Chamber evaluation of a portable GC with tunable retention and microsensor-array detection for indoor air quality monitoring†

Chia Jung Lu,‡[a] Chunguang Jin[a] and Edward T. Zellers*[ab]

Received 4th November 2005, Accepted 8th December 2005
First published as an Advance Article on the web 9th January 2006
DOI: 10.1039/b515696c

The evaluation of a novel prototype instrument designed for on-site determinations of VOC mixtures found in indoor working environments is described. The instrument contains a miniature multi-stage preconcentrator, a dual-column separation module with pressure-tunable retention capabilities, and an integrated array of three polymer-coated surface acoustic wave sensors. It was challenged with dynamic test-atmospheres of a set of 15 common indoor air contaminants at parts-per-billion concentrations within a stainless-steel chamber under a range of conditions. Vapours were reliably identified at a known level of confidence by combining column retention times with sensor-array response patterns and applying a multivariate statistical test of pattern fidelity for the chromatographically resolved vapours. Estimates of vapour concentrations fell within 7% on average of those determined by EPA Method TO-17, and limits of detection ranged from 0.2 to 28 ppb at 25 °C for 1 L samples collected and analyzed in <12 min. No significant humidity effects were observed (0–90% RH). Increasing the chamber temperature from 25 to 30 °C reduced the retention times of the more volatile analytes which, in turn, demanded alterations in the scheduling of column-junction-point pressure (flow) modulations performed during the analysis. Reductions in sensor sensitivities with increasing temperature were predictable and similar among the sensors in the array such that most response patterns were not altered significantly. Short-term fluctuations in concentration were accurately tracked by the instrument. Results indicate that this type of instrument could provide routine, semi-autonomous, near-real-time, multi-vapour monitoring in support of efforts to assess air quality in office environments.

Introduction

Indoor volatile organic compounds (VOCs) can arise from sources such as building materials, furniture, paint, human activity, indoor chemical reactions and microorganisms, and outdoor infiltration.[1–5] Concentrations of such indoor contaminants will vary spatially and temporally due to changes in generation and ventilation rates and levels of indoor activity.[6] Monitoring the diversity of VOCs encountered at the low concentrations typical of residential, office, and school environments has been a challenge for environmental researchers and health professionals. The most common methods employed entail collection with adsorbent-packed tubes or evacuated canisters followed by laboratory analysis by gas chromatography with mass spectrometric (GC-MS) detection.[7–11] These methods can achieve sub-part-per-billion (sub-ppb) detection limits but typically require long sampling times and are costly because of the need for laboratory work-up and analysis.[9]

Unfortunately, relative few direct-reading instruments are available that can provide field determinations of indoor vapour mixtures. Open-path FT-IR[12,13] and transportable GC-MS systems [14,15] have been used for this purpose but their size, cost, complexity and limited sensitivity prohibit their use for routine or large-scale monitoring campaigns of indoor air contaminants. Portable GCs with conventional detectors (*e.g.*, photo- or flame-ionization) are not generally suitable for this application because of limited resolving power and sensitivity. Short-term SPME-fiber sampling followed by direct portable-GC analysis has been used to reduce detection limits to useful levels but continual operator intervention and sample handling are required.[16] Less sophisticated instruments based on photo- or flame-ionization detectors alone can only provide composite measures of so-called 'total volatile organic compounds' (TVOC),[17,18] which may be useful for source identification or for monitoring general trends in overall vapour concentrations but are not useful for compound-specific analyses or for correlating exposures with health effects.[19]

The objective of the current study was to assess the suitability of a new type of portable multi-vapour monitoring instrument for near-real-time determinations of indoor-VOC mixtures. The instrument is essentially an enhanced portable GC. Unlike standard portable GC instruments equipped with gas sampling loops, on-board carrier-gas supplies, single columns, and single detectors,[20] this instrument employs a multi-stage adsorbent preconcentrator, a dual-column

[a] *Center for Wireless Integrated Microsystems, Department of Environmental Health Sciences, Ann Arbor, MI 48109-2029*
[b] *Department of Chemistry, University of Michigan, Ann Arbor, MI 48109-2029. E-mail: ezellers@umich.edu*
† Electronic supplementary information (ESI) available: vapour recognition. See DOI: 10.1039/b515696c
‡ Current address: Department of Chemistry, Fu Jen Catholic University, 510 Chung Cheng Rd, Hsinchuang, Taipei Hsien 24205 Taiwan.

separation module, and a detector consisting of an integrated array microfabricated chemical sensors. In addition, air is used as the carrier gas. The combination of tunable retention afforded by the separation module and rudimentary vapour recognition afforded by the patterns generated from the microsensor array allow the analytical burden to be distributed, with a net enhancement in versatility and performance.

In a recent series of articles we have described the development of key instrument components[21–26] as well as initial laboratory tests illustrating the operation and advantages of such a system.[26] In this article we report on our first series of tests with the instrument housed inside a chamber and challenged with steady and fluctuating concentrations of VOCs in the ppb range. Performance is also examined over a wide range of ambient humidity and at two temperatures typical of office environments. Quantification accuracy is assessed by comparison with an established reference method (*i.e.*, EPA TO-17). An approach to assessing the fidelity of sensor-array response patterns to calibration-library patterns of chromatographically resolved vapours is also presented. Results are considered in the context of monitoring air quality in indoor (office) working environments.

Experimental

Instrument description

The prototype instrument measures 36 cm (L) × 30 cm (W) × 10 cm (H), weighs about 10 kg, and in its current configuration operates on 115V AC power.[26] It was constructed by Microsensor Systems Inc. (Bowling Green, KY) according to a mutually agreed upon set of operating and design specifications. Fig. 1a presents a block diagram of the key analytical components. The multi-stage preconcentrator/focuser (PCF) consists of a thin-wall stainless-steel tube 1.32 mm id packed with 8 mg of Carbopack B, 2.5 mg of Carbopack X, and 1.8 mg of Carboxen 1000 in sequence separated by small plugs of stainless steel mesh.[21,22] The PCF was designed to provide sufficient adsorption capacity to quantitatively capture up to ~40 VOCs, each at a maximum concentration of 0.1 ppm, in a 1 L sample volume. Rapid heating (*i.e.*, up to 300 °C in <3 s) with backflushing generates a concentrated injection plug that enhances the concentrations of the trapped vapours by factors as high as 5000.[22]

