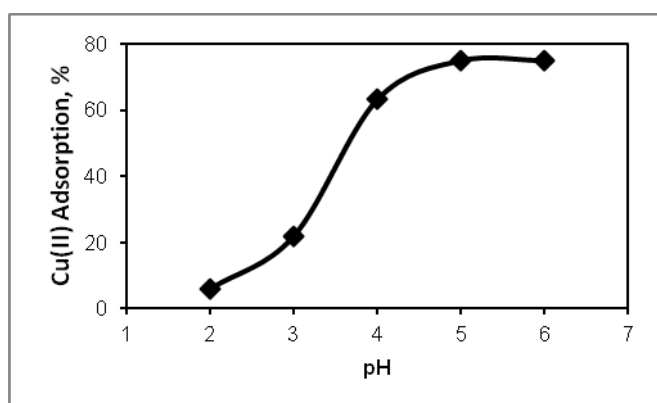


Figure 1. Effect of solution pH on Cu(II) adsorption by DWTS

KEY WORDS: Adsorption, Treatment sludge, Copper(II), Flame Atomic Absorption Spectrophotometry (FAAS)

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**Using the Method of Experimental Design in the Determining Rate
Biosorption of Cr(III)**

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The adsorption capacity of trivalent chromium (Cr(III)) by activated sludge was studied at room temperature. The optimum conditions for the biosorption of this element are determined: contact time 30 min, pH of the suspension equal to 4. The adsorption rate observed 25.66 mg/g.

On the basis of data from the biosorption of chromium, we conducted a modeling study to the variation of adsorption of Cr (III) by activated sludge as a function of contact time and pH of the medium using the method of design of experiments. The explicit mathematical model is adequate for our study area. Indeed, for eight (8) experiments performed, the study showed that the factors have significant influence on the variation of the amount adsorbed. Also, we made a comparison between the model and experimental design model of least squares.

The experimental design allows us to obtain effective information and proper mathematical model representing our results in function of the parameters studied in a given field of study and, as soon as possible, at lower cost and with less testing practices.

KEYWORDS: biosorption, modelisation, experimental design, Cr(III)

Determination of Some Heavy Metals in Four Medicinal Plants

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This study was carried out to identify the levels of heavy metals: Zn, Cu, Fe, Pb, Cd and Cr in the following medicine plants: *Rosmarinus officinalis*, *Thymus vulgaris*, *Mentha varidies* and *Matricaria chamomilla* which are used widely in Libyan society as hot drink and for treatment of some diseases. The samples were collected from Misurata supermarkets. They are prepared to be analysed by heating to boiling in bi-distilled water. The levels of heavy metals were determined by atomic absorption spectrometry. The levels of Pb, Cd, Cu, Zn, Fe and Cr were 0.13 - 0.76, 0.25 - 0.59, 0.28 - 1.85, 3.78 - 11.30, 2.09 - 6.83 and from less than instrument sensitivity to 1.73 ($\mu\text{g/g}$), respectively. According to the present data, the daily doses for lead and cadmium which may be going to human body with a mass of 50 kg by taking the drink prepared by boiling of 10 g medicine plants in water were calculated.

Investigation of Antioxidant Capacity of *Elaeagnus angustifolia* L. by Using CUPRAC and DPPH Methods

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Free radicals are defined as unstable and very reactive molecules that consist unpaired electron [1]. Excessive production of free radicals in human tissue cause oxidative stress, which can damage lipids, proteins, enzymes, carbohydrates and DNA [2]. Several epidemiological studies suggest that a high intake of foods rich in natural antioxidants increases the antioxidant capacity of the plasma and reduces the risk of oxidative stress related diseases [3].

In the present study, antioxidant capacities of leaf, peel, mesocarp and seed parts of oleaster (*Elaeagnus angustifolia* L.) were valuated by using cupric reducing antioxidant capacity (CUPRAC) and 1,1-diphenyl-2-picrylhydrazyl radical scavenging capacity (DPPH) assays. Moreover, each part of oleaster was separately extracted with ethanol/water (1:1,v/v) and methanol/water (1:1,v/v) in order to compare contribution of extraction solvent to antioxidant capacity methods.

KEYWORDS: *Elaeagnus angustifolia* L., oleaster, antioxidant capacity

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Determination of Arsenic and Zinc Concentration in Some Brands of Tea Sold In Gharian-Libya

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Tea is the most popular beverage in the world. Since tea contains several essential nutrients, drinking of tea is considered beneficial for human health. The presence of heavy metals in trace level in tea has received special attention because they are directly related to health.

A study has been carried out on the determination of Arsenic (As) and Zinc (Zn) concentration of some tea brands sold in the area of Gharian-Libya. In this study As and Zn were analyzed by Atomic Absorption spectrophotometer (AAS). The results of analysis showed that the level of As was from 0,0150 mg/Kg to 0,0800 mg/Kg and of Zn was from 13 mg/Kg to 29 mg/Kg. The results are under the level of the limits of the national center for standardisation.

KEYWORDS: Tea, arsenic, zinc

Effect of Silane Treatment on the Structural, Thermal and Morphological Properties of Short *Spartium Junceum* Fibers Reinforced Polypropylene

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The use of vegetable fiber reinforced polymer composites is an important branch in the field of composite materials [1]. Vegetables fibers like jute, flax, hemp coir, and sisal have been proved to be good reinforcement in thermoset and thermoplastic matrices and being used in automotive applications, construction as well as packaging industries with few drawbacks [2]. Vegetables fibers have many advantages as they are biodegradable, renewable and environmentally friendly. However, the main disadvantage of natural fibers is their hydrophilic nature that lowers the compatibility with hydrophobic polymeric matrices during composite fabrication [3].

To address the weak interfacial bonding between natural fibers and a polymer matrix, a number of flour surface modification techniques have been developed. These surface treatment agents include silane, sodium hydroxide, isocyanate, permanganate, maleic anhydride and peroxide [4].

The aim of this work is to elaboration and characterizes composites with *Spartium junceum* fibers. So, the surface of SJ fibers is treated with silane (Z-6020) at 3, 4 and 5 wt % of the fibers content. The treated *Spartium junceum* fibers were subsequently used to fill polypropylene. Thermal analyses by DSC, ATG, structural by XRD and morphological by SEM were used to characterize these composites. DSC measurements showed that the incorporation of *Spartium junceum* fibers to the polypropylene matrix increases the crystallinity of polypropylene. From ATG analysis, it can be concluded that the decomposition temperature and the temperature at the maximum degradation rate increase with increasing fibers content. The polypropylene filled with modified *Spartium junceum* fibers has a more homogenous surface compared to polypropylene-untreated SJ fibers composites.

KEYWORDS: composites, vegetable fibers, surface treatment, thermal analysis.

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Properties of Poly(Vinyl Chloride)/Spartium Junceum Fibers Composites

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Natural fibers/polymer composites, defined as polymer matrix reinforced with wood or other natural fibres, are principally produced from commodity thermoplastics. Due to the advantages of low cost, good mechanical and thermal properties, low density, water resistance, availability of renewable natural resources and biodegradability, natural fibres/polymer composites are widely used in various purposes such as construction materials, decorative parts, aerospace components, and vehicles' compartments [1,2].

Polyvinyl chloride is a versatile thermoplastic which has a range of applications in domestic as well as industrial uses by virtue of its high abrasion and solvent resistance. However, the cost of the products based on PVC can be significantly reduced if weight reducing filler (or plasticised PVC) can be used which will make the composite lighter and will not be detrimental to the mechanical or physical properties of base polymer. In view of its versatility, this polymer was chosen as the base polymer matrix for the present study for developing composites [3].

The objective of the present work is to fabricate composites from raw and chemically treated Spartium junceum fibers and Polyvinyl chloride (PVC/SJ) and subsequently investigate the effects of chemical treatment on the mechanical properties of the composites. The Spartium junceum fibers were modified with sodium hydroxide (NaOH) solution and a coupling agent vinyltrimethoxysilane. The Spartium junceum fibers amounts used were 10, 20, 30 and 40%.

KEYWORDS: composites, naturel fibers, surface treatment, mechanical properties.

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Determination of Cu, Fe, Mn and Zn Contents after Heat Treatment in Some Vegetables Grown in the Middle Black Sea

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The micronutrients copper (Cu), iron (Fe), manganese (Mn) and zinc (Zn) are not only constitutive elements with specific functions in plant growth, photosynthesis and respiration [1]. At the same time, these elements are essential for living organisms at low concentrations. However, the high concentrations of even the essential are toxic and cause various metabolic abnormalities [2].

One of the routes of entry of metals into the living organisms is through foodstuff. Vegetables naturally contain the necessary metals for our body but at the same time they may contain highly toxic heavy metals which can be carried in various ways from such as soil, air and water, those contaminated during industrial processing [2,3].

In this study, the determination of Cu, Fe, Mn and Zn contents after heat treatment of spinach (*Spinacia oleracea*), leek (*Allium porrum*), lady's finger (*Phaseolus vulgaris*), lamb's-quarters (*Chenopodium album*) and mad parsley (*Oenanthe pimpinelloides* L.) grown in Samsun, in the Middle Black Sea region was aimed. In this way, it has been aimed to contribute to the subject of whether the boiled liquors of the vegetables and fruits are to be shed or not which is confusing for people.

The concentrations of Cu, Fe, Mn and Zn were determined by flame atomic absorption spectrometer (FAAS) after digestion by wet-ashing method.

When compared with the values in chemistry literature it was found that plants except for leek have great deal of metal. Being shed of the plants depends on the kinds of fruits or vegetables. Especially pot liquors of mad parsley, lady's finger and lamb's-quarters must be shed. On the other hand, boiled pot liquor of spinach and leek can be consumed without being shed.

KEYWORDS: Samsun, micronutrients , vegetables, FAAS

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Fluoride Content of Turkish Tea Samples

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Fluoride is a necessary element to human health. Fluoride intake reduces dental caries among children and adult, however, excessive intake of fluoride increases the risk of dental fluorosis and can lead to potentially skeletal fluorosis. Thus, the fluoride content of food and drinks gets attention.

The purpose of this study is to determine the fluoride content of various Turkish tea samples using fluoride ion selective electrode. Fluoride concentrations were determined in twelve commercial tea brands including black tea, green tea and herbal tea samples. Tea bags were brewed in hot water for 5 minutes as advised on their labels. The level of dissolved fluoride in infusions showed variety according to tea types. Fluoride concentration ranges were found as; 0.487-2.22 mg/L for black teas, 1.09-1.99 mg/L for green teas, and 0.0060-0.011 mg/L for herbal teas, respectively. The fluoride concentrations obtained from measurements were compared with the permissible values given by the World Health Organization. Intake of fluoride can be beneficial or deleterious depending on the daily amount for mankind. Currently, the recommended upper limit of fluoride in drinking water is 2.0 mg/L. Since drinking water is not fluoridated in Turkey, black tea infusion is a good fluoride source for people; however excessive black tea consumption should be balanced with herbal teas especially for children.

KEYWORDS: Fluoride, ion selective electrode, tea.

Beneficial Effect of Popular Tea Samples Such as Black-Green-Rosemary-Sage in Terms of Their Antioxidant Profile

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Tea is the most popular beverage that is widely consumed all over the world. Due to the significant increase of tea consumption, tea quality and content have taken great attention concerning human health. Recent research shows that regular tea consumption is associated with reducing cardiovascular disease, certain types of cancer and also insulin sensitivity. It is known that all health effects of tea come from its antioxidant profile of phenolic components. Nowadays in addition to black and green tea, some herbal teas such as rosemary and sage are becoming popular. In the present study, a total of 14 tea infusions were performed. Four Black (B1-B4) and two green (G1 and G2) tea-bag samples were obtained from local markets as known commercial brands. The B1 sample consists of teas from the East Black Sea region of Turkey. The others are tea blends. According to labels, B2 is a blend of Kenyan and Sri Lankan teas. B3 is a blend of Turkish, Kenyan, and Indonesian teas. B4 is a blend of Turkish, Sri Lankan, Kenyan, and Indian teas. Two Sage (S1 and S2) and two Rosemary (R1 and R2) dry herb samples were purchased from local markets as known commercial brands. Two Sage (S3 and S4) and two Rosemary (R3 and R5) dry herb samples were obtained from Boston-USA markets as known commercial brands. This study reports the antioxidant activities and total phenolic contents of the tea infusions. Antioxidant activities of samples were determined by ferric reducing/antioxidant power (FRAP). Total phenolic (TPs) contents were determined by using Folin-Ciocalteu reagent as Gallic acid equivalent. The FRAP values of the tested black and green teas ranged between 449.2-601.4 $\mu\text{mol Fe}^{2+}/\text{g}$, compared with 63.80-81.86 $\mu\text{mol Fe}^{2+}/\text{g}$ for herbal (sage and rosemary) tea infusions. The TPs values also ranged between 113.6-67.61 mg GAE/g for black and green tea. Data between 4.91-17.16 mg GAE/g were calculated for herbal tea infusions. There was a significant linear correlation between TPs and FRAP values (0.985) of all tested tea infusions, as expected.

KEYWORDS: Tea , FRAP, total phenolics, antioxidant

Characterization of Fatty Acids, Essential Oils and *In vivo* Emitted Volatiles from Tunisian *Rosa canina* L. Leaves

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Rosa canina L. is an ornamental plant, belonging to the subgenus of *Rosa*, Section Caninae and the family of Rosaceae [1]. This plant grows naturally along hedges, in thickets and over wastelands. It is well represented in Mediterranean areas and temperate regions of Asia and North Africa [2]. *Rosa canina* is known by its medicinal properties. It is traditionally used as an antidiarrheal and in cases of asthenia and urolithiasis. Each part of this plant includes different bioactive compounds and present one or more biological activities (anti-inflammatory, antioxidant power...) [3]. The floral fragrance of *R. canina* is used for cosmetic and aromatherapy purposes [4].

The aim of this work is to establish a quantitative and qualitative description of fatty acid composition of *Rosa canina* leaves. We have also to study the essential oil composition and the volatiles spontaneously emitted *in vivo* by leaves and collected by solid phase micro-extraction (SPME). These extracts are analyzed by GC-FID and GC-MS systems.

Twenty fatty acids were identified and the unsaturated oleic acid was reported as the major constituent (40.24%), followed by the two saturated lignoceric (35.18%) and Behenic acids (18.04%). For the volatile fractions, chromatographic analysis showed that the essential oils of *Rosa canina* leaves are dominated by the oxygenated monoterpene linalool (16.5%), followed by α -terpineol (9.57%). We found also some other compounds as geraniol, linal, 6,10,14-trimethyl-2-pentadecanone...

