Determination of material emissions signatures by PTR-MS and its correlations with acceptability index

Han, Kwanghoon; Zhang, Jensen; Wargocki, Pawel; Knudsen, Henrik Nellemose; Guo, Beverly

Published in:
Healthy Buildings 2009

Publication date:
2009

Document Version
Publisher's PDF, also known as Version of record

Determination of Material Emission Signatures by PTR-MS and its Correlations with Acceptability Index

Kwanghoon Han[1,*], Jensen Zhang[1], P. Wargocki[2], H. N. Knudsen[3] and Beverly Guo[1]

[1] Building Energy and Environmental Systems Laboratory (BEESL),
Department of Mechanical and Aerospace Engineering, Syracuse University, Syracuse, NY13244, USA
[2] International Centre for Indoor Environment and Energy, Department of Mechanical Engineering, Technical University of Denmark, Kgs. Lyngby, Denmark
[3] Danish Building Research Institute, Aalborg University, Hørsholm, Denmark

[*]*Corresponding email: kwhan@syr.edu*

SUMMARY
The objectives of this study were to determine VOC emission signatures by PTR-MS, and to explore the correlations between PTR-MS measurements and acceptability index levels previously measured by human subjects. Emissions from nine materials, the same ones previously studied by DTU and SBi to investigate human exposure-response relationships in terms of acceptability index, were measured individually in a 50-*L*-small-scale chamber with similar area-specific airflow rates as in the test with human subjects. Chamber air was sampled by PTR-MS to determine emission signatures followed by sorbent tube sampling for identifying major VOCs emitted from each material and for comparing with PTR-MS emission signatures. The study focused on the analysis of the concentration level and composition of emitted VOCs causing acceptability differences among the tested materials. Results show high correlation between PTR-MS measurements and acceptability when the sum of individual VOC odor indices was used to represent the emission strength by PTR-MS.

KEYWORDS
Emission signature, PTR-MS, GC/MS, VOC odor, signal processing

INTRODUCTION
Proton transfer reaction mass spectrometry (PTR-MS) is relatively a new instrument that has attracted many engineers' and scientists' interests in the recent few years. Unlike Gas Chromatographic (GC) methods, PTR-MS allows numerous VOCs of interest to be monitored with a high sensitivity (detection limit: 10-100 *pptv*) and a rapid response time, usually less than 100 *ms* (Lindinger et al. 1998). Due to its ability for on-line monitoring, practical/handy identification and detection of VOCs, there have been many applications in atmospheric, food research, forensic investigation, environmental science and medical research (Lindinger et al. 1998). In this study, we explored the feasibility of using PTR-MS to determine the VOC emission signatures of building materials and furnishings, and to investigate the relationship between the emission signatures and the emission acceptability determined by human subjects. The results of this study will be useful for further development of methods for: 1) on-line material identification and detection, 2) VOC source detection under field conditions and 3) deeper understanding of VOC behaviors in a material and its impact on human sensory responses.

MATERIALS and METHODS
The same nine (9) building materials (Table 1) previously studied in the subjective sensory assessments by human subjects were tested for their VOC emission compositions and concentration levels by using PTR-MS and GC/MS to analyze air samples taken from the exhaust of an environmental chamber containing a test specimen. For each test, the material

specimen was placed in a 50-*L* small-scale environmental chamber with similar ranges of area-specific airflow rates (Table 1) that resulted in the similar pollution level in the chamber as that in the previous acceptability test (Wargocki et al. 2007). Air at the chamber exhaust was sampled by PTR-MS to determine the emission signature of each material (*i.e.*, the PTR-MS ion mass spectrum of the air sampled). Tests were done for low, mid and high ventilation rates. An effective signal processing method was applied to extract a VOC emission signature for each material from the relatively noisy signals of the PTR-MS device, by removing the background and noise parts from the raw measured signals. We also investigated the relationships among the concentration level of each identified VOC relative to their respective odor thresholds, the measured ion mass pattern (*i.e.* the shape of the emission signature) and the acceptability index defined in Knudsen et al. (2006).

Table 1. Specimen sizes and its ventilation rates used in the BEESL/SU chamber tests.