The tunable separation module takes advantage of differential retention factors in two series-coupled columns having complementary stationary phases in addition to junction-point pressure/flow modulation, which allows strategic separation of certain mixture components that would otherwise co-elute.[23–25] The first column (4.5 m long, 0.25 mm id) has a 0.5 μm thick wall coating of a non-polar polydimethylsiloxane stationary phase (Rtx-1, Restek, Bellefonte, PA). The second column has the same dimensions but has a polar polytrifluoropropylmethylsiloxane stationary phase (0.25 μm thick, Rtx-200, Restek). These two columns can be heated rapidly and independently using dedicated embedded heater wires in a so-called 'at-column' heating configuration (RVM Scientific, Santa Barbara, CA). The pressure-tuning valve connects the inlet of the first column to the junction point of two columns,

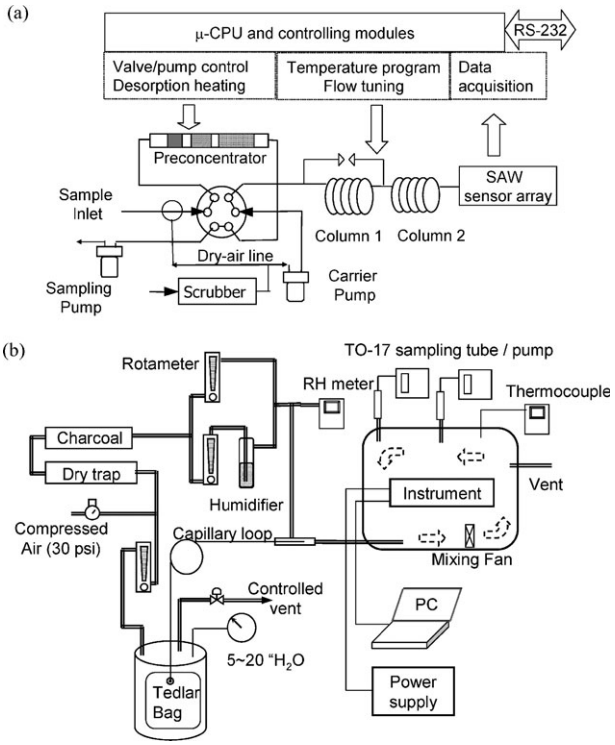

Fig. 1 System diagrams of (a) the prototype instrument, (b) the chamber test system.

which allows the carrier flow to bypass the first column and stop (column 1) or accelerate (column 2) the elution of compounds at several points in time during an analysis.

The sensor array was designed and developed at Sandia National Laboratories, Albuquerque, NM and consists of four surface acoustic wave (SAW) sensors.[27,28] One of the sensors is used as a reference and is uncoated, while the other three were coated, respectively, with polyisobutylene (PIB), ethyl cellulose (ECEL), and a co-polymer of polydimethylsiloxane with hexafluorobisphenol A (BSP3).[29,30] The sensor array can generate a response pattern for each vapour based on differential partitioning into the polymer coatings that is used to discriminate and identify the vapours *via* principal components analysis and comparison with reference patterns established during calibration. When simple mixtures co-elute, the identity and concentration of each component can be extracted from the composite response patterns, as described previously.[31–33]

The parameters for instrument operation (*e.g.*, column temperature program, column-junction-point pressure/flow modulation intervals, sampling time, preconcentrator heating temperature and time, *etc.*) were written as a text file in a personal computer and uploaded to the instrument's microcontroller through the RS-232 interface. Software for data acquisition was written in Lab View® 5.0 (National Instrument Inc., Austin, TX). The separation parameters for a given mixture were determined prior to chamber testing. During initial calibrations to determine response factors and optimal separation conditions, samples of the target vapours diluted in air in a Tedlar bag were introduced into the instrument sampling port by a gas-tight syringe. Chromatographic data

Table 1 Instrument detection limits and comparisons of chamber measurements from the instrument and the reference (TO-17) method

	Vapour	Instrument LOD[a]	Mean[b]	CV (%)	TO-17 Mean[c]	CV (%)	Difference (%)
1	Trichloroethylene	12.4	81	10.0	95	8.3	−15.2
2	2,4-Dimethylhexane	25.1	148	16.5	151	6.8	−2.3
3	Toluene	11.0	125	8.9	144	5.0	−13.2
4	2-Methylheptane	27.6	116	9.3	145	7.8	−4.2
5	Perchloroethylene	5.8	132	4.5	141	6.6	−6.4
6	Chlorobenzene	3.8	116	4.0	129	7.2	−10.1
7	Ethylbenzene	3.8	125	4.4	132	6.6	−5.6
8	*m*-Xylene	3.3	130	8.4	134	5.1	−3.0
9	Styrene	3.0	115	12.1	125	6.7	−7.7
10	Nonane	2.7	126	5.3	131	7.2	−3.4
11	α-Pinene	3.4	128	7.4	134	5.8	−3.9
12	Mesitylene	1.3	56	8.3	59	5.8	−5.2
13	3-Octanone	0.5	58	1.2	61	5.4	−4.8
14	D-Limonene	0.2	63	9.3	68	6.0	−7.2
15	D5	0.2	30	6.6	31	5.8	−3.5
	Average			7.7		6.4	−6.4

[a] LOD = 3 × (baseline standard deviation)/sensitivity for the most sensitive sensor (unit: ppb). [b] Average of five measurements with the instrument (unit: ppb). [c] Average of five pairs of TO-17 measurements (unit: ppb).

from the instrument were stored as a data file and then imported to Grams 32 (Thermogalactics, Inc. Salem, NH) for peak integration. A sample volume of 1 L collected at a flow rate of 180 mL min^{-1} was used for every analysis. The carrier gas was room air drawn through a scrubber by one of the instrument's diaphragm pumps. The carrier gas flow rate through the columns was maintained at 2.5 mL min^{-1}.

Dynamic test atmospheres

Fifteen common indoor volatile organic compounds (VOCs) from several different functional group classes were chosen for the evaluations (Table 1). All of the liquid test compounds were obtained from Aldrich (Milwaukee, WI) except for 2-methylheptane (Acros/Fisher, Pittsburgh, PA) and decamethylcyclopentasiloxane (D5, Gelest Inc., Morrisville, PA). All compounds were used as received.