The study of *in vivo* emitted volatiles showed that *Rosa canina* leaves produce frequently the Z-3-hexenol acetate (33.19%) and myristic acid (12.66%). Chromatographic profile describes also the presence of different volatile compounds with different proportions (α -bisabolol oxide, isophytol, cis-methylidihydrojasmonate...)

Rosa canina leaves could be considered as a potential source of nutritional and functional components.

KEYWORDS: *Rosa canina*, Tunisia, Fatty Acids, SPME, Essential Oils

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Determination of Catechin In Differently Brewed Tea

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The black tea trades in Europe, including Turkey, become widespread during the 17th and 18th centuries [1]. Today, tea is the most commonly consumed tein-containing beverage in the World after drinking water. Tea plant belongs to the family *Theaceae* from the genus *Camellia*[2]. There are three botanically described varieties of *Camelliasinensis*. The first of these is grown mainly in China and Japan, the second is the Assam variety grown in tropical climate (Sri Lanka, India, Bangladesh, Indonesia) and the last variety is the Irrawadiensis [3].

Tea is one of the major polyphenols (falavan-3-ol and flavonol) sources for human nutrition. The oxidation of falavan-3-ol has led to the formation of teaflavin and tearubijin which are important in the formation of the characteristic color and flavor of fermented black tea. The most reliable biochemical methods are based on assays of polyphenol oxidase activity and the catechin content of tea leaves [2]. It is a well known fact that tea catechins have many health benefits such as prevention of cancers, cardiovascular diseases, microbial diseases, diabetes and obesity [4].

In this study, different brands of common black-Ceylon tea were purchased from the market. Tea samples were brewed using different techniques and changing the brew-time. After brewing, the samples were cooled and filtered. Tein in the samples was extracted with concentrated chloroform by means of a separator funnel. Then, the liquid phases were treated with ethyl acetate to extract catechins. Catechins in the extracts were determined by high performance liquid chromatography.

KEYWORDS: Ceylon tea, phenolic components, HPLC

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Response Surface Optimized Ultrasonic Extraction of Antioxidant Compounds from *Pyracantha coccinea*

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The phenolic compounds have been shown to have anticarcinogenic, antimicrobial, antiviral, antimutagenic and antioxidant properties. This diverse range of biological properties makes phenolic compounds an interesting target for optimising extraction from natural source. The extractions such as heating, boiling, or reflux can be used to extract phenolic compounds. New techniques have been developed for the extraction of target compounds from different materials including ultrasound-assisted extraction [1]. This extraction is an inexpensive, simple and efficient alternative to conventional extraction techniques [2]. Because of difference in antioxidant compounds with respect to polarity, acidity, number of hydroxyl groups and aromatic rings, concentration, and matrix complexity, specific extractions techniques must be designed and optimised for target antioxidant compound [3].

The ultrasonic-assisted extraction of *Pyracantha coccinea* was optimized using the Box–Behnken design (BBD) combined with response surface methodology. The BBD was employed to evaluate the effects of extraction time (50–150 min), ethanol concentration (20–80%, v/v), HCl concentration (0.5–1.5 M) and liquid/solid ratio (8–16 mL/g plant) on the antioxidant capacity. The optimum conditions were determined as extraction time 107 min, ethanol concentration 54% (v/v), HCl concentration 1.46 M and liquid/solid ratio 15.6 mL/g plant. The extraction conditions of antioxidant compounds optimized with regard to the antioxidant capacity. The antioxidant capacity of *Pyracantha coccinea* extracts was determined by ABTS method. The predicted antioxidant capacity was 16.24 mg trolox/g dried plant under the optimal conditions and the subsequent verification experiment with 16.85 mg trolox/g dried plant confirmed the validity of the predicted model. The experimental value agreed with the predicted value by BBD, thus indicating suitability of the model employed and the success of response surface methodology in optimizing the extraction conditions.

KEYWORDS: *Pyracantha coccinea*, response surface analysis, antioxidant, BBD

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Isolation of Phenolic Compounds from *Prunella* L. Extracts and Investigation of Their Anticarcinogenic Properties

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The phenolic compounds have been shown to have anticarcinogenic, antimicrobial, antiviral, antimutagenic and antioxidant properties. *Prunella* L. species (*Prunella vulgaris* L., *Prunella laciniata* L., *Prunella grandiflora* L. and *Prunella orientalis* Bornm.) have been used in Western and Chinese herbal medicine that possesses antioxidant properties. *Prunella* L. species have a broad chemical composition, consisting of bioactive molecules as phenolic acids, flavonoids and anthocyanidins [1,2]. *Prunella* L. species have exhibited anti growth effect on different cancer types [3].

The bioactive methanolic fraction of four *Prunella* L. species (*Prunella vulgaris* L., *Prunella laciniata* L., *Prunella grandiflora* L. and *Prunella orientalis* Bornm.) was separated using Sephadex LH-20 column chromatography. Methanolic fractions were measured by spectrophotometry at 280 nm. Based on the absorbance data, fractions were pooled to obtain three fractions for *Prunella vulgaris* L., *Prunella laciniata* (L.) L., *Prunella grandiflora* L., and four fractions for *Prunella orientalis* Bornm. which exhibited antioxidant property. Total phenolic content and antioxidant activity of each fraction were determined with Folin-Ciocalteu and ABTS method, respectively. Phenolic compounds were determined in four methanolic extracts of *Prunella* L. species as rutin, rosmarinic acid and caffeic acid. The amounts of phenolic compounds of extracts and fractions determined by HPLC-DAD. The results show that the phenolic compounds were isolated from *Prunella* L. species with high phenolic contents ranged from 74% (*Prunella grandiflora* L.) to 99% (*Prunella orientalis* Bornm.).

Anti-growth effect of the *Prunella* L. extract was assessed by the MTT and ATP viability assays. MCF-7 and MDA-MB-231 cells were treated for 48 h with increasing doses of *Prunella* L. extracts and then IC₅₀ values were calculated. , the *Prunella* L. extracts significantly inhibited the growth of the MCF-7 cells in a dose-dependent manner (p<0.05). In MDA-MB-231 cells, the *Prunella* L. extracts significantly reduced the viability levels at relatively higher doses (p<0.05). *Prunella* L. extracts reduced the ATP levels in MCF-7 and MDA-MB 231 cells in a dose-dependent manner. The anti-growth effect of *Prunella* L. extracts were related to high content of rosmarinic acid in the *Prunella* L. extracts. The anti-growth effect of *Prunella* L. species were investigated on MCF-7 and MDA-MB 231 human breast cancer cell lines and the results indicated that *Prunella* L. species had anti-growth effect.

KEYWORDS: *Prunella* L., isolation, anti-growth effect, antioxidant

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Isolation of Phenolic Compounds from Black Mulberry (*Morus Nigra* L.) by Column Chromatography

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Tropical and subtropical fruit species, mulberry (*Morus* spp.) is involved in the genus *Morus*, the tribe *Moraceae* tribe, and the family *Moraceae*. East, West and South East Asia, South Europe, South of North America, Northwest of South America and some parts of Africa are areas of distribution of this species. The most commonly grown species in the *Morus* genus are white mulberry, black mulberry, and red mulberry [1].

Types of consumption of this fruit vary from fresh fruit, molasses, dried fruit, and fruit juice to alcoholic beverages. Black mulberry (*Morus nigra*) is a delicious fruit with a sugary-sour taste and refreshing flavor due to its aroma components and sugar/acid ratio [2].

Recent studies revealed that black mulberry has essential effects in human diet and health with the help of its compounds such as organic acids, phenolics, and sugar contents [1]. Positive effects of fruits on health are supposed to originate mainly from their antioxidant compounds. Antioxidant properties of black mulberry are generally attributed to their phenolic compounds, especially anthocyanins. Anthocyanins are becoming increasingly important not only as food colorants, but also as antioxidants. Anthocyanins are reported to have some therapeutic benefits including vasoprotective and antiinflammatory properties, anticancer and chemoprotective properties, as well as antineoplastic properties [3]. Major anthocyanins detected in the black mulberry are cyanidine-3-glucoside and cyanidine-3-rutinoside, which are reported to have an inhibitory effect on the lung cancer cells, pelargonidin-3-glucoside and pelargonidin-3- rutinoside [4,5].

In this study, phenolic compounds from black mulberry juice were isolated using Sephadex LH-20 column chromatography (10x400 mm) and methanol as eluent. The methanolic fractions (3 mL/tube) were measured by UV-visible spectrophotometer at 280, 360, 530 nm. Based on the absorbance data, fractions were pooled for black mulberry which exhibited antioxidant property. These fractions were analyzed and phenolic compounds were determined by HPLC-DAD. Total phenol content and antioxidant capacity of each fraction were determined with Folin–Ciocalteu and ABTS method, respectively. The results showed that the black mulberry juice has significant antioxidant property and rich in anthocyanins.

KEYWORDS: Black mulberry, anthocyanin, isolation, column chromatography, HPLC-DAD,

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Antioxidant Effects of Resveratrol, Carvacrol and Ellagic Acid Against Fenton Reaction

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Resveratrol (3,4',5-Trihydroxy-*trans*-stilbene) is a naturally occurring antioxidant present in grapes and other plants. In addition, resveratrol has been shown to possess cancer chemopreventive activity. Therefore, the past few years have witnessed intense research devoted to the biological activity, especially the antioxidative activity, of this compound, since free-radical-induced peroxidation of membrane lipids and oxidative damage of DNA are considered to be associated with a wide variety of chronic health problems, such as cancer, atherosclerosis and ageing [1]. Carvacrol (5-Isopropyl-2-methylphenol), the predominant monoterpene phenol which occurs in many essential oils of the family Labiatae including *Origanum*, *Thymbra*, *Thymus* and *Corydanthus* species used through the ages as a source of flavour in food. Substantial antioxidant, antibacterial, antifungal and insecticidal effects of carvacrol on different organisms have been described in several studies [2]. Ellagic acid (4,4',5,5',6,6'-hexahydroxydiphenic acid 2,6,2,6'-dilactone) is a natural compound that is very abundant in vegetables in the form of ellagitannins. It shows high antioxidant activity; probably because of the greater number of hydroxyl groups in its structure capable of sequestering and neutralizing free radicals. Several applications have been found for this acid in the pharmaceutical, chemical, and food industries. Antioxidant, chemopreventive, antiviral, or anticarcinogenic activities have been attributed to ellagitannins [3]. Free radicals and other reactive oxygen and nitrogen species (ROS and RNS) are generated by all aerobic cells and are known to participate in a wide variety of biological and biochemical processes. H_2O_2 is a major ROS in living organisms, and its homeostasis can have diverse physiological and pathological consequences. In addition, H_2O_2 and Fe (II) can produce reactive $\bullet OH$ radicals by the Fenton reaction. H_2O_2 and other ROS oxidants are connected to aging and severe human diseases such as cancer, cardiovascular disorders, and Alzheimer's, and related neurodegenerative diseases. Endogenously produced ROS and RNS are essential to life, being involved in many different biological functions. However, when overproduced, or when the levels of antioxidants become severely depleted, these reactive species become highly harmful, causing oxidative stress through the oxidation of biomolecules. The very important fact is that Fenton chemistry plays a crucial role in both physiological and pathological processes in living organisms [4].

In the present study, antioxidant effects of resveratrol, carvacrol and ellagic acid were investigated against the Fenton reaction. H_2O_2 and Fe (II) were added to each antioxidant solution. Oxidation of each antioxidant was monitored at time period by UV-visible spectrophotometer until the stabilization of reaction. Oxidative products and intact antioxidants were determined by HPLC-DAD. While resveratrol and ellagic acid oxidize to quinone intermediates, carvacrol also produces another antioxidant compound of thymoquinone. The results showed that the food antioxidants such as resveratrol, carvacrol and ellagic acid are effective as the free radical scavenger for a potential Fenton reaction at biological fluid level.

KEYWORDS: Fenton reaction, antioxidant, resveratrol, carvacrol, ellagic acid

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Pine and Tannins

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The purpose of this work is to study the effect of some parameters on batch extraction of tannins from bark of Aleppo pine (*Pinus Halepensis* Mill). An optimization study was conducted by the methods of factorial design of experiments and response surfaces. Total phenol was measured by the Folin-Ciocalteu [1] procedure (UV&VIS) to monitor the efficiency of the extraction under different experimental conditions.

KEYWORDS: tannins, pine, extraction, analysis, optimization.

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Determination of Essential Oils Constituents from *Caryopteris Incana* by Retention Time Locking Gas Chromatography Flame Ionization Detector and Retention Time Locking Gas Chromatography Mass Spectrometry.

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The exploration of traditional knowledge for cure to common diseases is attractive since antiquity. The medicinal plants are responsible for the most of the medicine and food used in modern society. It is estimated that an amount of 20,000 species from several families are useful for these purposes [1]. Pharmacology, pharmaceutical botany, medical and clinical microbiology, phytopathology, and food preservation are some fields in which the essential oils can be applied. The pharmaceutical properties of aromatic plants are partially attributed to essential oils [2]. Analysis of essential oils composition can be challenging because flavor and fragrance are usually complex mixtures that may contain many constituents that could include terpenes, diterpenes, sesquiterpenoids, etc. Common techniques used to analyze these types of samples are gas chromatography (GC) coupled to either flame ionization detector (FID) or mass spectrometer (MS). GC/MS is widely used to separate and tentatively identify flavor constituents. The identity obtained with the mass spectrometer for the flavor components is considered tentative. Identification of flavor components with an MS detector is difficult because usually they are mixtures of compounds with similar mass fragmentation. Since isomers give similar spectra, retention indices are commonly used to complement the information obtained with the MS. There are published libraries with retention indices for flavor and fragrances, but these libraries depend on the column type, linear velocity of the carrier gas, oven profile, etc. Due to the dependence of these experimental conditions, the retention indices can be difficult to reproduce. A technique known as retention-time-locking (RTL) can compensate for the disadvantages mentioned before of using GC/FID or GC/MS [3]. The aim of the present study was to investigate chemical composition of the essential oils from the herb, roots and shoots of *Caryopteris incana*. Simple and rapid methodology based on gas chromatography with flame ionization detector (GC-FID) and mass spectrometry (GC-MS) using Retention Time Locking method has been developed. In this study, an RTL flavor databases created by Agilent research group [4] and by research authors was used to analyze different essential oils extracts. GC-MS analyses were performed on an Agilent 5975 gas chromatograph equipped with a split/splitless inlet. Separation was done on a 30 m x 0.25 mm x 0.25 µm DB-5MS column. The inlet pressure was adjusted at 7.29 psi to lock a retention time at 27.500 min for n-pentadecane. GC-FID analyses were performed on an Agilent 7890A gas chromatograph equipped with a split/splitless inlet. Separation was done on a 60 m x 0.25 mm x 1 µm DB-5MS column (Agilent part number 122-5563). The inlet pressure was adjusted to give a retention time of 70.000 min for n-pentadecane which was set up at 38.032 psi. The analytical conditions in this GC-FID method are typical conditions used in quality control of essential oils. The column choice and the slow temperature program offer high resolution and a detailed sample profiling. The column also offers high sample capacity, which is also important in essential oil profiling, because important trace constituents can be present and elute close to major constituents.