Material	Q_v/A (L/s/m^2)				A
	#0	#1	#2	#3	(cm^2)
Ceiling 2	0.287	0.889	2.663	7.963	290.7
Wood	0.314	0.814	2.419	7.144	265.5
Carpet 1 **Linoleum 2** **PVC** **Polyolefine**	0.347	0.888	2.662	7.963	240
Gypsum	0.200	0.412	1.233		416
Paint 1	0.207	0.412	1.233	3.704	402
Paint 2	0.170	0.411	1.233		490.2

* T=24.0 ±0.02°C, RH=31±0.1%, Background concentrations: less than 1 $\mu g/m^3$ for each species.
* A detailed description about these building materials was reported in Wargocki et al. (2007).

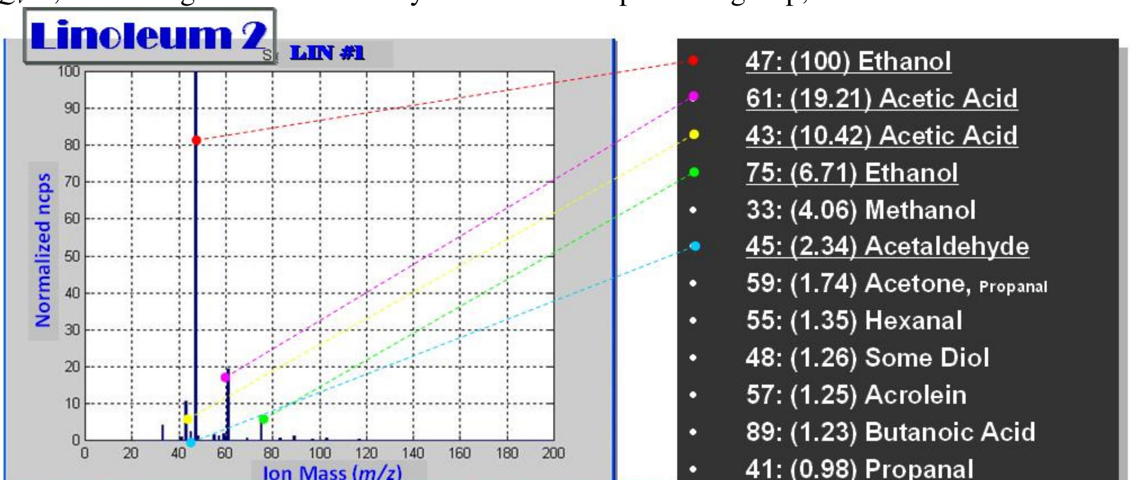
Environmental Chamber Conditions. A 50-*L* small-scale environmental chamber (0.5 *m* length × 0.4 *m* width × 0.25 *m* height) made of electro-polished stainless steel was used with precise controllers for flow (±0.1% of L/min accuracy) and humidity (±1% of RH accuracy).

GC/MS Analysis. For the identification and quantification of VOCs, air samples collected by Tenax sorbent tubes were analyzed using a conventional GC/MS instrument (*Perkin Elmer Auto System XL GC, TurboMassGold MS EI detector, Thermal desorber TuboMaxtrix ATD-GC/MS system* and *Elite-624 GC Column* were used). Sample volumes were from 6 *L* to 10 *L*. The response factor of Toluene from the GC/MS calibration was used only.

PTR-MS Analysis. A PTR-MS device (*Ionicon Analytik, Austria*) was operated at the standard conditions (Drift tube pressure: 2.3~2.4 mbar, PC: 455, FC: 6.5, V SO: 75, V S: 100, Drift tube voltage: 600 V and Source: 6.0 cc/min). As for a detailed description of the device and its conditions, it can be found in the literature (Lindinger et al. 1998). PTR-MS raw measurements, count rates (*cps*), were normalized by per million H_3O^+ ion count rates (*ncps*) which were used in this paper because these values are directly proportional to the concentration level of each target VOC.

RESULTS and DISCUSSION

A complete version of the PTR-MS emission signatures for the nine materials was obtained. As an example, Figure 1 shows an emission signature by PTR-MS for Linoleum 2. A short form of the dataset is illustrated in Figure 2. Unless confirmed by GC/MS spiking analysis, the VOCs identified in the PTR-MS results should be considered as probable or tentative. These emission signatures have the property of steadiness in its shape of the mass spectrum over time and even over different area-specific ventilation rate (Q_v/A) (In the present study, the flow rate was changed and the exposure area of a material was fixed). Due to these characteristics of the emission signature by PTR-MS specific to each material, by measuring the emission pattern of a given material, the detection and identification of the material is possible even in real time. Generally, most of the ion mass components show the similar trend in the change of its relative peak values over Q_v/A. A slight change among components over Q_v/A, but having the same tendency for several components' group, could be examined.