Vapour mixtures were prepared by injecting from 2–10 μL of each liquid compound into a 12 L Tedlar bag pre-filled with 7 L of clean air from a compressed cylinder using a dry gas meter. Concentrations were calculated from the ideal gas law assuming complete evapouration of the injected liquids and were within the range of 50 to 200 ppm for each component. The vapour mixture was delivered into an initial dilution-air stream (~20 L min^{-1}) at a relatively low continuous flow rate (5–20 mL min^{-1}) by placing the Tedlar bag within a plastic container with a gas-tight seal and applying pressure to the outside of the bag. The plastic container had four connection ports, one each for the compressed air inlet, controlled vent, pressure measurement, and vapour outlet (Fig. 1). Container pressure was monitored by a differential pressure meter. A 1.5 m long, 0.52 mm id deactivated fused silica capillary was inserted into the Tedlar bag through its injection-port septum and connected to the main dilution flow stream *via* another septum in a tee junction. The large pressure drop across the capillary tubing stabilized the sample flow delivery. The delivery flow rate varied approximately linearly with container pressure in the range of 5–20 inches of water, with a differential pressure of 10 inches of water providing a flow rate of 10 mL min^{-1} through the capillary. For dilution factors ranging from 1000–4000, ppb-level concentrations are obtained.

The main dilution-air source was house compressed air passed through traps to remove moisture and trace organic vapours. The stream was divided into two branches, each controlled by a rotameter equipped with a needle valve. One branch was routed through two thermostatted Greenburg–Smith impingers in series containing 500 mL of distilled water each and then returned to the dry air stream. The flow ratio could be adjusted to set the humidity level downstream. A fraction of the well-mixed airflow was bled through a 20 mL Pyrex cell containing a humidity probe (Oakton 35612, Cole-Parmer, Vernon Hills, IL) pre-calibrated using saturated salt solutions.

Exposure chamber

The exposure chamber was fabricated from a 50 L cylindrical stainless steel container (40 cm id, 40 cm deep) with one end open and flanged. The open end allowed the placement of the instrument and mixing fans into the chamber and was sealed with a Teflon gasket and 0.64 cm thick glass cover plate held in place with four C-clamps. Several holes were drilled in the backside of the chamber and equipped with bulkhead fittings for the test atmosphere inlet and outlet, two sampling ports for sorbent-tube samplers (reference method), power cord, data cable, and thermocouple. Stainless steel Swagelok® connectors were used for the fluidic ports. The power cord and data cable were connected through Swagelok® bulkhead connectors with Teflon ferrules pressed tightly on each cord. The thin thermocouple wire was threaded through a Teflon-lined septum inserted in a 1/4″ Swagelok® connector and then extended into the center of the exposure chamber.

The test atmospheres were delivered to the exposure chamber at ~20 L min^{-1}. Assuming ideal dilution with perfect mixing, 12.5 minutes are required to reach 90% of the steady state concentration. Two small fans (15 cm × 15 cm, 12 V DC) enhanced mixing within the chamber. Since the chamber had no active temperature control mechanism, the temperature

was adjusted by changing the thermostat that controlled the laboratory air temperature. Due to the heat generated by the instrument, the chamber temperature remained at 5 ± 1 °C above room temperature. Normally, ~30 minutes was needed to establish a stable temperature within the chamber after resetting the room thermostat. Once established, the temperature was quite stable due to the large mass of the chamber. As a quality control measure, duplicate blank samples (clean air) were collected and analyzed by the instrument prior to initiating an exposure test. In addition, a span calibration was performed before and after each test. This entailed collection of matched instrument and reference measurements and use of the latter to adjust sensitivities as necessary to account for minor sensor drift over the course of the study.

Reference method

US EPA Method TO-17 was used to measure the concentration generated inside the chamber. Sample preparation and analysis followed the criteria in the compendium of methods published by the US EPA.[10] Stainless steel sampling tubes (1/4″ od) were packed with 80 mg of Carbotrap C, 120 mg of Carbopack B, and 60 mg of Carboxen 1000 (Supelco, Bellefonte, PA), separated by silanized glass wool, and preconditioned at 300 °C for 8 hours in a GC oven under a continuous N_2 flow. Sampling pump (224-PCXR7, SKC Inc, Eighty Four, PA) flow rates were set to 100 mL min^{-1} and were calibrated with an electronic flow meter before and after sampling. The TO-17 sampling time was limited to 5 min (~0.5 L volume) to approximate that of a single instrument sampling cycle.

Calibration solutions, prepared by diluting the neat chemicals in CS_2, were spiked sequentially into an adsorbent tube, flushed with clean air, and analyzed. There was no significant difference in peak areas for samples flushed with 0.5 L and 1.0 L of clean air. Spiked calibration sampling tubes were subjected to the same thermal desorption and GC analysis as the chamber samples. Fluorobenzene was used as the internal standard. Statistical analyses were performed using Matlab 7.0 (MathWorks Inc., Natick, MA).

Results and discussion

Optimization of separation conditions

The chromatographic conditions necessary for separation of the representative set of 15 target compounds selected for this study were established in preparation for the chamber tests and are shown in Fig. 2 above the set of three chromatogram traces from the sensors in the array. The temperature program was as follows: 0–120 s at room temperature; 120–190 s at 50 °C, 190–310 s at 70 °C, and 310–450 s at 130 °C. All compounds except for 2-methylheptane and toluene were fully resolved by this temperature program. Since these two compounds are separated in the first column, but re-converge by the end of the second column, they were amenable to pressure-tuned separation.

Toluene elutes from the first column in 82 seconds and 2-methylheptane in 87 seconds. By opening the pressure tuning valve at the column juncture at t = 85 s and leaving it open for three seconds the toluene was accelerated through the second column relative to the 2-methylheptane, which was temporarily retained in the first column, resulting in a 10 second separation between these two compounds at the end of the second column. All compounds eluting after 2-methylheptane therefore had a 3 s shift in retention time. Note that there is no significant peak broadening associated with this procedure. As shown in Fig. 2a–c, all 15 compounds can be adequately separated under these conditions. Limits of detection (LOD) range from 0.2–28 ppb (1 L sample volume) and generally decrease with decreasing vapour pressure as expected for sorption-based detectors (Table 1).