KEYWORDS: essential oils, biological matrices, retention time locking, *Caryopteris incana*, flavors, gas chromatography, mass spectrometry, flame ionization detector

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Antioxidative Responses to Lead Phytotoxicity on Germination and Seedlings Growth of Strong Wheat *Triticum durum* Desf

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Two Cvs. Gta and Vitron of durum wheat (*Triticum durum* Desf.), were grown in six lead (Pb) concentration levels (T_0 , 10^{-3} M, 1/750M, 1/500M, 1/250M, 10^{-2} M) in germination assay to analyze the antioxidant enzyme system in the leaves.

The obtained results showed that change in activity occurred at lower Pb concentration in solution leading to lower threshold values of Pb contents in plants. In fact, there was a significant decrease in guaiacol peroxidase (GPX) and glutathione sulfotransferase (GST) for the two varieties. However, there was a significant increase in the peroxidase (POD) activities for the two wheat cultivars subjected to concentrations of Pb ($0-10^{-2}$ M). In General, the application of increasing doses of lead induced an oxidative stress response in wheat seedlings characterized by an increase in the ascorbate peroxidase (APX) activity and a decrease in the catalase (CAT) activities in the first cultivar Gta. In the contrast, for the second cultivar Vitron, the opposite phenomenon was observed a decrease in the activity of APX and an increase in CAT activity.

KEYWORDS: germination- lead- enzyme activity- antioxidative response

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Desorption of Copper from Lewatit Loaded with Copper Ions

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Adsorption and ion exchange methods are frequently applied to dispel the metal ions from the arising effluents after various industrial processes. In these methods, the metal ions in solution are removed by using insoluble solid matters in aqueous medium, like activated carbon and ion exchange resins. Adsorption of heavy metal ions by ion exchange resins from the resulting wastewaters after various industrial processes has been a popular research area in recent years. In ion exchange process, metal ions in solution are adsorbed by chelating or ion-exchange resins, which have high adsorption capacities, selectivity and durability [1-3].

A desorption process after adsorption is important to gain the removed metal ions and to reutilize the resin after recycling [2, 4]. Thus, desorption of copper from a cation-exchange resin loaded with copper ions was investigated in this study. Lewatit S 108, which is a strongly acidic, gel-type cation exchange resin in the Na-form with beads of monodisperse based on a styrene-divinylbenzene copolymer, was used for the adsorption of copper ions from aqueous solution [5]. After adsorption, the resin loaded with copper ions was utilized in desorption process.

Adsorption test before desorption process was performed as follow: After 50 mL of Cu²⁺ solution with a concentration of 0.005 mol/L prepared by dissolving CuSO₄.5H₂O in distilled water was poured into 100 mL conical flask placed on magnetic stirrer, 0.3 g of resin was added to the solution. While performing adsorption test, the values of the contact time, temperature, pH, and agitation speed of solution were 60 min, room temperature (23±1 °C), natural pH, and 250 rpm, respectively. The amount of copper adsorbed by resin was calculated by complexometric method from difference between the metal ion concentration in the solution before and after adsorption process. Under the experimental conditions mentioned above, the efficiency of copper adsorption by resin was 99%. The desorption of copper ions from the loaded resin was examined using strong mineral acids, including H₂SO₄, HCl, and HNO₃. After the loaded resin obtained was washed by distilled water, desorption of copper (II) ions was performed by mixing the loaded resin and strong acid eluent solutions into 100 mL conical flask placed on magnetic stirrer. During desorption, the temperature and stirring speed of solution were 23±1 °C and 350 rpm, respectively. The effects of acid type, acid concentration, and time on desorption process were investigated. The amount of the desorbed copper ions was calculated complexometrically from difference between the copper amount in loaded resin and the copper amount passing into stripping solution. It was determined that the percentage of the desorbed copper increased with an increase in concentrations of acids, and time. It was found that sulfuric acid solution was quite effective for desorption of copper ions from the loaded cation exchange resin. Depending on the experimental conditions, it was determined that almost all of copper ions were removed from the loaded resin.

KEYWORDS: copper, ion-exchange, resin, Lewatit, desorption

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Copper Removal from Aqueous Solution by Lewatit

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The resulting effluents at the end of many industrial processes can contain various heavy metals. The wastewaters discharged directly into environment without applying any purification or separation process can cause serious damages on the environment and human health due to their metal contents. Therefore, heavy metals in industrial wastewaters should be disposed by using appropriate separation method(s), or they must be reduced to allowable levels. Several treatment methods have been developed to eliminate heavy metals ions from wastewaters because they cannot be destroyed chemically like organic pollutants. For the recovery or removal of metal ions from aqueous solutions, many techniques, like chemical precipitation, ultra-filtration, reverse osmosis, electro-deposition, solvent extraction, filtration, ion exchange, cementation, and adsorption, can be applied [1-3]. When they are compared with each other, each of these methods can be some advantages and disadvantages. Thus, the most effective technique or techniques must be applied to remove heavy metals from aqueous solutions.

Among the methods mentioned above, ion-exchange process is one of the most widely used methods for the removal of metal ions from an aqueous solution. In this method, metal ions in solution are adsorbed by chelating or ion-exchange resins, which have high adsorption capacities, selectivity and durability [4]. In the present study, Lewatit S 108 resin was used for the removal of copper from aqueous solution. This resin is a strongly acidic, gel-type cation exchange resin in the Na-form with beads of monodisperse based on a styrene-divinylbenzene copolymer [5]. This type of resin can be used for the elimination or separation of heavy metals from the resulting wastewaters after various industrial processes.

The solutions containing Cu^{2+} ions were prepared by dissolving weighed quantities of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ in distilled water. The initial pH of sample solutions was adjusted by using diluted H_2SO_4 . All adsorption experiments were carried out at laboratory temperature (23 ± 1 °C). The batch tests were performed in 100 mL conical flasks placed on a magnetic stirrer. In each test, after a volume of 50 mL copper solution at a definite concentration was placed into the glass flask, a given amount of resin was added to the solution. The process was performed for various contact times. At the end of each contact time, the contents of the flask was filtered by using filter paper, and the amount of copper ions in the solution was determined complexometrically by using Titriplex III solution (0.01 N) as titrant and murexide as indicator. The amount of copper adsorbed by resin was calculated from difference between the metal ion concentration before and after process. The effects of the initial concentration of copper (II) ions, initial pH of solution, resin dosage, and stirring speed on the process were studied. It was determined that the percentage of the adsorbed copper increased with an increase in resin dosage, initial pH and stirring speed, and with a decrease in initial ion concentration. It was found that the maximum adsorption occurred at natural initial pH values. Depending on the experimental conditions, it was observed that almost all of copper ions were removed from solution. While the initial solution concentration, initial pH, contact time, stirring speed, and resin dosage were 0.005 mol/L, natural, 60 min, 250 rpm, and 6 g/L, respectively, the efficiency of copper adsorption by resin ore was 99%.

KEYWORDS: copper, ion-exchange, resin, Lewatit

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Determination of Trace Elements of *Prunus avium* L. (Pulp, Bark, Stalk and Glue)

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The basis of medical treatment, which co-exists with human life, presents the plants and substances in the nature. For thousands of years, natural products have played an important role throughout the world in treating and preventing human diseases. People have noticed that some plants are useful in various diseases by the method of trial and error, and throughout the years, implemented a variety of ways, and still applied [1].

Prunus avium L., in the public, with the name of cherry, its human-edible and nonedible organs are used for therapeutic purposes, it is seen in written and oral sources. Cherry in particular has been found to offer a good source of antioxidants and contain compounds believed to aid in pain relief of arthritis, gout and headaches. Cherry has assisted to cut back the potential risk of most cancers, cardiovascular disease. **Keeps heart healthy by lowering the cholesterol level.** Cherry's bark removes constipation and is used as a fever reducer and is diarrhea. Cherry's glue is antitussive and is good for bowel inflammation [1 - 3].

Trace elements such as zinc (Zn), manganese (Mn), iron (Fe) even after making an extremely low amount in the body has many important functions for organism. Also researches have shown that the trace elements' such as selenium (Se), cadmium (Cd), copper (Cu), aluminum (Al) existence at large amounts create toxic effects. A diet regime, which these elements will receive enough, is of great importance for a healthy life [4-6].

As a result of research literature, cherry's parts' -used for therapeutic purposes- trace element content has not been done. The aim of this study, is to determine seven trace elements (Zn, Mn, Al, Cu, Fe, Cd and Se) of cherry's pulp, bark, stalk and glue and determine the amount of daily consumed. 0.5 g of the pulp, bark, stalk and glue samples were transferred into PTFE vessels, one by one. Then 7 mL of concentrated HNO₃ (65%) and 2mL of H₂O₂ were added into the vessels. The vessels were closed, placed on the rotating turntable of the micro-wave oven and the digestion process was started. The digestion was allowed to 500 W and temperature range from 85 to 200 °C and maintained at this condition for 14 min. The digested solutions were diluted to 25mL with deionized water. The microwave digestion method tested by standard reference material (NIST SRM 1515 Apple Leaves). Then Zn, Mn, Al, Cu, Fe, Cd and Se in each samples (pulp, bark, stalk and glue) were analyzed using atomic absorption spectrophotometer (Perkin Elmer A Analyst 800) equipped with flame and graphite furnace. The results obtained for Zn, Mn, Al, Cu and Fe in mg per 100 g dry weight and for Cd and Se in µg per 100g dry weight. The average concentrations of Al, Cu, Fe, Mn, Zn, Cd and Se detected in cherry's pulp, bark, stalk and glue were 4,99±0,47, 0,32±0,012, 0,42±0,0049, 0,061±0,0066, 0,17±0,025, 0,17±0,16, 5,0, and 12,92±5,35, 0,46±0,094, 146±50,99, 3,63±1,88, 2,50±0,51, 4,94±0,78, 17,96±8,87 and 20,61±0,77, 1,61±0,12, 18,80±3,02, 0,93±0,037, 3,46±0,38, 1,67±0,44, 6,82±0,33 and 7,48±1,14, 0,51±0,097, 2,36±1,09, 0,05, 0,56±0,055, 0,13±0,028, and 3,59±0,28, respectively.

KEYWORDS: Trace elements, AAS, Cherry, Microwave digestion

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The Utilization of Revised BCR Sequential Extraction Procedure for the Fractionation of Copper in Asphaltite Combustion Waste (Silopi, Turkey)

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Fuel and combustion waste contain many elements. Asphaltite, originating from petroleum, contains many kinds of mineral matter elements derived from its generation. These elements exist in different forms which may change their forms throughout the asphaltite combustion process. Different veins of asphaltic materials have different physical and chemical characteristics depending on the location of asphaltite, geological formation and degree of metamorphosis. The Silopi reserve was classified as a substance between asphaltite and asphaltic pyrobitumen and the Harbul vein is the major part (approximately 2.5.10⁴ tonnes) of the Silopi asphaltites. It is used in power plant in the production of electrical energy [1]. Asphaltite combustion waste (ACW), the inorganic residue derived from the burning of asphaltite, represents the noncombustible impurities originally present in asphaltite [2]. It is crucial to perform a complete chemical and mineralogical characterization of ACW in order to establish the contamination risk potential of power plants over their surrounding environment and human health, as well as their possible industrial usage [3]. A true understanding of the dynamics of elements in the natural environment requires an expanded knowledge of its oxidation–reduction cycling [4]. Copper (Cu) is a characteristic element associated with airborne particulates originating from the fossil fuel combustion. Although the total concentration of Cu is still useful in many areas, the knowledge of speciation is of primary importance because the toxicity, mobility, bioavailability, and bioaccumulation depend on the chemical species. The advantages of the technique include a high degree of automation, good reproducibility, and short analysis time and thus make it the method of choice for the speciation of Cu. A revised sequential extraction procedure for the fractionation of Cu, proposed by the Commission of the European Communities Bureau of Reference (BCR) has been applied to ACW from Harbul asphaltite vein in Silopi, SE Anatolia, Turkey. Analyses were carried out by inductively coupled plasma optical emission spectrometry (ICP-OES). The 327.393 nm line was used because it offers better detectability and was free from major spectral interferences. The fractions extracted were: exchangeable (extraction step 1), reducible-iron/manganese oxides (extraction step 2), oxidizable-organic matter and sulfides (extraction step 3). The sum of the Cu content in the three fractions plus aqua-regia extractable content of the residue (extraction step 4) was compared to the aqua-regia extractable content of Cu (total copper concentration) in the ACW [5]. The accuracy obtained by comparing the determined content of Cu with certified values, using NCS DC73301 Rock – constituents, certified for the extractable contents of Cu, in ACW following a modified BCR-four step sequential extraction procedure, was found to be satisfactory. Total Cu concentration in the ACW is 104.56 mg kg⁻¹ dry weight (d.w). The most abundant copper fraction in studied ACW sample was found as residual fraction of Cu (57.33%). Relative abundances of the remaining Cu fractions in ACW are as follows: Exchangeable +water and acid soluble (19.24%) > oxidizable (16.73%)> reducible (7.32%). Cu compounds are mainly bound to the oxidizable-organic matter/sulfides and residual fractions (74.06 % of total copper extracted). Revised BCR sequential extraction procedure can also provide useful information for migration assessment in ACW since the amounts of Cu mobilizable under different changes in environmental conditions can be determined [6]. Cu fractionation scheme allows quantitative knowledge of copper distribution in ACW.

KEYWORDS: ICP-OES, copper, sequential extraction, asphaltite, chemical speciation

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Microwave Digestion Followed by ICP-OES for the Simultaneous Determination of Metals in Hazelnut (*Corylus avellana* L.)

