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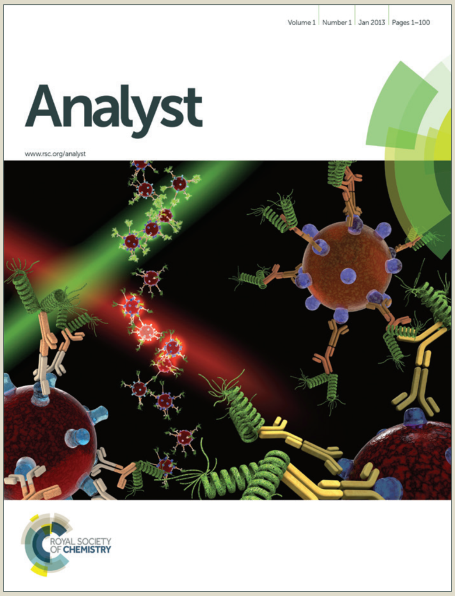

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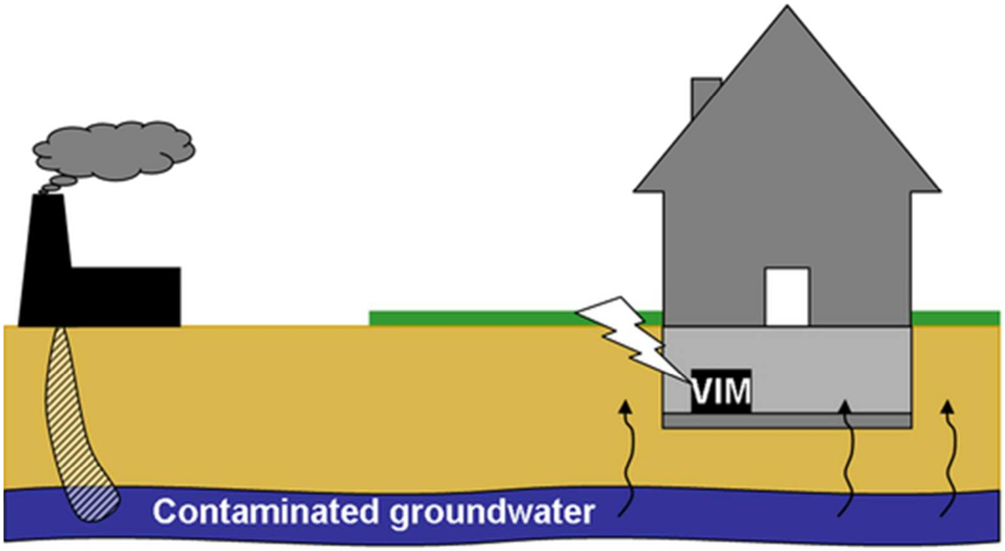

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ARTICLE TYPE

Developments toward a Low-Cost Approach for Long-Term, Unattended Vapor Intrusion Monitoring

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There are over 450,000 sites contaminated by chemicals in the US. This large number of contaminated sites and the speed of subsurface migration of chemicals pose considerable risk to nearby residences and commercial buildings. The high costs for monitoring around these site stem from the labor involved in placing and replacing the passive sorbent vapor samplers and the resultant laboratory analysis. This monitoring produces sparse data sets that do not track temporal changes well. To substantially reduce costs and better track exposures, less costly, unattended systems for monitoring soil gases and vapor intrusion into homes and businesses are desirable to aid in the remediation of contaminated sites. This paper describes progress toward the development of an inexpensive system specifically for monitoring vapor intrusion; the system can operate repeatedly without user intervention with low detection limits (1 x 10^{-9}, or 1 part-per-billion). Targeted analytes include chlorinated hydrocarbons (dichloroethylene, trichloroethane, trichloroethylene, and perchloroethylene) and benzene. The system consists of a trap-and-purge preconcentrator for vapor collection in conjunction with a compact gas chromatography instrument to separate individual compounds. Chemical detection is accomplished with an array of chemicapacitors and a metal-oxide semiconductor combustibles sensor. Both the preconcentrator and the chromatography column are resistively heated. All components are compatible with ambient air, which serves as the carrier gas for the gas chromatography and detectors.

Introduction

Regulatory agencies are currently discussing and developing policy recommendations from the U.S. Environmental Protection Agency (EPA) regarding a framework for assessing vapor intrusion from subsurface sources. Vapor intrusion occurs when vapor-phase contaminants migrate from subsurface sources into buildings and may occur anywhere down-gradient from sites where hazardous chemicals have been used, stored or abandoned, whether releases of the contamination was inadvertent or intentional.[1] Volatile chemicals in buried wastes and/or contaminated groundwater migrate through subsurface soils and seep through cracks or other openings in basement walls or foundations to reach air spaces of overlying buildings.[2] Liquid contaminants and contaminated groundwater flow in response to gravity or disperse through diffusion, allowing the noxious contaminants to travel great distances from their source. In the U.S., there are over 450,000 brownfields[3,4] and 1,319 Superfund[5] sites with hazardous chemicals that contaminate watersheds, aquifers, and municipal water systems[6]. Sites include former drycleaners (chlorinated solvents), military installations (solvents and petrochemicals) industrial facilities (solvents), gas stations (petrochemicals) and even isolated sites where people have discarded wastes. Hence, vapor intrusion is considered a significant cause of human exposure to hazardous chemicals in indoor spaces, as concentrations of vapors may accumulate indoors to levels that pose inhalation and/or flammability risks.