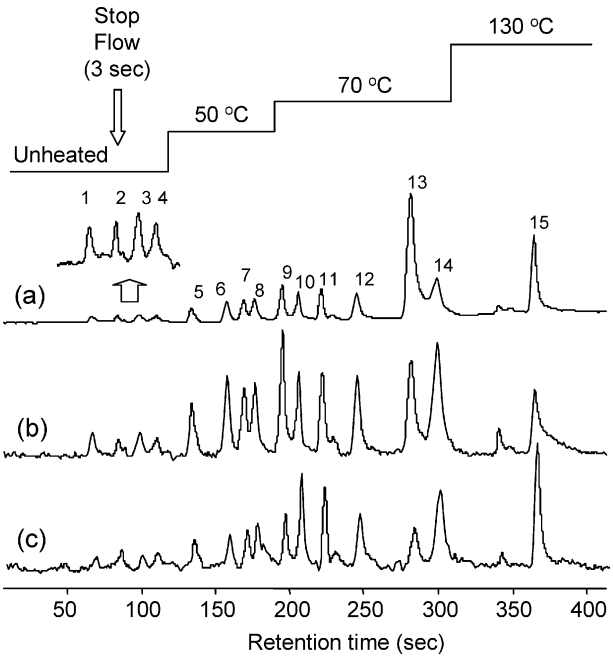

Fig. 2 Temperature program and pressure tuning sequence for the separation of the 15-vapour mixture; chromatograms from (a) BSP3-, (b) ECEL-, and (c) PIB-coated SAW sensors. Compounds are numbered as in Table 1. The y-axis of trace (b) was enhanced by 8× and that of trace (c) by 4× for improved visualization.

Reproducibility

Instrument response stability was evaluated in the chamber by generating a test atmosphere containing all 15 compounds at fixed concentrations and collecting a set of five consecutive measurements over a 1 h period. During the course of this test, the chamber temperature varied by <1 °C and the relative humidity was <4% RH (referred to henceforth as '0% RH'). For each instrument measurement, a pair of TO-17 samples was taken simultaneously. Fig. 3 compares TO-17 and instrument data for an arbitrarily chosen subset of four compounds. Error bars represent the range of each pair of TO-17 measurements. Estimates of the concentration for each vapour i, C_i, were made by combining responses from all three sensors in the array using the following equation:[34]

$$C_i = \frac{(M_{i1}S_{i1} + M_{i2}S_{i2} + M_{i3}S_{i3})}{(S_{i1}^2 + S_{i2}^2 + S_{i3}^2)} \quad (1)$$

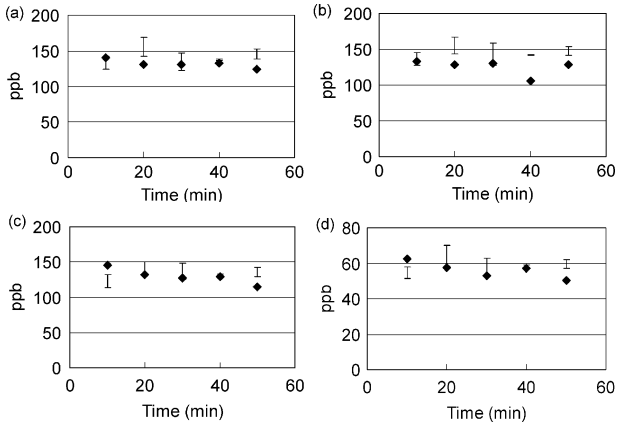

Fig. 3 Representative examples of measurement reproducibility: (a) perchloroethylene, (b) 2-methyl heptane, (c) *m*-xylene, (d) mesitylene (filled diamonds represent instrument responses and vertical brackets mark the range of duplicate TO-17 measurements).

where M_{ij} is the response of each sensor j, and S_{ij} is the corresponding calibration slope.

Table 1 compares the data for all 15 vapours. The average coefficient of variation (CV) of the TO-17 measurements is 6.4%, which reflects a composite of chamber concentration variations and TO-17 measurement uncertainty (*e.g.*, sampling pump flow variation, thermal desorption efficiency variation, FID response variation, *etc.*). The average CV of the instrument measurements is 7.7%, which is similar to that of the reference method. However, the CVs from the TO-17 measurements do not vary much among the different compounds (range = 5.0 to 8.3%), whereas with the instrument some compounds show a particularly large variation (*e.g.*, 2,4-dimethyl hexane, CV = 16.5%) while others show quite a small variation (*e.g.*, 3-octanone, CV = 1.2%). The majority of this variability can be attributed to differences in sensitivity. Retention time variations were very small (*i.e.*, <0.5 s) in all cases.

The average difference between the instrument and TO-17 mean concentration values is -6.4% for the 15 test compounds. While the instrument shows a systematic negative bias, this difference is within the CV range of the measurements. Thus, the accuracy of the instrument appears to be reasonably good.

Vapour recognition using retention time and sensor array response pattern

The advantage of using multi-sensor array detection is the capability for vapour recognition afforded by the pattern of responses, shown in Fig. 4 for the vapours studied here. The response patterns provide information about the physical and/or chemical interaction between vapours and sensor coatings as determined by their chemical structures. The sensor array output can be considered a crude spectrum, akin to IR or MS, but based on differential sorption. Note the similarity among response patterns of vapours from the same chemical classes. Fortunately, homologous vapours are generally readily separated chromatographically due to differences in volatility. Furthermore, by dividing the chromatogram into retention

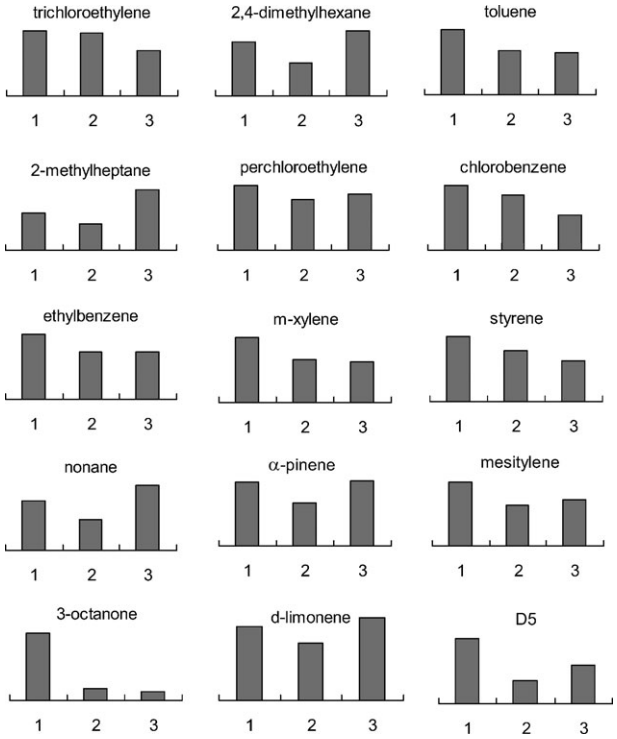

Fig. 4 Sensor-array response patterns of the 15 target compounds in order of elution. Each pattern is normalized by dividing all sensor responses by that for the most sensitive sensor for a given vapour.