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Food is the primary source of essential elements for humans and it is an important source of exposure to toxic elements. In this context, levels of essential and toxic elements must be determined routinely in consumed food products. Hazelnut plays a major role for human nutrition because of its very special nutrient contents such as proteins, carbohydrates, fats, vitamins and minerals. It has a high nutritional value, containing, generally, 65 % oil, 14 % protein, and 16 % carbohydrates. More than 90 % of its oil consists of unsaturated fatty acids, especially oleic (C 18:1, 80 %) and linoleic (C18:2, 12%) acids [1]. Turkey is the world's leading country in hazelnut production and export. High-quality hazelnuts with much economic importance in Turkey are cultivated mainly in the Black Sea Region, which has suitable climate conditions [2]. Based on the importance of hazelnut as a mineral source and on the necessity of understanding its mineral composition, the present work reports the results obtained by the proposed method for the simultaneous determination of metals (Cd, Co, Cr, Cu, Fe, Ni, Pb, Zn) by inductively coupled plasma optical emission spectrometry (ICP-OES) following digestion using diluted oxidant mixture in a closed-vessel microwave oven [3].

In this study, wet acid microwave digestion was used as the sample preparation method. The selected sample preparation procedure involves the task to obtain the best results in the shortest time, with minimum contamination, using the smallest quantities of reagents and samples, and having little residue and waste generation. In addition it is of importance to maintain the integrity of the sample and the traceability of the results, to have quality and confidence in the measurements [4]. The ICP-OES analytical method was applied due to its simplicity and reliability. It also offers a wider linear dynamic range and has multi element detection capability, high selectivity and has low spectral interference problems from other elements. The method was validated through the analysis of an SRM with good recoveries. The analytical ICP-OES technique which has been developed and validated for hazelnut samples proved to be simple, rapid, accurate, and precise for the simultaneous determination of eight essential and non-essential elements [5]. It can also be considered a useful method for the routine analysis of trace elements in foods and possibly similar matrices, and for quality control purposes. The results presented here enlarge the knowledge of the elemental composition of hazelnut (*Corylus avellana* L.) and will be useful and of interest in the toxicological and nutritional fields [6]. The results showed that the concentrations of heavy metal are below the daily intake recommended by the international organizations. This nut is therefore shown to be safe for public consumption.

KEYWORDS: food, MW digestion, metal, ICP-OES

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The Effects of Various Drying Conditions and Total Phenolic Content of Apple Slices

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Apple which is one of the widely produced fruit in Turkey and many new products are obtained with apple processing. Even though drying is a commonly-used and old processing method of agricultural materials but problems and their solutions associated with apple drying are unclear. In addition, the total phenolic content which at the end of drying methods, is obscure.

Many researchers have studied either total phenolic content or drying methods [1-2]. Some researchers worked about the contents of total phenolic compounds of various temperatures [3-4]. Mrad et al. observed that phenol content was significantly influenced by air temperature [5]. Furthermore, Harbourne et al. worked on both total phenolic compounds and drying methods of meadowsweet and willow. Their work shown that for meadowsweet and willow, freeze-drying and oven or tray drying at 30°C had no significant effect on the phenolic constituents or the colour of the extracts in comparison to traditional air-drying. Although increasing the drying temperature to 70°C resulted in an increase in the drying rate of both herbs it also led to the loss of some phenolic compounds [6]. Hereby, the aim of our study was investigated the total phenolic content of each apple slices at the end of drying processes.

In this study, three different drying methods selected which are natural drying under open atmosphere, laboratory oven drying and microwave drying. Firstly, each apple sample was sliced to 5 mm thick and dipped in one of chemical solutions for a certain time period. Afterwards, prepared samples were divided into three equal parts. The first part was dried under open atmosphere in 72 hours. The second part was dried with laboratory oven in 5 hours. And the last part was dried in microwave in 15 minutes. At the end of the drying processes, samples were taken from each of the methods and then total phenolic content of these samples were compared.

KEYWORDS: drying methods, total phenolic content, apple

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Determination of Bioavailability and Bioaccessibility in soil and plant by in Vitro Digestion

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Bioavailability is the fraction of a substance that is released from the soil matrix in the human gastrointestinal tract and is available for absorption [1]. Bioavailability processes are described as the individual physical, chemical, and biological interactions that determine the exposure of plants and animals to chemicals associated with soils [2]. A simpler way of considering bioavailability is to assess bioaccessibility, which is defined as the fraction of an analyte released from its matrix in the gastrointestinal tract, because bioavailability can only be smaller than or equal to bioaccessibility. The bioaccessibility of an element depends not only on the matrix, but also on the chemical form of the analyte and the model used [3]. An *in vitro* digestion model has been improved as a easy, cheap, and reproducible tool to quest the bioaccessibility of soil contaminants [4]. Contaminants can be comparatively or totally released from soil by ingestion, depending upon their speciation under gastrointestinal conditions. In vitro tests obtain guesses of bioaccessibility, which corresponds to the proportion of contaminant that dissolves in the artificial gastrointestinal fluids and is potentially available for absorption [5].

Bioaccessibility intends to the fraction of a contaminant that is released from soil into solution by digestive juices. It indicates the maximum proportion of contaminant that is substantial for intestinal absorption. Only a fraction of these contaminants can be absorbed by the intestinal epithelium and afterwards transported to the liver via the portal vein for biotransformation. The fraction of fundamental compound that arrives the systemic circulation is meaned to as the bioavailable fraction [6].

The main aim of this study was an investigation of the influence of selected soil and plant properties on the bioaccessibility of trace elements and hence, their potential impacts on human health in urban environments. In this study, an artificial environment was prepared which constitutes human digestive systems. Soil and plant samples were taken to these media. Position of the levels of the trace elements was investigated by determining the effect on human health. The artificial environment of the digestive tract was created with saliva, stomach, intestine and bile waters. The body temperature of 37 °C was adjusted based on the environmental temperature. Artificial media was prepared by adjusting digestion times and media pH. Temperature, pH, mixing time, and the solution volumes prepared in ambient conditions, such as bioavailability of soil and plant samples were investigated thereby prepared ambient conditions (such as temperature, pH, mixing time and the solution volumes).

Antioxidant Activities of the Extracts from *Anemone albana* Stev by Different Extraction Techniques

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When it is taken into consideration of Turkey's flora from the point of view of nutrition and medicinal purposed plants, it can be seen that there are myriad species and their applications. One of these species is *Anemone albana* Stev whose base and leaves have been using the treatment of some illness such as headache and sinusitis by the local people of north-eastern provinces of Turkey [1]. No data was found in the literature about total phenolic content and antioxidant activity values of extracts from its grounded leaves by using Soxhlet and Ultrasound Assisted Extraction techniques.

Ultrasound Assisted Extraction Technique is a promising method with superior features, e.g. shortened extraction time and reduction of solvent volume used, upon conventional Soxhlet Extraction Technique in the extraction of bioactive phenolic compounds [2]. In this method, extraction efficiency depend on degradation of vegetal cell walls, reduced particle dimension, and mass transfer phenomena occurred by the effect of cavitation bubbles [3].

Air dried and grounded to pass 125 µm sieve of *A. albana* leaves were subjected to methanolic extraction by using two different extraction techniques, Soxhlet and Ultrasound Assisted Extraction techniques, respectively. Solvents of the extracts were evaporated and extraction yields were calculated. After that, stock solutions were prepared by using the same solvent and kept in 4°C for further analyses. Total phenolic contents of the extracts were determined according to Folin-Ciocalteu's assay [4]. Antioxidant capacities of the extracts were determined by using DPPH (2,2-diphenyl-1-picrylhydrazyl) radical scavenging [5] and CUPRAC (cupric reducing antioxidant capacity) [6] methods.

In the Soxhlet extraction procedure, slightly higher total phenolic content was obtained when compared to that of ultrasound assisted extraction procedure (2.77 and 2.22 mg Gallic Acid Equivalent (GAE)/100 g air dried sample, respectively). In contrast to total phenolic content values, ultrasound assisted extracts showed slightly better antioxidant capacity values in both assays with the IC₅₀ value of 58.0 µg/mL and CUPRAC value of 0.229 mmol TEAC/g dried sample. For Soxhlet extracts, these values were 60.0 µg/mL and 0.172 mmol TEAC/g dried sample, respectively. Although both extraction techniques exhibited similar results, among them, ultrasound assisted extraction technique stood out with the properties of diminishing extraction time and solvent used.

KEYWORDS: *Anemone albana* Stev, Soxhlet Extraction, Ultrasound Assisted Extraction, DPPH assay, CUPRAC assay.

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**The effect of different extraction conditions on the antioxidant properties of
Cranberry (*Cornus mas* L.)**

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A antioxidant has an important role to neutralize the excess of free radicals, to protect the cells against their toxic effects and to contribute to disease prevention [1]. Antioxidants from our diet play an important role in helping endogenous antioxidants for inhibition of the reactive oxygen species [2]. Each nutrient is unique in terms of its structure and anti-oxidant function. Especially fruits, vegetables, and herbs attract great attention due to their high content of bioactive compounds with antioxidant characteristics [3]. Cranberry phenolics include simple phenolic acids, and flavonoid that include anthocyanins, proanthocyanidins (PACs), as well as flavonols [4]. Cranberry phenolics have important positive effects on human health.

In this study, antioxidant properties of different extracts of cranberry (*Cornus mas* L.) obtained from Elazig were investigated. Acidified water, acidified acetone, acidified acetonitrile, acidified methanol and acidified ethanol were used to prepare extracts. The antioxidant profiles of these extracts were determined by ABTS and DPPH radicals scavenging power, reducing power, total phenolic content, total flavonoid content and total anthocyanin content. These results showed that *Cornus mas* L. extracts have high content of total phenolic compounds and free radical scavenging power. In addition to, antioxidant properties of *Cornus mas* L. extracts changed depend on extraction solvent. The results indicated that cranberry is a potential source of natural antioxidant.

KEYWORDS: *Cornus mas* L., Extraction, Antioxidant Activity.

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Antioxidant Properties of Different Extracts of Strawberry (*Fragaria vesca*)

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Antioxidants are molecules which can safely interact with free radicals and terminate the chain reaction before vital molecules are damaged [1]. Antioxidants from fruits and vegetables are considered an important protection factor against oxidative stress and its harmful effects to human health. Strawberries potentially contain bioactive compounds such as flavonoids and phenolic acids. All of these phenolic compounds have been shown to prevent oxidative processes, particularly those caused by reactive oxygen species (ROS). These compounds make strawberries a highly antioxidant fruit with potential health benefits. Among the numerous healthy properties described in the literature are anti proliferative effects on cancer cells and the antioxidant and anti-inflammatory effects that have been shown to reduce cardiovascular disease risk factors in several prospective cohort studies [2].

The aim of this study, antioxidant properties of different extracts of strawberry (*Fragaria vesca*) obtained from Elazig were investigated. Acidified water, acidified acetone, acidified acetonitrile, acidified methanol and acidified ethanol were used to prepare extracts. The antioxidant profiles of these extracts were determined by ABTS and DPPH radicals scavenging power, reducing power, total phenolic content, total flavonoid content and total anthocyanin content. In addition to, antioxidant properties of *Fragaria vesca* extracts changed depend on extraction solvent. The results indicated that strawberry is a potential source of natural antioxidant.

KEYWORDS: Antioxidant Activity, *Fragaria vesca*, Extraction.

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Comparison of Head-Space GC MS and Head-Space Solid-Phase Microextraction Methods of Volatile Constituents and Antimicrobial Activity of Essential Oils of *Salvia staminea* Montbret & Aucherex Bentham

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The volatile components from *Salvia staminea* Montbret & Aucherex Bentham plant growing on natural grasslands in Bayburt, Turkey, selected for the broad qualitative and quantitative diversity of their terpenoid fractions, was analyzed by gas-phase chromatography and mass spectrometry (GC-MS) after the essential oils were obtained by steam distillation in 500 ml dis. water in a Clevenger-type apparatus and headspace and headspace solid-phase microextraction (HS-SPME) were done to comparison the each others. HS-SPME allowed all the plant material to be analyzed under the same conditions even though its wide-ranging composition. This is not always feasible with other extraction methods. Using an apolar poly(dimethylsiloxane) (PDMS) phase, numerous terpenoid hydrocarbons, together with alcohols, cyclic ethers, and esters, were extracted. Its ease of use and the high resolution of the chromatographic profiles obtained make HS-SPME well suited to the rapid characterization of the main components of the volatile fraction of plants. Twenty-six and seventeen and two components were identified and the main component of this taxon was Sclareoloxide, Linalyl Acetate and Isopropyl formate for essential oil, HS-SPME and HS methods, respectively. Linalool and Linalyl Acetate compounds were common to three of each method and in headspace method, essential oil component to form a total of these two compounds is an important finding for this article.

KEYWORDS: Headspace; SPME; GC-MS; PDMS; Linalool; *Salvia staminea* Montbret & Aucherex Bentham.

Chemical Composition of Essential Oil of *Hyssopus officinalis* Cultivated in Greece

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Recently, *Hyssopus officinalis*, a plant of Lamiaceae family commonly known as hyssop, is systematically cultivated to the prefecture of Aetoloakarnania in Greece. Hyssop's essential oil is of great commercial interest. The chemical composition of an essential oil is strongly influenced by environmental factors like temperature, climate, soil and it differs qualitatively and quantitatively among taxa of different geographic origin and between wild and cultivated species [1-3].

In the present work, the chemical composition of the essential oil of *Hyssopus officinalis* cultivated in Greece is described. Hyssop's samples of different developmental stage and of different growers are examined. The oil yield, obtained from leaves and flowers by hydrodistillation, ranged between 2.2 – 2.6%. The Gas Chromatography – Mass Spectrometry (GC-MS) analysis of essential oil allowed to the identification of its chemotype, which is isopinocampone / β -pinene / pinocarvone. Isopinocampone was found as the major compound (65.6 – 44.6%), followed by β -pinene (8.0 – 14.4%) and pinocarvone (3.9 – 11.4%).

Hyssop essential oil from all the samples demonstrated similar qualitative profile, while differences observed to the relative percentages of the compounds among samples provided from different growers. The qualitative characteristics of each soil, but also the cultivation practices between growers by means of more or less irrigation can explain the observed fluctuation to the volatile composition of hyssop samples [4].

KEYWORDS: *Hyssopus officinalis*, essential oil, GC-MS, isopinocampone

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Chemical composition and antimicrobial activity of the essential oils from the flower, leaf, and stem of *Sempervivum brevifolium* Muirhead from Turkey

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The genus *Sempervivum* contains about 50 species which occur predominantly on rocky places, old walls, chimneys and at higher altitudes [1,2]. *Sempervivum* L.(Crassulaceae; common houseleek) represented with 14 species in Turkey [3,4]. Some species as *Sempervivum tectorum* L. and *Sempervivum armenum* Boiss. et Hue are used in Anatolian folk medicines [5,6]. *Sempervivum brevifolium* is an evergreen endemic species and distributed in C. Anatolia. This species is named as "Kader Çiçeği" in Turkish and used as an ornamental plant [3-6]. They occur from Morocco to Iran, through the mountains of Iberia, the Alps, Carpathians, Balkan mountains, Turkey, the Armenian mountains, in the northeastern part of the Sahara Desert, and the Caucasus. Their ability to store water in their thick leaves allows them to live on sunny rocks and stony places in the mountain, subalpine and alpine belts. The name "*Sempervivum*" has its origin in the Latin *Semper* ("always") and *vivus* ("living"). *Sempervivum* are called "always living" because this perennial plant keeps its leaves in winter and is very resistant to difficult conditions of growth.