GCMS Analysis VOC Compound	M.W.	Formula	CAS#	Conc.[a] ug/m3	Threshold[b] ppb	Threshold[b] ug/m3
ACETIC ACID, ANHYDRID	88	C3H4O3	2258-42-6	V		
PENTANAL	86	C5H10O	110-62-3	V	6.03	21.90
ETHANOL, 2-NITRO-, PRC	147	C5H9O4N	5390-28-3	V		
HEXANAL	100	C6H12O	66-25-1	V	13.80	57.5
BUTANOIC ACID	88	C4H8O2	107-92-6	V	3.9	14.50
HEPTANAL	114.2	C7H14O	111-71-7	V	4.79	22.90
CYCLOTETRASILOXANE,	296	C8H24O4Si4	556-67-2			
PENTANOIC ACID	102	C5H10O2	109-52-4	V	4.79	20.40
BENZALDEHYDE	106	C7H6O	100-52-7	V	41.70	186.00
HEXANOIC ACID	116	C6H12O2	142-62-1	V	12.60	60.30
NONANAL	142	C9H18O	124-19-6	V	2.24	13.5

* In the order of Ion Mass, Magnitude, VOC Name
* Range of Q_v/A = 0.35, 0.89 & 2.66 (L/s/m²)
* The underlined above are the major peaks

Figure 1. An example of the emission signature of Linoleum 2 by PTR-MS.

Effect of Airflow on Emission Rate

This phenomenon is related to the different emission characteristics of different VOCs in a material, and can be explained from a decomposed ncps trend plot by each ion mass as shown in Figure 3. Each ion mass corresponds to a VOC. A material may contain VOCs that are either slowly or fast decreasing (decaying) in emission rates. A clear linear-relationship can be established between concentration and area-specific flow rate (Q_v/A) on a log scale for slow decaying compounds (Figure 3). In order to clearly see this trend, the order of the tests was intentionally conducted in this way: mid (Test #1) → high (Test #2) → low level of Q_v/A (Test #0). Methanol (m/z = 33) was one of the fast decaying VOCs over time (Figure 3A), and many compounds in Paint 2 had this trend (Figure 3B). However, there are still several compounds even in this material having the aforementioned linear relationship with the logarithm of Q_v/A.

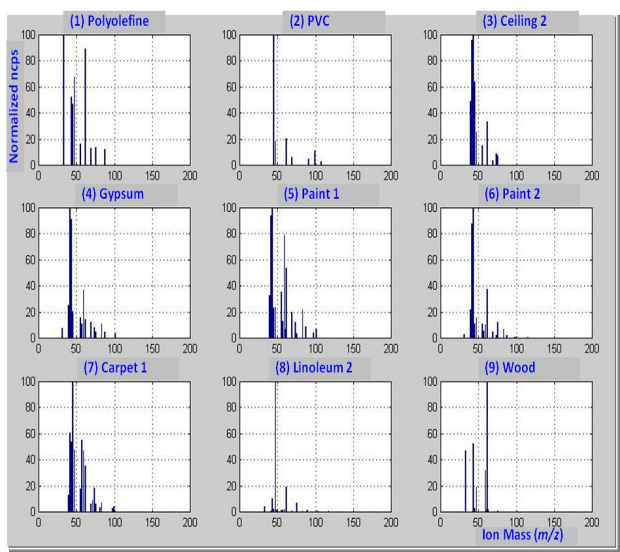


Figure 2. A dataset of emission signatures.

Acceptability vs. *ncps*

Wargocki et al. (2007) reported the linearity of the relationship between the logarithm of Q_v/A and the acceptability with a positive slope. The consecutive three plots indicating the relationship of the acceptability with PTR-MS measurements (*ncps*) are illustrated in Figure 4A. Keeping the relative shape of the mass spectrum over Q_v/A, the linear decrease of the peak values can be found as Q_v/A increases logarithmically. In this case, most of the compounds in the material were less time-dependent decaying species, so the clear linearity of the response to the change of Q_v/A can be seen following inherent emission physics. The higher the ncps values, the lower the acceptability.