time windows, each pattern recognition analysis can be confined to only those vapours falling within the window under consideration.[26] In this case we have complete resolution of all compounds, which simplifies the analysis. However, as mentioned above, it has been shown that co-elution of two, or at most three, vapours within a retention-time window could be tolerated while maintaining the capability for recognition and quantification of the vapours *via* pattern recognition.[31–33]

In virtually all reported applications of sensor arrays, pattern recognition entails comparisons between a measured pattern and a set of possible calibrated-vapour patterns, with identities being assigned on the basis of pattern matching. Similar problems are encountered in GC-MS and have been addressed by a number of methods for matching an unknown sample spectrum to a reference spectrum stored in a database.[35] The problem faced here cannot be solved by such methods, but rather relies on establishing a test of fidelity to a single calibrated pattern of a measured pattern that may become distorted to varying extents by aging of the sensors, by the presence of uncalibrated interferences, or possibly by shifts in temperature or humidity (see below). Placing a statistical threshold on the allowable degree of distortion is required in order to make meaningful assignments of vapour identity from response patterns of fully resolved peaks. This is an ostensibly simple problem, but one that has not yet been addressed in the context of vapour recognition with sensor arrays used as GC detectors.

To address this problem we have employed a multivariate statistical goodness-of-fit method commonly used in chemometric classification models such as SIMCA[36] to assess fidelity

at a known level of confidence. Briefly, calibration data are used to define clusters in the 3-dimensional space whose boundaries are defined by the spread among replicate sensor-array response vectors for a given vapour over the range of calibrated concentrations. The so-called Mahalanobis distance is then calculated and used to establish a spatial threshold (boundary) for deciding whether subsequent sample vectors fall within an acceptable distance from the cluster mean to be considered to have been generated by the vapour corresponding to that cluster. In order to establish decision rules with known error rates, we use an F statistic with the degrees of freedom determined by the sample size and number of sensors in the array.

A confidence level of 95% was selected in all cases addressed in this study. Details of the fidelity test as applied to this type of problem are given in the Supporting Information accompanying this article.

The fidelity test methodology was applied initially to a series of eight chromatograms collected successively from the instrument in the chamber at 25 °C and <4% RH. The vapour concentrations were all well above the limits of detection in all cases (Table 1). Thresholds on the allowable variability in response patterns (vectors) were first established from a training set consisting of data from a series of chromatograms collected during calibrations and independent exposures under the same environmental condition. Individual-vapour peak areas (n = 9–15) were pooled in order to get good estimates of response variation in the training set. Among the 120 test-set samples (8 replicates of 15 vapours) 111 (93%) were correctly recognized and there were at most two errors in recognition for any vapour (7 of the 15 vapours were recognized without error). This recognition rate matched that for the training set (194/210 = 93%).

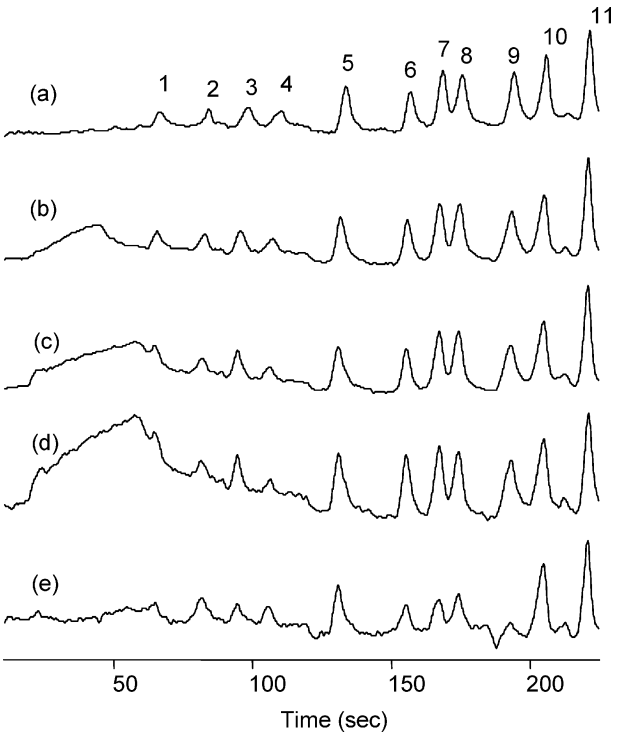

Fig. 5 Chromatograms obtained from the BSP3-coated sensor at (a) 0, (b) 45, and (c) 90% RH; (d) ECEL- and (e) PIB-coated sensors at 90% RH. See Table 1 for vapour identities. Only the first 11 (of 15) vapours are shown. The y-axis for each chromatogram was scaled independently to enhance visual comparisons such that peak heights between traces are not comparable.

Humidity effects

The instrument was then challenged with the 15-vapour mixture at a constant chamber temperature (25 °C) and 0, 45, and 90 ± 2% RH. The normal operating cycle of the instrument incorporates a dry air purge of the PCF after sampling to reduce the influence of environmental humidity.[21] That is, following sample collection, the inlet valve directs the incoming air stream through a cartridge containing a small bed of $CaSO_4$ and then across the PCF for 50 s prior to heating. Fig. 5 shows sections of the chromatograms from the BSP3-coated sensor at the three different RH levels as well as the corresponding sections of the chromatograms from the other two sensors at 90% RH. Although the dry-air purge step removes the majority of water vapour trapped in the adsorbent, there is still a residual quantity, believed to be retained on the Carboxen 1000,[37] which is thermally desorbed along with the trapped VOCs and detected primarily by the more polar BSP3 and ECEL-coated sensors. The water vapour elutes rapidly because it is not retained strongly on the GC stationary phases and it can be seen clearly in Fig. 5 that trapped humidity has no effect on the later eluting compounds under any conditions. At high humidity (90% RH), the residual water vapour elutes as a broad peak in the 0–75 second retention time range, and can affect the integration of early eluting peaks (*e.g.*, trichloroethylene) on the BSP3 and ECEL-coated sensors. Note, however, that the PIB coated sensor does not respond to residual water vapour even at 90% RH, and that effective quantification is possible even for these early eluting vapours on the basis of responses from all three sensors by baseline subtraction.