Previous works on the genus *Sempervivum* L. were especially about the biological activities for the isolate obtained by various extraction techniques [1-2,7-8]. The juice of *S. tectorum* was applied to herpetic eruptions of the skin, minor burns and wounds [2]. And also antinociceptive, liver-protecting, membrane stabilizing effect, antimicrobial, antiinflammatory and in vitro antioxidant properties of *S. tectorum* extracts have described in recent studies [1-2,7-8]. The leaf extract of *Sempervivum marmoreum* L. was investigated and showed anti-oxidant and antimicrobial activities [1]. To date, no previous reports dealing with any investigation of the volatiles of this species growing in Turkey can be found in the literature. The aim of this work was set to perform a detailed compositional analysis of the volatiles isolated from the flowers, leaves and stems of *S. brevifolium*. Furthermore, we also tested the antimicrobial activity of the essential oils against a panel of microorganisms as well as against fungal strains.

The essential oils from the fresh flower, leaf, and stem of *Sempervivum brevifolium* Muirhead. (Crassulaceae) were isolated by hydrodistillation in a modified Clevenger-type apparatus, and characterized by GC-FID and GC-MS. Identification of the substances was made by comparison of mass spectra and retention indices with literature records. A total of fifty, forty-three, and thirty-one compounds were identified, constituting over 92.6%, 92.6%, and 94.3% of oil composition of the flower, leaf, and stem of *S. brevifolium*, respectively. The components of essential oils were classified into five groups which were terpenoids (monoterpene hydrocarbons, oxygenated monoterpenes, sesquiterpene hydrocarbons, oxygenated sesquiterpenes, oxygenated diterpene, terpen related compounds), hydrocarbons, aldehydes, alcohols and others. The chemical profile reveals the dominance of hydrocarbons (flower: 65.3%, leaf: 47.6%, stem: 71.1%). The main compounds of essential oils from *S. brevifolium* were tetracosane (20.2%) in flower, 1,2-diphenyl ethandione (16.1%) in leaf and docosane (30.5%) in stem. Monoterpene hydrocarbons were the major class of terpenoids in flower (2.2%) and in stem (1.8%), oxygenated diterpene was the major class of terpenoids in leaf (4.5%). Oxygenated monoterpenes were in minor amounts in all parts (flower: 0.3%, leaf: 0.7%, stem: 0.1%) of the plant. In addition, antimicrobial activities of the essential oils of *S. brevifolium* were investigated. The oils didn't show any antimicrobial and antifungal activity against tested bacteria, but showed high antituberculostatic activity against *Mycobacterium smegmatis*.

KEYWORDS: Crassulaceae, *Sempervivum brevifolium* Muirhead, essential oil, GC-FID, GC-MS

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Heavy Metal Determinations in Ruderal *Verbascum olympicum* Boiss. Growing Under Cadmium Stress by ICP-MS

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Toxic metal pollution of waters and soils is a major environmental problem. The use of specially selected and engineered metal-accumulating plants for environmental clean-up is an emerging technology called phytoremediation [1].

Verbascum olympicum Boiss. (Scrophulariaceae) is an endemic species of Uludağ (Bursa-Turkey) and it has the capability to remediate heavy metal-contaminated soils by accumulating the metals in different parts [2].

V. olympicum seeds were collected from Uludağ Mountain in August 2011. Cd treatments (0.0, 50.0, 100.0 and 250.0 µM Cd) were applied for 7 days to 8 week-old seedlings in a growth chamber [3]. A triplicate digestion procedure was applied for leaves and roots of the samples. The accuracy of the method was confirmed by the analysis of the certified reference material (NIST 1570a spinach leaves). The detection and quantification limits of Mn, Mo, Zn, Cu, Cd are 0.32, 0.16, 0.42, 0.21, 0.21 mg/kg and 1.06, 0.52, 1.39, 0.69, 0.70 mg/kg, respectively (n=10).

The high concentration of organic matrix in plant samples may give rise to matrix and/or spectral interferences from polyatomic ions. These effects were eliminated or minimized by the use of alternative isotopes and interference correction equations from software.

The accumulation of Cd and variations in the content of some trace elements (Cu, Mo, Mn and Zn) were used for the assessment of Cd stress.

KEYWORDS: *Verbascum olympicum* Boiss., heavy metals, ICP-MS.

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Total Antioxidant Capacities of Methanol and Water Extract of the horse tail (*Equisetum Arvense*) Species Wildly Growing in Kutahya and Trakya

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Equisetum Arvense, commonly known as the Field Horsetail or Common Horsetail, is a rather bushy perennial with a rhizomatous stem formation native to the northern hemisphere. In this study, horse tail (*Equisetum Arvense*) also known as Kırkkilit which is a plant found in large amounts in Turkey was collected from two different areas and was extracted with water and methanol. Dried samples were analyzed with modified CERAC[1], spectrofluorimetric CERAC[2] and CUPRAC[3] methods. The optimization studies were made to compare the total antioxidant capacities (TAC) of Horsetail plants which are collected from different areas in order to get the highest yield. Extraction samples were prepared with three different methods such as boiling, infusion and methanol extraction. Firstly, 2.0 grams of Horsetail plant was extracted in 250 mL water for 1 hour using three different techniques such as hotplate heating with the aid of a magnetic stirrer for an efficient homogenization, shaker, and ultrasonic bath, respectively. The same procedures were repeated for methanol extraction. As a result, the highest yield was observed at hot plate magnetic stirrer. To determine the optimization of heating temperature of water extraction with the modified CERAC method, the extraction solutions were heated at 40, 60, 80, 100 °C and the most appropriate heating temperature was found to be 60 °C. In order to determine the optimized heating time period, the extracts were heated at 5, 10, 20, 40, and 60 minutes and the highest yield was determined at 10 minutes. After 10 minutes the decreasing value of TAC was observed. For the infusion method, 2.0 g of horse tail plant was dipped in 250 mL of boiling distilled water for 3 minutes and after which had been kept 2 minutes. For horse tail plants the highest TAC value was obtained with the plants originating from Trakya with the infusion procedure when compared to the plants from Kutahya.

KEYWORDS: Antioxidant, Total antioxidant capacity, CERAC, Horsetail,

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Fullerene C₆₀ Functionalized γ -Fe₂O₃ Magnetic Nanoparticle: Synthesis, Characterization, Analytical And Biomedical Applications

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Magnetic nanoparticles (MNPs) shows magnetic behaviour while exposed to magnetic fields that they don't retain any magnetism after applied magnetic field is removed have been found an important application area in biotechnology [1]. Metallic, bimetallic, and superparamagnetic iron oxide nanoparticles (SPIONs) are classified as MNPs. Among SPIONs γ -Fe₂O₃ and Fe₃O₄ have been attained special attention due to their biocompatibility, biodegradability, availability, stability and high magnetic susceptibility. They have been widely used for protein adsorption, bacterial detection, protein purification, targeted drug delivery, and cancer diagnosis and therapy, photodynamic therapy, bioanalytical sensor, supporting materials for enzymes etc. SPIONs are sized between 10 and 100 nm and are used for *in vivo* and *in vitro* studies due to size similarities with biological macromolecules, cells and enzymes [2]. MNPs could be converted to biocompatible forms by coating of poly(ethyleneglycol), dextran, chitosan, copolymers, polyethyleneimine, liposomes and micelles for *in vivo* studies. Additionally, it was highlighted that surface coating could also significantly influence the cytotoxicities of SPIONs [4]. Increasing in blood circulation time by decreasing the protein adsorption on SPION could be achieved by surface coating [3].

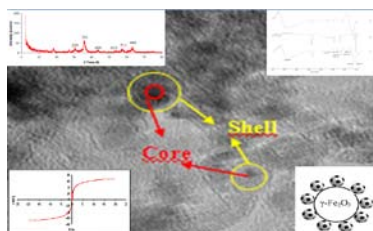


Fig. 1. Representative image of synthesis procedure of γ -Fe₂O₃ magnetic nanoparticle functionalized with fullerene C₆₀

Hybrid magnetic nanoparticles composed from C₆₀ fullerene and γ -Fe₂O₃ were synthesized by hydrothermal method. A representative image of synthesis procedure was given in Fig. 1. X-ray diffraction (XRD), fourier transform infrared spectrometry (FT-IR), vibrating sample magnetometry (VSM), scanning electron microscopy (SEM), high resolution transmittance electron microscopy (HR-TEM) were employed to characterize the C₆₀ conjugated with γ -Fe₂O₃ magnetic nanoparticles. Concentrations of Fe in synthesized magnetic nanoparticle and fullerene C₆₀ were determined by inductively coupled plasma optical emission spectrometry (ICP-OES). The magnetic saturation value of C₆₀- γ -Fe₂O₃ magnetic nanoparticles was found as 66.5 emu/g. Concentration of Fe in nanoparticle was found as 40.7% Fe. Particle size of C₆₀- γ -Fe₂O₃ magnetic nanoparticles was found lower than 10 nm. Maximum adsorption capacity of C₆₀- γ -Fe₂O₃ for flurbiprofen, non-steroidal anti inflammatory drug was calculated from Langmuir isotherm as 142.9 mg/g. No antimicrobial activity for C₆₀- γ -Fe₂O₃ was observed against Gram positive and Gram negative bacteria.

KEYWORDS: Nanobiotechnology; maghemite; fullerene C₆₀; biomedical application; characterization

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γ -Fe₂O₃ Magnetic Nanoparticle Functionalized with Carboxylated Multi Walled Carbon Nanotube: Synthesis, Characterization, Analytical and Biomedical Applications

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Synthesis, characterization, analytical and biomedical applications of magnetic nanoparticles are of growing interest in nanoscience that significant efforts have been devoted to develop nanometer sized products for nanobiotechnology and nanomedicine. Such materials include polymeric nanomaterials, carbon based structures such as fullerene, single walled carbon nanotube (SWCNT) and multi walled carbon nanotube (MWCNT), quantum dots (QD), magnetic nanoparticles (MNPs), all of which are of great interest for in a variety of applications [1]. Magnetic nanoparticles have been found special applications in nanobiotechnology and nanomedicine due to their unique properties and biocompatibility. These include bioanalytical sensor, drug carrier, enzyme support material, magnetic resonance imaging (MRI) enhancement, targeted drug delivery, cancer diagnosis and therapy [2].

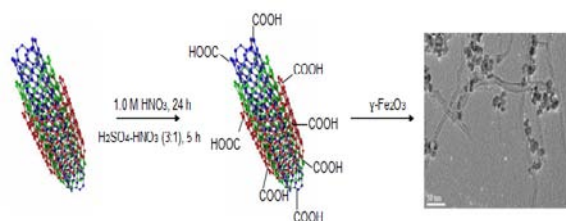


Fig. 1. Representative image of synthesis procedure of γ -Fe₂O₃ magnetic nanoparticle functionalized with carboxylated multi walled carbon nanotube

From this perspective, hybrid nanostructure from γ -Fe₂O₃ magnetic nanoparticle and carboxylated multi walled carbon nanotube was synthesized and characterized by FT-IR, VSM, SEM, HR-TEM, TGA, ICP-OES. Microscopy images showed that magnetic nanoparticles were spherical structure that arranged on carboxylated MWCNT with particle size lower than 10 nm. A representative image of synthesis procedure was given in Fig. 1. VSM results showed that the obtained functionalized magnetic nanotubes show superparamagnetic properties at room temperature are preferred because they don't show any magnetism after magnetic field is removal. The magnetic saturation value of these magnetic nanoparticles was found as 35.2 emu/g. The synthesized magnetic nanoparticle were used for their analytical and biomedical applications through the adsorption of harmaline, indicator of Essential Tremor. Antimicrobial activity of MNPs were investigated against Gram positive and Gram negative bacteria.

KEYWORDS: Nanobiotechnology; maghemite; carboxylated carbon nanotube; biomedical application; characterization

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Catalytic Activity of Ag Nanoparticles Modified Polymer Film Electrode for Dimethylamine Borane Oxidation

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Investigations of renewable and clean power sources have been studied for several decades. In this way, fuel cells have been considered as candidates for minimizing the usage of fossil fuels. Electrocatalysts play an important role in new type of electrochemical systems for energy generation in fuel cells. The high cost of the platinum is one of the reasons for its limited use. In order to improve the reaction kinetics and decrease the cost, it is necessary to develop new catalysts. Thus, great efforts have been devoted to the development of fuel cell electrocatalysts with a focus in increasing their electrocatalytic activity and reducing the noble metal content [1-3].

Sodium borohydride derivatives such as ammonia borane and dimethylamine borane that have capacities, as hydrogen storage materials and fuel of the direct liquid-feed fuel cell, have attracted much attention since the early 2000s. Dimethylamine borane, which is safe, chemically stable, easy to transport in its dry state and high solubility in water appears as an attractive fuel for fuel cells. Until nowadays, the electrochemical studies of dimethylamine borane have not been produced enough data for hydrogen carriers or fuels for fuel cells. Real improvement opportunities still exist. Yet dimethylamine borane has potential in specific applications. [4, 5].

In this work, p-aminophenol monomer was polymerized electrochemically at glassy carbon electrode surface by repetitive potential cycles using cyclic voltammetry and electrode donated as PAP/GCE. After aminophenol polymerization, Ag nano particles were also formed at modified electrode surface by cyclic voltammetry. Modified electrodes were characterized with atomic force microscopy and scanning electron microscopy (Fig.1). Dimethylamine borane oxidation was investigated at all prepared electrodes. The obtaining results were comparing with bare and PAP modified glassy carbon. While there wasn't any oxidation peak observed at bare and PAP/GCE, silver nano particles incorporated polymer film electrodes have high catalytic activity towards dimethylamine borane oxidation at -980 mV.