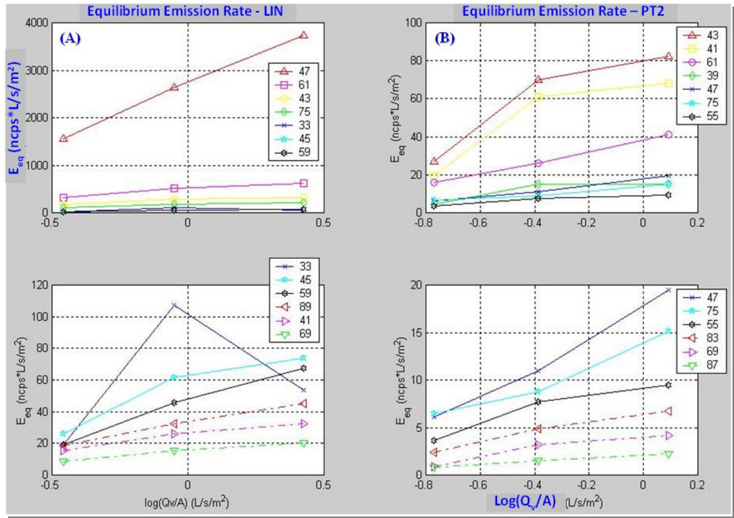


Figure 3. (A) vs. E_{eq} for Linoleum 2. (B) for Paint 2.

VOCs corresponding to Poor Acceptability

Generally, the perceived order intensity of an individual VOC is better correlated with its ratio of concentration to odor threshold. In this sense, a VOC odor index (VOI) may be defined as $VOI = \Sigma\ Ci/Thresh$ (*ppbv/ppbv*) based on the odor thresholds in the VOCBASE of the Danish National Institute of Occupational Health. Since VOI is mostly influenced by VOCs having high OI and threshold values are not available for all compounds detected, we only included up to 3 VOCs with highest OI values to calculate VOI for each material (Figure 4B). Except for Paint 2, the relative ranking based on VOI coincides with that based on the acceptability.

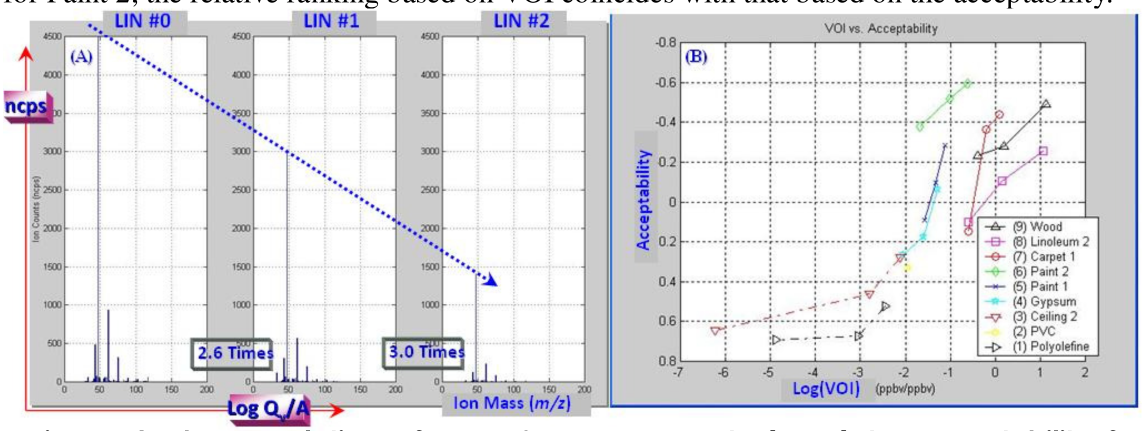


Figure 4. The correlation of PTR-MS measurements (*ncps*) to acceptability for Linoleum 2.
(A) PTR-MS measurement trend for Linoleum 2. (B) VOI vs. Acceptability.

SUMMARY and CONCLUSIONS

Steady emission signatures enabled us to observe material properties and their relationships. The acceptability index was strongly correlated to the log(VOI) forming an S-shaped curve.

REFERENCES

Knudsen, H.N., Wargocki, P. (2006). "Effect of Ventilation on Perceived Quality of Air polluted by Building Materials." *Proc. of HB2006*, Vol. 1, 57-62.

Lindinger, W. et al. (1998). "On-line Monitoring of Volatile Organic Compounds at Pptv Levels by Means of PTR-MS." *Int J Mass Spectrom,* 173, 191-241.

Wargocki, P., Knudsen, H.N. (2007). "Effect of using Low-Polluting Building Materials and Increasing Ventilation." *Proc. of CLIMA 2007*, Helsinki, Finland.