Tests were duplicated at each RH level using the same vapour-mixture challenge. Table 2 reports the sensitivity ratios at the different RH levels. The average 45 : 0 and 90 : 45 ratios are 0.95 and 0.99, respectively, across all compounds, and the average 90 : 0 ratio is 0.93. It appears that increasing RH causes a systematic negative bias. However, the overall −7% error is within the instrument short-term CV (±7.7%).

The independence from humidity effects observed in this data set is consistent with results reported from other studies of polymer-coated SAW-sensor based instruments employing adsorbent preconcentrators without a separation column.[38,39] To more rigorously assess the consistency of the response patterns as a function of humidity, fidelity tests were run using data derived from the pooled set of array responses at 0% RH as a training set and response patterns obtained at 45 and 90% RH as test sets. F-tests performed on the 30 response patterns at the higher RH levels (average of duplicate exposures at each elevated RH level for each vapour) indicated that 29 had no significant difference in pattern (the exception was α-pinene at 90% RH).

Table 2 Effects of ambient humidity on vapour sensitivities from 0–90% RH[a]

Vapour	RH45 : 0	RH90 : 0	RH90 : 45
Trichloroethylene	1.12	0.96	0.86
2,4-Dimethylhexane	1.00	0.98	0.99
Toluene	0.84	1.08	1.31
2-Methylheptane	0.93	0.77	0.82
Perchloroethylene	0.96	0.87	0.91
Chlorobenzene	0.99	0.98	0.99
Ethylbenzene	0.92	0.89	0.97
m-Xylene	0.93	0.87	0.94
Styrene	0.96	0.94	0.97
n-Nonane	0.91	0.93	1.01
α-Pinene	0.84	0.91	1.08
Mesitylene	0.96	0.92	0.96
3-Octanone	0.94	0.94	1.00
D-Limonene	0.95	0.92	0.97
D5	0.94	1.05	1.12
Average	0.95	0.93	0.99
Range	0.84–1.12	0.77–1.08	0.82–1.31

[a] Entries in the table are ratios of sensitivities at the indicated ambient %RH levels determined from duplicate determinations in the range of 20–163 ppb.

Temperature effects

Table 3 presents the shifts in retention times and sensor responses incurred with a change in chamber temperature from 25 to 30 °C. This is a relatively small temperature change but not too different from what would be expected in an air-conditioned office environment.[40] Since the separation conditions employed rely on an unheated column for the first two minutes in order to separate the least volatile compounds in the mixture, it is not surprising that the initial column temperature increase accompanying a rise in ambient temperature causes a decrease in retention time for the early eluting compounds. As shown in Table 3, the early eluting compounds are accelerated to a greater extent than the later eluting compounds, which are not as mobile at 25–30 °C within the column.

These retention time shifts can have an impact on pressure tuning. The timing of actuation of the tuning valve to selectively separate certain pairs of compounds relies critically on their respective elution times across the column junction. Originally, the separation of 2-methylheptane and toluene at 25 °C relied on the 3 s stop-flow interval at $t = 85$ s into the run. When the chamber temperature rises to 30 °C, toluene and 2-methylheptane pass through the first column at approximately $t = 74$ and 78 s, respectively, and co-elute from the column ensemble because the timing of the pressure-tuning event was not adjusted to account for the reduced retention. The shift in retention time with temperature reported in Table 3 for 2-methylheptane is therefore larger than expected on the basis of temperature effects alone.

The reductions in sensor sensitivity are fairly consistent among the sensors and test compounds, averaging about 20% except for perchloroethylene (PCE) which was reduced by ~50% (note: the ratio of the composite toluene + heptane peak area at 30 °C to that of the sum of the individual peaks at 25 °C was within the expected range). The larger value for PCE, however, is an artifact of the accelerated elution of this compound, which fortuitously passed across the sensor array at a point ($t = 120$ s) when the column temperature was stepped up and the sensor baselines experienced a transient shift due to poor isolation of the column heater circuit. The integrity of the PCE peak was affected. This is more apparent in the ECEL- and PIB-coated sensors than in the BSP3-coated sensor because the ECEL- and PIB-coated sensors give smaller PCE signals.

The temperature dependence of the sensitivities of several polymer-coated SAW vapour sensors is reported in ref. 40. One coated sensor (PIB) and two vapours (trichloroethylene and *m*-xylene) were tested in both that previous study and this one. Temperature coefficients of sensitivity near 25 °C of

Table 3 Temperature effects on retention times and sensor responses

		Sensitivity ratio[b]			
Vapour	Reten. time shift/s (%)	BSP3	ECEL	PIB	Avg
Trichloroethylene	−6.5 (−9.6)	0.92	0.79	0.71	0.81
2,4-Dimethylhexane	−9.6 (−11.3)	0.87	0.90	0.81	0.86
Toluene[c]	−11.0 (−11.1)	0.75	0.71	0.73	0.73
2-Methylheptane[c]	−22.4 (−20.3)	0.75	0.71	0.73	0.73
Perchloroethylene	−13.7 (−10.2)	0.63	0.50	0.49	0.54
Chlorobenzene	−9.9 (−6.3)	0.81	0.79	0.70	0.76
Ethylbenzene	−8.8 (−5.2)	0.83	0.80	0.60	0.74
m-Xylene	−8.2 (−4.6)	0.83	0.83	0.75	0.80
Styrene	−8.0 (−4.1)	0.74	0.73	0.74	0.74
Nonane	−6.2 (−3.0)	0.97	0.91	0.72	0.87
α-Pinene	−4.4 (−2.0)	0.81	0.74	0.76	0.77
Mesitylene	−4.5 (−1.8)	0.76	0.86	0.85	0.82
3-Octanone	−4.5 (−1.5)	0.75	0.80	1.02	0.86
D-Limonene	−5.4 (−1.9)	0.78	0.76	0.88	0.81
D5	−2.9 (−0.8)	0.77	1.14	0.87	0.92
Average[d]		0.81	0.83	0.78	0.81
CV(%)		10.4	7.3	15.0	7.5

[a] Average shift from 25 °C to 30 °C; $n = 4$ at each temperature. [b] Average ratio of responses at 30 °C to those at 25 °C; $n = 4$ at each temperature. [c] Retention time shifts and response ratios are calculated from the sum of the individual peaks for toluene and 2-methylheptane at 25 °C and the composite (toluene + 2-methylheptane) peak at 30 °C. The unusually large retention shift for 2-methylheptane arises from the absence of the pressure-tuned increase in retention at 30 °C (see text). [d] Excluding perchloroethylene (see text).