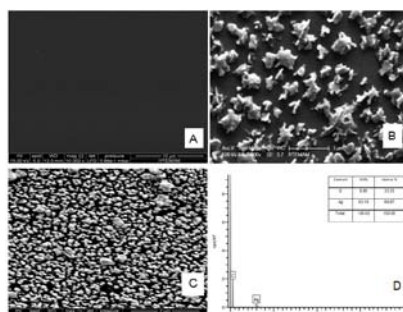


Fig.1 SEM images of a)GC, b) PAP/GC, c) Agnano/PAP/GC electrodes and d) EDX result of Agnano/PAP/GC electrode.

KEYWORDS: Dimethyl aminoborane oxidation, polymer film, silver nano particles

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Metal Oxide Synthesized Materials for a Textile Dye Removal

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Dyes are widely used in industries such as textiles, rubber, paper, plastics, cosmetics etc. to color their products but these dyes are highly colored and the disposal of these wastes into receiving water causes damage to the environment. Color removal from textile effluent is a major environmental problem due to the difficulty of treating such streams by conventional chemical and biological treatment methods [1, 2].

Among several chemical and physical methods, the adsorption process is one of the effective techniques that have been successfully employed for color removal from wastewater. To improve the efficiency of the adsorption processes, it is essential to develop the more effective and cheaper adsorbents with higher adsorption capacities. Especially sol-gel which has due to their high surface area, low density and open pore structure are intensively researched.

In this study, the synthesis of SiO₂ and SiO₂ composites including clay, surfactant and, both clay and surfactant were carried out with TEOS in acidic media by using various parameters SiO₂ composites were prepared at room temperature and then aged time on the adsorption was investigated. The effect of pH on the adsorption was also examined at a range of pH 1.0-9.00. The results indicated that the optimum pH was 1.5 for a textile dye with SiO₂ including clay as an adsorbent.

KEYWORDS: SiO₂, Sol-gel, adsorption, dye

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Characterization of SiO₂ Materials Prepared by Using Sol-Gel Method

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SiO₂ materials are commonly produced by sol-gel process. The sol-gel process is defined as formation of an oxide network through hydrolysis and condensation reactions of a molecular precursor in a liquid. The precursors used in the preparation of the sol are typically inorganic metal salts or metal organic compounds such as metal alkoxides. Sol-gel process can be used to produce a wide range of oxides in various forms, including powders, fibers, coatings and thin films, monoliths and porous membranes. In addition, the surfactants which have different alkyl chain length on structures have been used modifying on surface of SiO₂ particle. In this manner, some properties of SiO₂ particles such as, tensile yield strength, strain, and highest fracture toughness has been improved[1]. Moreover, sol-gel method has been widely used to produce porous SiO₂/clay composite materials. The SiO₂ network in which has clay minerals, has been composed through sol-gel procedure in presence of surfactants as intercalation. These composites have unique properties such as high surface area and porosity, and they can be used some applications such as adsorption, encapsulation, insulation[2].

In this study, various kinds of SiO₂ materials were synthesized with sol-gel method. These SiO₂ materials are including surfactant, clay and both surfactant and clay. All synthesized materials were performed under ambient conditions. The materials which were obtained four different forms were characterized with XRD, XRF, FTIR, SEM, BET and zeta potential measurements.

KEYWORDS: Sol-gel, SiO₂, clay, characterization

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Determination of Zeta Potential Surface of Nanoporous Polymer Membranes

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Implementation of membrane separation processes involves complex phenomena which control optimizes the separation. In fact, the selectivity (or separation ability) of a porous membrane vis -a-vis a mixture of solutes (ions and molecules) result both of a sieve effect (that is to say a discrimination function of the size of the species to be used) and the effects of the electric charges resulting from the chemical nature of the membrane material and the species to be separated.

It is therefore essential to optimize the operating conditions of a membrane prior to study its electrical properties and electrokinetic. This consists of measuring the potential and the current streaming can then be connected directly to the surface charge density of the material studied [1].

A preliminary characterization of dense films made with Teflon allowed us to validate the method of measuring the current streaming. The zeta potential calculated from both current and potential streaming lead to the same value. However, the zeta potential, obtained with a polyamide membrane NF 270, calculated from the streaming potential was significantly lower than the zeta potential obtained from the streaming current. This was due to the contribution of the membrane porous body [2]. The results obtained with a polyamide membrane NF270 helped to highlight the presence of a negative surface charge (due to the presence of carboxylic acid functions) and understand the differences in permeability of different types of electrolytes through the membrane.

KEYWORDS: Membrane, current streaming, potential streaming, zeta potential, nanofiltration.

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Synthesis and Antibacterial Activity of Thiosemicarbazide from Amino Acids Derives

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The synthesis of nucleoside and its derivatives have attracted considerable attention of organic and medicinal chemists for many years¹⁻⁴. Triazoles reverse nucleoside 5,6 were prepared by reaction of thiosemicarbazide 3 with ammonium thiocyanate in the presence of chloridric acid. The thiosemicarbazide 4 were prepared from amino acid ester 2. The nucleoside of triazoles compound present a interesting biological activities with *Staphylococcus aureus*, *Bacillus cereu,s* *Acinitobactère* and *Salmonelle shiguer* .

The synthesized compounds were characterized by elementals analysis, NMR data and infrarouge.

KEYWORDS: Triazoles, thiosemicarbazide, amino acid ester and nucleoside

**System Action of Copper Diacetate and Triphenylbismuth Diacetate
on The Arylation of a Variety of Heteroaryl Amine**

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The heterocyclic belong to the family of compounds having particular importance in medicine, biology, agronomy, cosmetic and various pharmaceutical activities (anti-parasitic, anti-fungal, anti-inflammatory, psychotropic) [1].

In this context, we then proposed to synthesize heteroarylamines secondary by action of the system copper diacetate and diacetate triphenylbismuth on various groups heteroarylamines primary [2],

The heteroaromatics products are obtained with the excellent yields, separated and purified by column chromatography and their structure was identified by the usual spectroscopic methods such as proton NMR and carbon-13.

KEYWORDS: Copper diacetate, diacetate triphenylbismuth , heteroarylamines primary , heteroarylamines secondary.

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Investigation of The Solvent Effect on The Fluorescence Properties of Some New Synthesized Schiff Bases

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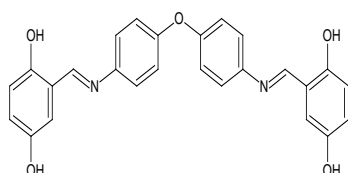
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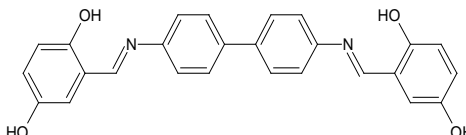
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Schiff bases play a central role as chelating ligands in main group and transition metal coordination chemistry [1-2]. Schiff bases and their metal complexes are becoming increasingly important as biochemical, analytical, industrial and antimicrobial agents [3]. Determining the chemical properties of Schiff bases help to conduct studies with these ligands. Solvation dynamics of fluorescent molecule with its environment has an important effect on kinetics of many photochemical reactions and on a lot of photochemical parameters. The Stokes' shift observed in fluorescence emission has generally invoked the interaction between the solvent and fluorescent molecules [4]. Thus, the need to understand the effects of solvent polarity, specific solvent-fluorescent molecule interaction and charge separation in the excited state becomes essential in photochemistry.

The effect of solvent on the fluorescence properties of some new synthesized Schiff bases have been studied at room temperature in a series of solvents with different polarities and proton-donating abilities. Therefore, this study was carried out to investigate the fluorescence properties of N,N'-bis(2,5-dihydroxybenzylidene)-4,4'-diaminodiphenylether (DHDPE) [5] and N,N'-bis(2,5-dihydroxy benzylidene)-4,4'-diaminobenzene (DHDBP). Multi-emission spectra of these Schiff bases in N,N-dimethylformamide, methanol, ethanol and acetonitrile were measured by changing excitation wavelengths. Then fluorescence intensities of each Schiff base in excitation (λ_{ex}) and emission wavelengths (λ_{em}) were determined in these solvents and compared with each other. Furthermore, solvatochromic correlations were used to estimate the ground-state (μ_g) and excited-state (μ_e) dipole moments.



DHDPE



DHDBP

KEYWORDS: Fluorescence, solvent effect, Schiff base

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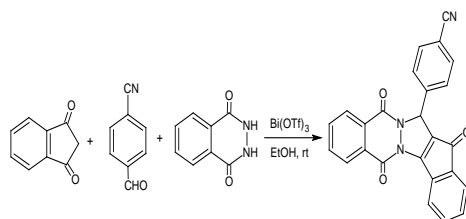
Spectroscopic Investigations Aromatic of 2*H*-indazolo[2,1-*b*]phthalazine-triones

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Nitrogen-containing heterocyclic compounds are widespread in nature, and their applications to pharmaceuticals, agrochemicals, and functional materials are becoming more and more important [1]. Among a large variety of N-containing heterocyclic compounds, those containing hydrazine moiety as 'fusion site' have received considerable attention because of their pharmacological properties and clinical applications [2]. Moreover, fused phthalazines were found to possess multiple biological activities, such as antimicrobial, anticonvulsant, antifungal, anticancer, and anti-inflammatory activities [3-7]. Nevertheless the development of new synthetic methods for the efficient preparation of heterocycles containing phthalazine ring fragment is an interesting challenge. Recently, several elegant multicomponent strategies for the synthesis of phthalazine-triones by the cyclocondensation of phthalhydrazide, benzaldehyde, and 1,3-diketone utilizing different types of catalysts have been reported [8-11]. The reported methods show varying degrees of successes as well as limitations, such as harsh reaction conditions, expensive catalyst/reagent, toxic organic solvents, low product yields, long reaction times, and co-occurrence of several side products. Thus, a simple, rapid and efficient procedure is still strongly desired for the synthesis of these important fused heterocyclic compounds. Therefore, the search continues for a better catalyst for the synthesis of phthalazine-triones in terms of operational simplicity, reusability, economic viability, and greater selectivity. Bismuth triflate has recently attracted much attention due to low toxicity, low cost, and good stability. It can efficiently catalyze through one-pot condensation of phthalhydrazide, 4-cyanobenzaldehyde and 1,3-indandione (Scheme). The product obtained was fully characterized by spectroscopic methods such as UV, FTIR, ^1H NMR, ^{13}C NMR, mass spectroscopy and elemental analysis and have been identified by comparison of the spectral data with those reported.



KEYWORDS: phthalazine, spectroscopy, synthesis

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Spectroscopic Investigation of Ethyl 4-(4-cyanophenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate

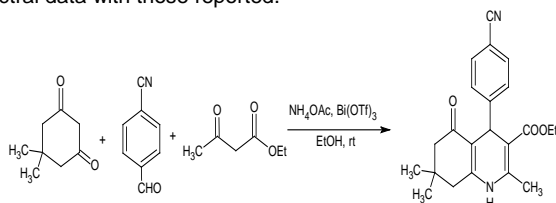
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1,4-dihydropyridines (1,4-DHPs) and their derivatives are an important class of bioactive molecules in the pharmaceutical field. They possess anti-inflammatory, anti-microbial [1], anti-oxidant, anti-ulcer activities [2]. DHPs are commercially used as calcium channel blockers for the treatment of cardiovascular diseases, including hypertension. Recently, the synthesis of DHPs with respect to Multidrug Resistance (MDR) reversal in tumor cell gave a new dimension to their applications [3]. In addition, 1,4-DHP class of compounds are excellent starting synthons for development of anti-tubercular agents [4]. Oxidative aromatization reactions of DHPs are taking place in biological systems in the presence of certain enzymes. The nitrogen heterocycles thus prepared by Hantzsch method are of great importance because of their role in biological systems. Realizing the importance of 1,4-dihydropyridine derivatives, several synthesis methods have been reported, like conventional heating [5], refluxing in acetic acid [6] and microwave irradiation [7] and ultrasound [8]. Different other approaches for the syntheses of 1,4-dihydropyridine derivatives using various catalysts have also been reported and some of the methods are associated with several shortcomings such as long reaction times, expensive reagents, harsh reaction conditions, low-product yields and the use of large quantity of volatile organic solvents. Therefore, the search continues for a better catalyst for the synthesis of 1,4-DHPs in terms of operational simplicity, reusability, economic viability, and greater selectivity. Bismuth triflate has recently attracted much attention due to low toxicity, low cost, and good stability. It can efficiently catalyze through one-pot condensation of 4-cyanobenzaldehyde, dimedone, ethyl acetoacetate and ammonium acetate (Scheme). The product obtained was fully characterized by spectroscopic methods such as UV, FTIR, ¹H NMR, ¹³C NMR, mass spectroscopy and elemental analysis and have been identified by comparison of the spectral data with those reported.



KEYWORDS: dihydropyridine, spectroscopy, synthesis

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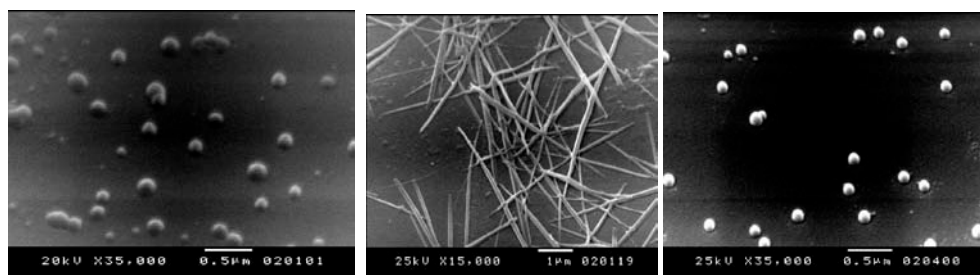
Fluorescent Chemosensors For Iron (III) and Cu(II) Based on Symmetric Tetradentate Ligands Nanoparticles

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Three Fluorescent sensors nanoparticles of the types $H_2L[C]$, $H_2L [O]$ and $H_2L[S]$ were successfully synthesized by ultrasonication of 2-hydroxynaphthaldehyde with three different diamines containing flexible linkages. The three fluorescent sensors were fully characterized. The fluorescent chemosensors $H_2L[C]$ and $H_2L[O]$ were obtained as well-separated spherical nanoparticles with average diameters of 38 and 76 nm, respectively, while $H_2L[S]$ chemosensor was obtained as rod-like nanoparticles with a diameter of 62 nm. The fluorescence properties of these compounds were studied in CH_3CN -DMSO (9:1, v/v) in a range of 400–650 nm. The effect of metal cations such as Mn^{+2} , Fe^{3+} , Co^{+2} , Ni^{+2} , Cu^{+2} , Zn^{+2} , Cd^{+2} and Hg^{+2} on the fluorescence spectra of $H_2L[C]$, $H_2L [O]$ and $H_2L[S]$ was investigated. The prepared nanoparticle showed specific metal response as remarkable fluorescence quenching to Fe^{+3} and Cu^{+2} over other cations. The binding stoichiometry and the stability constant of the formed complexes were detected. The effects of foreign ions were investigated and no obvious interference was observed during the detection of Fe^{3+} and Cu^{+2} in different mixtures of metal ions. The highly selective quenching of these ligands by Fe^{3+} and Cu^{+2} may be utilized for the diagnosis of various ferric or copper related diseases.



KEYWORDS: Sensors; iron (III) and Cu(II) ; fluorescence quenching; schiff bases.

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Separation of the Structural Isomers of Thiazolidin-4-one Synthesized from 1-(2,4-Dimethylphenyl)-3-(4-methylphenyl)thiourea by HPLC

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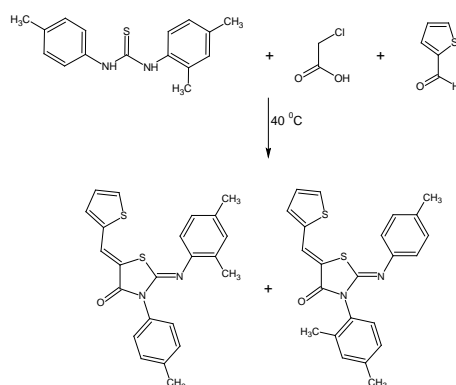
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Iminothiazolidinones are the derivatives of thiazolidinone which belong to an important group of heterocyclic compounds containing sulphur and nitrogen in a five member ring. Iminothiazolidinones are also known as wonder nucleus because they give out different derivatives with all different types of biological activities. These heterocyclic compounds have been used for photography, as synthetic intermediates, dyes and display diverse biological activities such as anti-arthritis, antibacterial, antiviral, inhibitors of bacterial type III secretion, anticonvulsant, anti-inflammatory, antidiabetic, antithyroidal, pesticidal, fungicidal, SHP-2 inhibitor and calcium tuberculostatic [1-4].

Besides, thioureas have an important role in the synthesis of sulfur- and nitrogen-containing heterocyclic compounds due to their ability to make advanced reactions. Addition to this, thiourea derivatives have attracted attention during the last decades due to their significant biological activities as antitubercular, antibacterial, antifungal, anti-HIV, antihypertensive, anticancer as well as good anticonvulsant properties [5-7].

In this study, new iminothiazolidinone derivative considered that may possess biological activity has been obtained via one-pot multicomponent method by using thiophene-2-carboxaldehyde, chloroacetic acid and 1-(2,4-dimethylphenyl)-3-(4-methylphenyl)thiourea. The product was separated by high-pressure liquid chromatography (HPLC) and the obtained structural isomers were unambiguously characterized by spectroscopic methods [8]:



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Synthesis of Substituted 6,7-Dihydrocyclopentapyrimidin-2-amine Compounds via One-Pot Method

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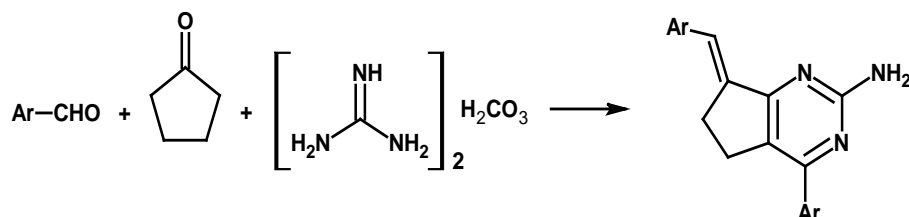
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Pyrimidine derivatives, as the nitrogen-containing heterocycles, are extremely important compounds with high biological activities as antimicrobial, antiinflammatory, antihyperlipidemic, antihypertensive and anticonvulsant properties [1-3]. They have an important place in the area of heterocyclic compounds because of their presence in the structures of macrocyclic complex drugs, their applications in industry and usage in pharmaceutical researches due to their biological properties.

In this study, some new substituted pyrimidine derivatives which are considered that may possess biological activity have been obtained via one-pot three-component reactions. These reactions, which are carried out using the method of multicomponent reactions (MCRs), proceed as domino processes, making them easier to occur than the conventional multistep organic reactions. This method enables new organic molecules to be synthesized in a single step, using a minimal amount of time and number of trials.

The study consists of one steps. Cyclocondensation of each of the previously substituted cyclic ketones with hetaryl carboxaldehydes and guanidine was achieved by the technique of one-pot multicomponent reaction; and structures of all the synthesized compounds have been determined and characterized by ultraviolet, infrared, nuclear magnetic resonance, mass spectral data [4].



Ar= Thiophen-2-ly, 3-methylthiophen-2-ly, 5-methylthiophen-2-ly

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Synthesizing Different Size Emulsion Polymers and Characterization

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Macroemulsions are thermodynamically unstable liquid/liquid dispersions, usually stabilized by emulsifiers, polymers or solid particles [1], and a latex product is a dispersion of a large number of tiny polymer particles (ca. 50-1000 nm) in water, which has been widely used in coatings, adhesives, plastics, and rubber industry [2]. Nano-emulsions are a new class of emulsion with droplet sizes in the range of nanometers. These emulsions, termed nano-emulsions, mini-emulsions or ultrafine emulsions are transparent or semi-transparent with droplet size between 50 nm and 200 nm, or milky up to 500 nm [1]. Emulsion properties depend on physicochemical variables (nature of components, composition, temperature and pressure), on preparation methods and on the order of addition of the components.

In this study, water-based emulsion copolymers were synthesized with small particles including nano-sizes and narrow particle size distribution. The latex particles concurrently resulted in small and the distribution of them was narrow with the using anionic and nonionic emulsifier mixture; which could not be achieved in a conventional water-based emulsion polymerization by using protective colloid.

KEYWORDS: latices, nanoparticles, particle size, surfactants.

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Synthesis Electrochemical, Spectroscopic and Biological Study of Benzidine's Ligand and its Complex Organometallic Cu (II) and Co (II).

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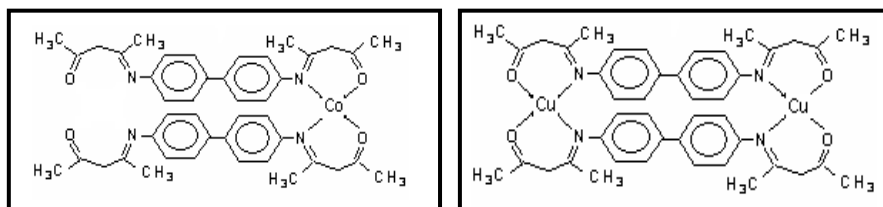
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The coordination chemistry of metals do the several object researches, among them, we find which concerns the complexation of the metals' ions with the organic compounds "schiff base". this ligands may be with a various forms and with a various' coordination sites'. it define as the chemicals compounds with one or several imin fonction. It is widely used in medicinal treatment to several diseases and in industry for the Anti against the corrosion. it may also have a wide application in the field of water treatment because it has a high complexing ability for the transition metals. including the recovery of heavy metals from industrial effluents harmful or radioactive elements in nuclear waste. [1]

For example, although benzidine is highly toxic, it is used in many areas such as ligands in organometallic complexes.

In February 2007 "The Korean Society of Mycology" published a study entitled "Design and synthesis of a macrocyclic ligand and its antifungal complexes. The work carried out is as follows: three new complexes of Cu (II), Co (II) and Zn (II) with a macrocyclic ligand derived from the condensation of diethyl phthalate and benzidine was designed. The analytical data showed that the geometry of the complex is square planar. The antifungal activity of the macrocyclic ligand and its metal complexes was tested in vitro against fungi such as *Aspergillus Niger*, *A. flavus harizantum* *Trichoderma viridae* T. and *Rhizoctonia solani*. Moreover, it is worth noting that these complexes disrupt the process of cell respiration, thus blocking protein synthesis, causing limiting further growth of the organism. [2]

In the extension of these studies is our job to know at first time the synthesis of a tetradentate Schiff base ligand and in second time with respect to the complexation of transition metals. This ligand is mainly based on the condensation of 2,4-pentanedione with 4,4'-diaminobiphenyl (benzidine) in absolute EtOH medium with a molar ratio 2:1. This condensation has led to the Schiff base 4,4'-(biphenyl-4, 4'-diyl)dinitrilo dipentan-2-one (denoted H₂L) which was subsequently used as a tetradentate. this ligand coordinate the Cu (II) and Co (II) chloride salts and it was gave a metallic complexes with a molar ratio (metal-ligand) 2:2 and 1:2.



All synthesized compounds were characterized by microanalysis, IR, UV-vis electronic spectroscopy, mass spectrometry and magnetic resonance SM ¹H NMR. The electrochemical behavior of the ligand and its complexes in dimethylformamide (DMF) was even addressed and discussed.

KEYWORDS: Benzidine, schiff base, ligand.

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Effects of Interchange Reactions on the Dynamical and Thermal Properties of PC/PET Blends

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Reactive extrusion is a polymer processing technique that mainly involves the use of an extruder as a chemical reactor. Chemical reactions associated with polymers are carried out in situ, while processing is in progress. Therefore, This process differs from conventional polymer manufacturing methods, where synthesis is a separate operation and the extruder serves only as a mixing tool. Reactive extrusion is receiving increased attention as a commercial technique because of its several advantages, which include lower cost and versatility, especially in polymer blends. Indeed, reactive extrusion allows the compatibilization of immiscible blends by the in-situ synthesis of copolymers serving as compatibilizers at the interface between the blended polymers [1-3].

Polycarbonate (PC) and polyethylene terephthalate (PET) are widely used as engineering plastics either alone or blended with other thermoplastics to ensure certain performances that cannot be provided by using the neat homopolymers. For this purpose, their reactive blending has received a great interest to get insight into all the parameters that may influence the ultimate properties of the final product. Among all transesterification catalysts, tetrabutylorthotitanate (TBOT) was found to be the most active in catalysing ester-carbonate exchange reactions in PC/PET systems, but it allows also the occurrence of side reactions which can have drastic effects on the properties of the blend [4,5].

This study was performed in order to evaluate the effects of TBOT as a transesterification catalyst on the dynamical and thermal properties of PC/PET blends as a function of homopolymer and exchange catalyst concentrations. Also, the dependence of PC rich-phase composition on the catalyst concentration was estimated according to Wood's equation.

Thermoanalytical Investigation of New Phenyl Tetrazoles

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In the last 20 years, the trend in energetic material research has been towards the synthesis of unstrained, therefore safer, molecules. In this fashion, today, nitrogen rich substances come out as the prominent energetic materials [1]. These substances are considered as relatively more environment friendly, since the explosion reactions mainly yield nitrogen gas. For the purpose of preparing such explosives, nitrogen rich aromatic molecules are designed and synthesized or nitrogen containing functional groups such as azide (N_3^-) are added to organic substances [2-4].

In this study, a number of phenyl tetrazole derivatives were designed and synthesized according to similar entries in the literature. These tetrazole substances are namely, 1-phenyl-1H-tetrazole (I), 1(4-chlorophenyl)-1H-tetrazole (II), 1(4-hydroxyphenyl)-1H-tetrazole (III), 1(4-methoxyphenyl)-1H-tetrazole (IV), 1(4-nitrophenyl)-1H-tetrazole (V), and bis-1,4-tetrazol-1-yl benzene (VII) Fig.1c.

	X: H	I
	X: 4-Cl	II
	X: 4-OH	III
	X: 4-OCH ₃	IV
	X: 4-NO ₂	V
	X: 4-CHN ₄	VI

They were characterized by means of elemental analysis, 1H -NMR, ^{13}C -NMR spectroscopies and kütte spectroscopy and further investigated by Thermogravimetry. The exothermic decomposition of tetrazole ring between 170 and 210 °C was observed. The mass spectra were proven helpful in interpretation of TG results. It was concluded that the remaining mass after the decomposition of the tetrazole ring accounted for newly formed phenyl isonitriles [5]. The theoretical formation enthalpies of the given tetrazole species were calculated by Gaussian 09 software and the corresponding reaction enthalpies were calculated accordingly. The experimental thermal decomposition enthalpy was determined by using Differential Scanning Calorimetry. The experimental findings fitted well with the theoretical result for compound II, III, IV and V where compound I and VI yielded incoordinate results. In conclusion, this study showed that the theoretical software can be employed for analytical purposes such as estimation of the reaction products.

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Synthesis and Characterization of Meloxicam Cu(II) Complex and Its Interaction with DNA

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The synthesis and the electrochemical characterisation of copper(II) complex of meloxicam is reported. Meloxicam is a nonsteroidal anti-inflammatory drug (NSAID) with analgesic and fever reducer effects. It is a derivative of oxicam, closely related to piroxicam, and falls in the enolic acid group of NSAIDs.[1] In addition to characterisation, the electrochemical properties of the Cu(II) complex of meloxicam were investigated by cyclic voltammetry (CV). The oxidation/reduction, reversibility and molecular transportation type depending on pH were investigated. The dependence of intensities of currents and potentials on pH, concentration, scan rate, was investigated. The oxidation/reduction mechanism was proposed and discussed.

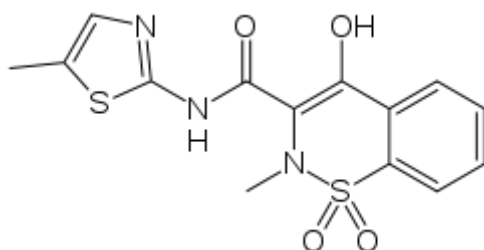


Fig. Structure of Meloxicam

Also, the interaction of Cu(II) complex of meloxicam with double-stranded DNA (dsDNA) and single-stranded DNA (ssDNA) was studied electrochemically by using differential pulse voltammetry (DPV) and cyclic voltammetry (CV). The changes in the experimental parameters (the concentration of complex and the concentration of DNA) were studied by DPV; in addition, the detection limit and the reproducibility were determined.

KEYWORDS: meloxicam, DNA, Cu(II) complex

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**Synthesis and Characterization of N, N'-bis
(salicylidene)ethylenediamine. Study of Mining Properties vis-à-vis the
Copper (II) in Sulphate Environment**

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The synthesis and characterization of N, N'-bis (salicylidene) ethylenediamine, Salen said were carried out. The behavior of this ligand has been studied in solution in solvent homogeneous and heterogeneous systems in sulphate medium. The use of pH-metric titration, GRAN [1] and JOB's[2] methods have permitted the determination of different parameters governing the behavior of Salen in solution such as the acidity constant, the stability constant, the nature of the interaction solvent-solute, the solvation number, the stoichiometry of extracted complex etc...