$-3.8\%\ ^{\circ}C^{-1}$ and $-4.6\%\ ^{\circ}C^{-1}$ were reported for trichloroethylene and *m*-xylene on a PIB-coated SAW sensor, respectively. Accordingly, a 5 °C increase should cause a 19% and 23% loss in sensitivity, respectively. In the current study, the sensitivity losses for these vapours on PIB were 29% and 25%, in reasonable agreement with expectations.

Fidelity tests of the data collected at 30 °C, excluding PCE (*vide supra*), indicated that only D5, which is a component of anti-perspirants, showed a significant change in response pattern at the elevated temperature relative to that at 25 °C (the test set consisted of the average of replicate peak areas collected at 30 °C for each of the 14 remaining vapours). Note that the pattern derived from the composite (co-eluting) toluene/2-methylheptane peak obtained at 30 °C showed no significant difference from the pattern derived from the concentration-weighted sum of the individual peaks obtained at 25 °C. These findings are consistent with those reported elsewhere showing no change in response patterns from polymer-coated SAW sensor arrays for most vapours over modest temperature ranges.[38,39,41]

Fluctuating exposure profiles

To assess the ability of the instrument to respond to vapour concentrations fluctuating on a time scale shorter than the 5 min sample collection period of the instrument, the generation rate of the 15-vapour mixture was altered to varying degrees and in different directions over the course of a 50 min test period. This was achieved by brief changes in the pressure applied to the Tedlar bag containing the test mixture while keeping the dilution flow rate constant. Although the chamber concentration could not achieve a steady-state level at this rate of concentration change, the mixing provided by the chamber fans should be sufficient to expect similar values from the instrument and the reference samplers.

Fig. 6 presents data for five samples from three representative vapours, showing the close correlation between the reference method results and those obtained from the instrument. The concentration spanned about a 4-fold range. The average error in concentration estimates for the five measurements among all 15 compounds was −2% (range: −9 to +15%) and the average CV was 10% (range: 5–24%), which is slightly larger than for the steady concentration test (*i.e.*, 8%) and can be ascribed to the greater influence of sensor baseline noise on the lower-concentration samples–for several of the vapours the largest errors occurred at the lowest test concentration. In fact, at the lower concentrations, some of the sensors did not yield reliable signals for the most volatile analytes. Fidelity testing of the 69 (out of 75) samples with measurable signals from all three sensors revealed only four in this series where the measured response pattern did not match the calibration pattern at the 95% confidence level.

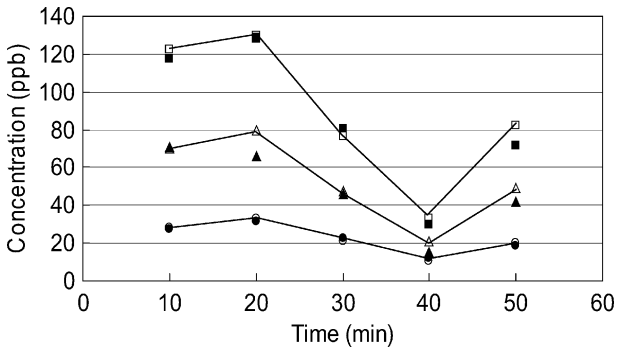

Fig. 6 Comparison of portable-GC (filled symbols) and TO-17 (open symbols) results for fluctuating concentrations of three representative compounds (out of 15): perchloroethylene (squares), styrene (triangles), 3-octanone (circles). Lines merely connect the points corresponding to the TO-17 results for a given vapour.

Conclusions

This study has explored the performance of a prototype portable GC with several unique design and operating features, including multi-stage adsorbent preconcentration; dual-column, tunable separation; and microsensor array detection. Results of this series of chamber tests confirm earlier laboratory tests indicating that these features afford several performance enhancements relative to more standard portable GC instrumentation. Detection limits in the low-/sub-ppb range are achievable with modest sample volumes and chromatographic resolution is sufficient to achieve baseline separation of a 15-component mixture of typical VOCs in ~6 minutes (overall duty cycle of <12 minutes). Accuracy and precision are comparable to those achievable with a standard reference method and humidity has little or no effect on performance. Using ambient air as the carrier gas eliminates the need for an on-board gas supply and the associated shortcomings. Although changes in ambient temperature influence both the separation and detection functions, the effects are well-behaved and compensatable. Still, the effect on retention of a relatively small temperature change is noteworthy and demands that the ambient temperature be monitored and changes be made to any pressure tuning program established during calibration.

The combination of rapid, tunable separation and sensor array detection is a key feature of this instrument. Response patterns obtained from the array increase the reliability of qualitative analysis relative to GCs that rely only on retention time for this function. The approach presented here for assessing the fidelity of the response patterns from a chromatographically resolved vapour to its corresponding library pattern is quite straightforward. The decision rule assigns vapour identities within a given retention time window at a known level of confidence. Additional testing of this approach in the presence of increasing concentrations of co-eluting vapours will permit an assessment of its sensitivity to this important source of 'pattern distortion'.[33]

Results obtained in this study have been used to guide the design and construction of a second-generation instrument with independent temperature programming of each column, improved isolation of column-heater and sensor-readout circuitry, continuous rather than step-wise changes in column temperature, and a different (thermostatted) microsensor technology that affords even lower detection limits. Preliminary tests focused on analyzing vapour-phase markers of environmental tobacco smoke are very promising.[42]

Acknowledgements

The authors are indebted to the following individuals: Patrick Lewis of Sandia National Laboratories, Albuquerque, NM for providing the SAW sensor arrays used in this instrument; Hank Wohltjen, Brent Busey, and Mark Klusty of Microsensor Systems, Inc. for constructing the instrument and providing on-going technical assistance throughout the project; and Daniel Normolle for assistance with the statistical analyses. Funding for this research was provided by Grant R01-OH03 692-04 from the National Institute for Occupational Safety and Health of the Centers for Disease Control and Prevention (NIOSH-CDCP). This work made use of Engineering Research Centers Shared Facilities supported by the National Science Foundation under Award Number EEC-0096866.