The extraction of the Salen was finally undertaken to words the copper (II) sulfate medium. The pH of complexation, extraction time, the number of protons exchanged and the number of ligands have been finally determined.

KEYWORDS: Salen; copper(II); metal complex; acid-base behavior; liquide-liquide extraction

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Synthesis of New Phthalocyanine Molecules and Characterization

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Phthalocyanines consisting of four interdependent isoindolin units with nitrogen atoms and having 18- π electron systems are macrocyclic structures. Colours of phthalocyanines are blue and green tones because of highly delocalized π -electron systems in their structures. Because of their chemical, thermal and photochemical stability, they have been used as pigments. Delocalized π -electron systems of phthalocyanines allow to bind more than seventy metal or nonmetal ions to their cavities and have different substituent groups. Thus, they have been utilized such as photodynamic therapy, optical disc, transducer, electronic sensor, catalyst and photovoltaic cell [1] [2]. Also general using synthesis methods of phthalocyanine molecules are phthalic acid and Rosenmund-von Braun, use of Diels-Alder and crosscoupling reactions. [3]

In this study, Metallophthalocyanine / metal free phthalocyanine have been synthesized and achieved characterization. Substituent groups have been bound to non peripheral positions of molecules. Characterization of these molecules have been achieved by nuclear magnetic resonance (NMR), atomic absorption spectrophotometer (AAS), fourier transform infrared spectroscopy (FT-IR), ultraviolet visible spectroscopy (UV-Vis), and MALDI-TOF mass spectrometry.

KEYWORDS: Metallophthalocyanine, metal free phthalocyanine, macrocyclic molecules

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Oxidation Of Thymol with Potassium Peroxy monosulfate Catalyzed by Iron(III) Phthalocyanine Tetrasulfonate

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Thymol can be oxidized to thymoquinone, which has a commercial value considerably higher than its precursor. Thymoquinone has antitumor and antioxidant effects and also protects against heart, liver and kidney damage [1,2]. It is limited only to certain plant resources such as *Nigella arvensis*, *Callitriche articulata* and *Monarda fistulosa* [3,4,5]; therefore, there is a growing interest for its production by the transformation of other chemicals. It is known that the chemical transformation of natural products can make them more valuable new products [6].

In this study, sodium salt of iron(III)phthalocyaninetetrasulfonate ([FePcTS]Na₄) was prepared using the Weber procedure [7]. Oxidation of thymol was carried out with potassium peroxy monosulfate (oxone) in the presence of iron(III) phthalocyaninetetrasulfonate in a 8:1 methanol-water mixture. The reaction yielded high conversion of thymol and selectivity of thymoquinone. Uncatalyzed oxidation of thymol did not proceed in the presence of the oxidant KHSO₅. Thymoquinone is the major product in this reaction. Catalytic activity of [FePcTS]Na₄ was investigated with relative to the concentrations of substrate, oxidant and catalyst. Products of the reaction were analyzed by GC-MS technique.

Graphical Summary

KEYWORDS: Iron(III)phthalocyanine tetrasulfonate, thymol, thymoquinone, oxidation

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The Photophysical and Photochemical Properties of New Unmetallated and Metallated Phthalocyanines Bearing Four 5-Chloroquinolin-8-Yloxy Substituents on Peripheral Sites

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Phthalocyanines (Pcs), which were discovered by coincidence in 1907 at the South Metropolitan Gas Company by Braun and Tcherniac [1], are planar macrocycles related to porphyrins constituted by four isoindole units presenting an 18 π -electron aromatic cloud delocalized over an arrangement of alternated carbon and nitrogen atoms [2]. Phthalocyanines and related derivatives, such as copper phthalocyanines, have been the subject of intense research because of their commercial importance as coloring agent. Apart from their intense colors, they also exhibit high chemical and thermal stability, inertness to acids and alkalis, fastness to light, redox versatility [3]. Metal complexes of N_4 -ligands, such as porphyrins and phthalocyanines, are also used for photodynamic cancer therapy [4]. Photodynamic cancer therapy (PDT) has developed over the last century because of its potential usage in the treatment of some cancers. PDT uses a photosensitizing agent (PS) which is introduced, followed by illumination using light of a specific intensity and wavelength to activate the particular PS agent [5]. Metallophthalocyanines have been used as photosensitizing agent for photodynamic therapy due to their intense absorption in the visible region [6]. The aim of this work is to synthesize and characterize novel unmetallated and metallated [zinc(II), lead(II), cobalt(II), copper(II) and nickel(II)] phthalocyanines bearing four 5-chloroquinolin-8-yloxy groups by miscellaneous spectral methods such as FT-IR, ¹H NMR, ¹³C NMR, mass spectra, UV/vis and thermogravimetric analysis. The photophysical (fluorescence lifetime and quantum yields) and photochemical (singlet oxygen production and photodegradation under light irradiation) properties of unmetallated, zinc(II), lead(II) phthalocyanines are investigated in DMF. The effect of the nature of the central metal ions in the phthalocyanine cavity is also studied for comparison.

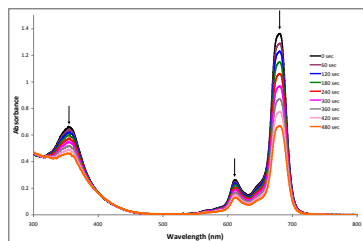


Fig.1. Absorption changes during the photodegradation studies of **ZnPc** in DMF showing the disappearance of the Q-band at one minute intervals. (Inset: Plot of absorbance versus time). 300W General Electric quartz line lamp was used as a light source. Power density was 18 mW/cm² and used energy was 100 watt.

KEYWORDS: Phthalocyanine; Photophysics; Photochemistry; Fluorescence, Photodegradation.

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Novel 4-(2-(Benzo[D]Thiazol-2-Yl)Phenoxy) Substituted Phthalocyanine Derivatives: Synthesis, Electrochemical and *in situ* Spectroelectrochemical Characterization

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Metal complexes of N₄-ligands, such as porphyrins and phthalocyanines, are widely studied due to their numerous physical-chemical properties and the great variety of their applications in many fields [1]. Both series of tetrapyrrole macrocycles (phthalocyanines and porphyrins) are able to form complexes with almost all the metals in Periodic Table [2] and at least seventy metal phthalocyanines have been prepared [3] thanks to their ability. Their favorable properties, such as extraordinary thermal and chemical stability, make them suitable as industrial pigments for several decades [4]. Phthalocyanines, which are an important class of compounds use in inks, dyestuff for textiles and colorant for metals and plastics, have been used other applications such as liquid crystal displays, optical applications, electrochromism, chemical sensors, semiconductors for organic field-effect transistors (OFETs) and photodynamic therapy. Metallophthalocyanines (MPcs) are used in many electrochemical technologies, especially electrosensing [5], electrochromic [6], and electrocatalytic [7] application due to the excellent redox properties. Changing the metal center and types, number and position of substituents alter the electrochemical responses as well as the usage fields of the MPc complexes [8]. Therefore in this paper we aimed to investigate the electrochemical properties and possible application fields of the newly synthesized MPc complexes. Here, we report the synthesis and characterization of novel 4-(2-(benzo[d]thiazol-2-yl)phenoxy)-substituted metal-free (H₂Pc), zinc(II), lead(II), cobalt(II) and copper(II) phthalocyanine derivatives. Furthermore, in this work voltammetric characterizations of the complexes were performed with cyclic voltammetry and square wave voltammetry for the first time. These organo-soluble phthalocyanines have been also characterized by using electronic absorption, FT-IR, ¹H NMR, ¹³C NMR, elemental analysis and mass spectra.

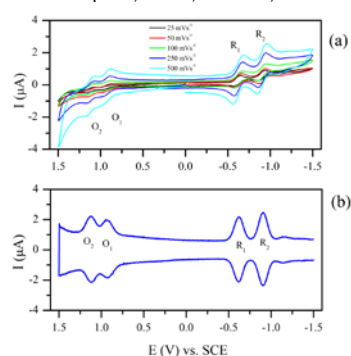


Fig. 1. (a) CVs of H₂Pc at various scan rates on a Pt working electrode in DCM/TBAP and (b) SWV of H₂Pc recorded with SWV parameters: step size = 5 mV; pulse size = 100 mV; Frequency = 25 Hz.

KEYWORDS: Metallophthalocyanine; Metal-free phthalocyanine; Electrochemistry; Demetallation; Spectroelectrochemistry

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Synthesis, Electrochemical, *in situ* Spectroelectrochemical and Electrocolorimetric Measurements of Novel Metal-Free and Metallophthalocyanines Bearing Oxadiazole Groups at The Peripheral Positions

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Prior to 1960, there existed only one well-established category of synthetic cyclic ligands which were the highly conjugated phthalocyanines. Phthalocyanines (Pcs) and their derivatives bear a strong structural resemblance to the natural porphyrin systems [1]. Their dramatic and useful chemical and physical features such as bright colors, conductivity [2], chemical and thermal stability [3] have made them comparatively desirable for many applications. Phthalocyanine complexes have been shown to behave as solar cells, catalysts, semiconductors, liquid crystals. In the last few decades, the application field of phthalocyanine derivatives in the use of as photosensitizers for photodynamic therapy (PDT) [4, 5]. Electrochemical applications, especially electrocatalytic, electrosensing, and electrochromic application criteria of metallophthalocyanines (MPcs) can be tuned by changing the metal center and types, number, and position of substituents [6]. In this paper we report the synthesis and characterization of metal-free, cobalt(II) and lead(II) phthalocyanines containing 4-(4-(5-phenyl-1,3,4-oxadiazol-2-yl)phenoxy) groups by the classical method. The characterization of novel compounds was achieved by using several spectral methods. Electrochemical characterizations of the complexes were performed with cyclic voltammetry, square wave voltammetry and *in situ* spectroelectrochemical measurements.

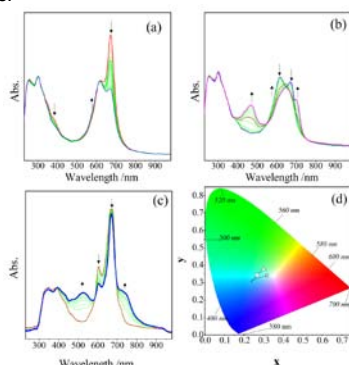


Fig. 1. In-situ UV-Vis spectral changes of **CoPc** in DCM/TBAP. **a)** $E_{app} = -0.30$ V. **b)** $E_{app} = -0.70$ V. **c)** $E_{app} = 1.00$ V. **d)** Chromaticity diagram (each symbol represents the color of electro-generated species; \square : $[Co^{II}Pc^{-2}]$, \bigcirc : $[Co^IPc^{-2}]^{-1}$ (aggregated); \triangle : $[Co^IPc^{-2}]^{-1}$; \star : $[Co^{II}Pc^{-1}]^{+1}$).

KEYWORDS: Metallophthalocyanine, Oxadiazole, Electrochemistry, Demetallation, Spectroelectrochemistry.

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Development and Validation of RP-LC Method for The Determination of Mirtazapine

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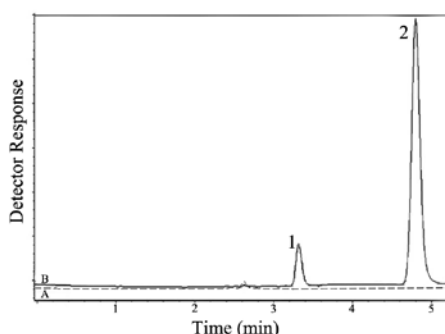
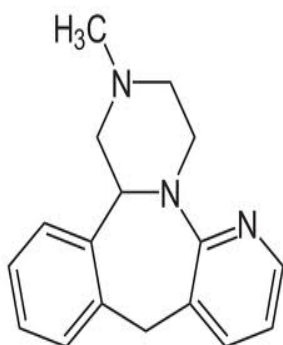
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Mirtazapine (MIR), (1,2,3,4,10,14b- Hexahydro-2 methylpyrazino[2,1-a]pyrido[2,3-c] benzazepine, is a tetracyclic piperazinoazepine, which has different structure from any other currently used antidepressant. It enhances central noradrenergic and serotonergic activity by blocking α_2 receptors and selectively antagonizing 5HT₂ and 5HT₃ receptors.

In this study rapid, sensitive, selective, accurate and precise analytical methodology was developed for the determination of antidepressant drug mirtazapine (MIR) by using liquid chromatography. The simple and fully validated reverse phase-liquid chromatography (RP-LC) method for the assay of MIR in tablets has been applied using X-Select RP-18 column (250x4.60 mm ID x 5 μ) at 25 °C with the mobile phase (containing 15 mM o-phosphoric acid) of methanol:water (30:70, v/v) adjusted to pH 3.0. The RP-LC method allowed quantitation over the 1.0-18.0 μ g/mL range of MIR. Retention times were 4.65 min for MIR and 3.27 min for hydrochlorothiazide (IS). The detection and quantitation limits of MIR have been obtained as 0.015 and 0.051 μ g/mL. Fully validated RP-LC method was applied for the analysis of MIR in pharmaceutical dosage forms without the necessity of sample pretreatment, or any time consuming evaporation or extraction steps prior to analysis.



Chemical structure of MIR and typical LC chromatograms of (A) methanol:water (30:70, v/v) adjusted to pH 3.0 as a mobile phase and (B) pharmaceutical dosage form of 5.0 μ g/mL IS (1) and 30.0 μ g/mL MIR (2).

KEYWORDS: Mirtazapine, RP-LC, validation, drug analysis.

Analysis and Identification of Chemical Components of Oil Dde Mastic (Fixed and Essential Oil)

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Given the preparation of *Pistacia lentiscus* L Algeria and especially its use in traditional folk medicine was studied in this work. Its chemical components were analyzed and identified. The extraction of vegetable oil from the berries was obtained with a yield of 43.25 ml/411g fruit. The physical, chemical and physicochemical characterization of oil mastic which allowed us to conclude that: the moisture content of the oil is moderately high. The presence of pigments responsible for the color. The existence of long-chain fatty acids by this index indicates relatively high saponification. Non cicative oil, this ranking is based on the value of the iodine under 100. U is predominantly unsaturated fatty acids (tri olein sort linoléine, trinolenine) analyzed by TLC and GC / MS. The extraction of essential oils from the leaves gave a yield of 0.0027 ml/100 mass. The results of the analysis of the essential oil by TLC and GC / MS indicated the *Pistacia lentiscus* L *Bétalinalool* chemotype. The physicochemical characterization of the essential oil, has been identified the chemotype of the plant. And secondly, to test biologically oil on laboratory animals confirm its pharmacological properties used in traditional medicine and toxicological tests to avoid any accident.