References

1 P. Wolkoff, *Indoor Air*, 1995, **5**(suppl. 3), 9–73.
2 H. C. Shield, D. M. Fleischer and C. J. Weschler, *Indoor Air*, 1996, **6**, 2–17.
3 A. Pasanen, S. Lappalainen and P. Pasanen, *Analyst*, 1996, **121**, 1949–1953.
4 D. Norback, G. Wieslander, G. Strom and C. Edling, *Indoor Air*, 1995, **5**, 166–170.
5 P. Wolkoff, T. Schneider, J. Kildeso, R. Degerth, M. Jaroszewski and H. Schunk, *Sci. Total Envrion.*, 1998, **215**, 135–156.
6 J. Ten Brinke, S. Selvin, A. T. Hodgson, W. J. Fisk, M. J. Mendell, C. P. Koshland and J. M. Daisey, *Indoor Air*, 1998, **8**, 140–152.
7 M. R. Van Winkle and P. A. Scheff, *Indoor Air*, 2001, **11**, 49–64.
8 S. K. Brown, M. R. Sim, M. J. Abramson and C. N. Gray, *Indoor Air*, 1994, **4**, 123–134.
9 C. Y. Peng and S. Batterman, *J. Environ. Monit.*, 2000, **2**, 313–324.
10 US EPA, *TO-17, Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air*, Report No. EPA/625/R-96/010b, US Environmental Protection Agency, Washington, DC, 2nd edn, 1997.
11 US EPA, *TO-14, Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air*, Report No. EPA/625/R-96/010b, US Environmental Protection Agency, Washington, DC, 2nd edn, 1997.
12 A. C. Drescher, D. Y. Park, M. G. Yost, A. J. Gadgil, S. P. Levine and W. W. Nazaroff, *Atmos. Environ.*, 1997, **31**, 727–740.
13 M. Y. Tsai, M. G. Yost, C. F. Wu, R. A. Hashmonay and T. V. Larson, *Atmos. Environ.*, 2001, **35**, 4791–4799.
14 M. A. Puskar and M. R. Plese, *Am. Ind. Hyg. Assoc. J.*, 1996, **57**, 843–848.
15 G. E. Spangler and R. A. Miller, *Int. J. Mass Spectrom.*, 2002, **214**, 95–104.
16 M. Jia, J. Koziel and J. Pawliszyn, *Field Anal. Chem. Technol.*, 2000, **4**, 73–84.
17 S. Batterman and C. Y. Peng, *Am. Ind. Hyg. Assoc. J.*, 1995, **56**, 55–65.
18 L. Mølhave, G. Clausen, B. Berglund, J. De Ceaurriz, A. Kettrup, T. Lindvall, M. Maroni, A. C. Pickering, U. Risse, H. Rothweiler, B. Seifert and M. Younes, *Indoor Air*, 1997, **7**, 225–240.
19 P. Wolkoff and G. D. Nielsen, *Atmos. Environ.*, 2001, **35**, 4407–4417.
20 http://www.clu-in.org/products/site/camp/photovac.htm.
21 C.-J. Lu and E. T. Zellers, *Anal. Chem.*, 2001, **73**, 3449–3457.
22 C.-J. Lu and E. T. Zellers, *Analyst*, 2002, **127**, 1061–1068.
23 A. J. Grall, E. T. Zellers and R. D. Sacks, *Environ. Sci. Technol.*, 2001, **35**, 163.
24 J. J. Whiting, C.-J. Lu, E. T. Zellers and R. D. Sacks, *Anal. Chem.*, 2001, **73**(19), 4668–4675.
25 J. J. Whiting and R. D. Sacks, *Anal. Chem.*, 2002, **74**, 246.
26 C.-J. Lu, J. J. Whiting, R. D. Sacks and E. T. Zellers, *Anal. Chem.*, 2003, **75**(6), 1400–1409.
27 E. J. Heller, V. M. Hietala, R. J. Kottenstette, R. P. Manginell, C. M. Matzke, P. R Lewis, S. A. Casalnuovo, G. C. Frye-Mason, M. Butler, N. Yamazoe, P. Vanysek and M. Aizawa, *Proceedings of Electrochemical Society Meeting*, ECS Inc., Pennington, NJ, 1999, vol. 99–23, pp. 138–142.
28 G. C. Frye-Mason, R. J. Kottenstette, P. R. Lewis, E. J. Heller, R. P. Manginell, D. R. Adkins, D. Dullock, D. Martinez, D. Sasaki, C. Mowry, C. Matzke and L. Anderson, *Proceedings of Micro Total Analysis Systems*, Kluwer Academic Publishers, Dordrecht, Netherlands, 2000, pp. 229–232.
29 J. W. Grate, S. J. Patrash and S. N. Kaganove, *Anal. Chem.*, 1999, **71**, 1033.
30 J. W. Grate, S. N. Kaganove, S. J. Patrash, R. Craig and M. Bliss, *Chem. Mater.*, 1997, **5**, 1201.
31 J. Park, W. A. Groves and E. T. Zellers, *Anal. Chem.*, 1999, **71**, 3877–3886.
32 J. Park, G. Z. Zhang and E. T. Zellers, *Am. Ind. Hyg. Assoc. J.*, 2000, **61**, 192–204.
33 M. D. Hsieh and E. T. Zellers, *Anal. Chem.*, 2004, **76**, 1885–1895.
34 M. A. Sharaf, D. L. Illman and B. R. Kowaski, in *Chemometrics*, John Wiely and Sons Inc., New York, 1986.
35 S. E. Stein and D. R. Scott, *J. Am. Soc. Mass Spectrom.*, 1994, **5**, 859–866.
36 B. G. M. Vandeginste, D. L. Massart, L. M. C. Buydens, S. De Jong, P. J. Lewi and J. Smeyers-Verbeke, in *Handbook of Chemometrics and Qualimetrics*, Elsevier, Amsterdam, Netherlands, 1998, pp. 228–232.
37 J. Gawlowski, J. Niedzielski, E. Pietruszynska, M. Gawrys and J. Niedzielski, *Analyst*, 2000, **125**, 2112–2117.
38 J. Park and E. T. Zellers, *Analyst*, 2000, **125**, 1775–1782.
39 M. D. Hsieh and E. T. Zellers, *J. Occup. Environ. Hyg.*, 2004, **1**, 149–160.
40 B. W. Olesen, *Indoor Air*, 2004, **14**(suppl. 7), 18–26.
41 E. T. Zellers and M. Han, *Anal. Chem.*, 1996, **68**, 2409–2418.
42 Q. Zhong, W. H. Steinecker and E. T. Zellers, *Rare Metal Mater. Eng.*, in press.