Hazardous chemicals present in vapor intrusion scenarios include halogenated hydrocarbons such as trichloroethylene (TCE) and perchloroethylene (PCE), and aromatic hydrocarbons such as benzene and xylene common to petroleum products.[7,8] Vapor plumes may emanate from contaminated sites (e.g. Superfund sites or leaking underground storage tanks) for many years after contaminating activities have ceased, and remediation may take years to complete. Whereas many types of bacteria can step-wise, reductively dechlorinate chloro-ethylenes (PCE→TCE→DCE→VC→ethylene),[9] these steps occur at different rates; thus, relative levels of each species measured over time can be used to track the attenuation process to assess the effectiveness of natural attenuation in soils and groundwater against established models. Furthermore, other processes (e.g. abiotic attenuation or hydrolysis) can produce other daughter products. Identifying these compounds enables researchers to study remediation progress.

Despite the large number of contaminated sites, careful monitoring of risks around these sites has been sparse. Regulatory agencies, indoor air quality (IAQ) experts and environmental remediation specialists currently lack analytical instruments that allow for frequent, long-term monitoring of potentially contaminated sites to assess exposures, identify contamination sources, and monitor remediation progress at sites.

Further complications arise in assessing exposures since concentrations of vapor intrusion chemicals vary from site to site, building to building, or floor to floor within a single building. Concentrations vary with distance from the source, physical integrity of the structure, and permeability of the subsurface soil. Any actions taken to ameliorate risks depend on the level of estimated risk using a number of methods. For example, the EPA's listed residential air screening level[10] for a 1 x 10^{-6} target risk factor is approximately 0.08 parts-per-billion by volume,[‡] (ppbV) for TCE.

Current Technology

Due to interest in improving public health, a number of approaches are being investigated for intrusion monitoring. At this time, the state-of-the art fielded system for measuring vapor intrusion is the HAPSITE field-portable gas chromatograph/mass spectrometer (GC/MS) (Inficon, Inc. East Syracuse, NY). This instrument offers 1 part-per-trillion (ppt) detection limits, and provides extremely high selectivity. The instrument consists of a conventional gas chromatograph with sorbent vapor trap and uses bottled carrier gas and battery power pack. The entire instrument weighs about 19kg with an approximately 3-hr run time before recharging is needed.[11]

Several research groups[12,13,14,15,16] are developing Micro-GCs to increase duty cycle, reduce instrument costs, and minimize consumption of consumables. Several reported micro-GC systems include microfabricated chromatographic columns, trap-and-purge preconcentrators and detectors. Kim, et al. recently reported that detection limits of 0.052 ppb could be estimated for TCE vapor intrusion in a test house using a chemiresistor array.[12] The state of development for these micro-devices ranges from laboratory research stage to field tested and commercialized.[17,18] Whereas these micro-devices have great potential for reducing size and power for improved portability, their prices have yet to drop to levels allowing mass deployment or long-term monitoring. Other techniques, such as Raman spectroscopy, have been show capable of detecting sub part-per-million levels of chlorinated compounds.[19] However, Raman instruments do not offer lower cost or greater sensitivity than current GC-based monitors. Issues slowing commercialization include low sample collection flow rates, requiring highly sensitive detectors to detect the low concentrations required for meaningful assessment of vapor intrusion risks.

While the HAPSITE and similar available instruments supply accurate snap-shot data regarding vapor intrusion conditions, their high cost and rapid depletion of consumables are not consistent with long-term monitoring in homes or offices. Vast efforts have been expended to develop instrumentation for vapor intrusion studies, but there is still an unfilled niche for low-cost instruments that can measure levels of vapor intrusion chemicals unattended for extended periods of weeks to months.[4,6]

Herein we report on the capabilities of a low-cost (< $2000 U.S.), unattended, long-term (1 - 12 months) monitor to detect ppb-levels of common vapor intrusion chemicals. In developing such an instrument, it is recognized that some sensitivity and speed may be sacrificed to achieve a low-enough cost such that multiple instruments that can be deployed at contaminated sites to provide long-term spatial and temporal trend data. The benefits of hourly or daily concentration tracking over periods of weeks to months is seen as impetus for further development of a low-cost instrument.

This vapor intrusion monitor (VIM) work builds on earlier developments of sorbent traps (preconcentrators)[20] and oven-less gas chromatographs for education[21] and industry[22]. The VIM system consists of a packed-tube preconcentrator, a resistively heated commercial chromatography column, and a detector array.

Experimental

VIM Validation Testing

VIM instruments were validated using a vapor mixing and delivery system consisting of a bank of computer-controlled mass flow controllers, gas cylinders, and valves.[23] House air was sourced from an air compressor (JUN-AIR #2000-40M) and dried with Drierite (W.A. Hammond Drierite Company, Xenia, OH). To deliver controlled chemical concentrations, calibrated dilute gas mixtures in air were delivered through the mass flow controllers as needed. Note that there are trace-levels of water present, which stem from the house air and drying system, and from leaks in the connections between the gas mixing station and the inlet of the preconcentrator. A LabVIEW 2011-based software program was developed to control the VIM and automatically record output from the detectors. Collection times, column and sensor temperatures, and flow pressure were all programmed in software for each experiment in order to compare different conditions.

Analytes

Target analytes (benzene, t-1,2-dichloroethylene (t-1,2-DCE), trichloroethylene (TCE), 1,1,2-trichloroethane (TCA), and perchloroethylene (PCE)) were purchased from MESA Specialty Gas (Santa Ana, CA) in the form of pre-mixed gas cylinders containing either 20ppbV of all five chemicals or 25 parts-per-million by volume (ppmV) of each of the four chlorinated compounds (balance dry air).

Sensors

In this work, two detector technologies were evaluated: a conventional heated metal-oxide semiconducting (MOS) detector and an array of polymer-filled microfabricated capacitors. The MOS detector (TGS #2620, general VOC detector) from Figaro USA, Inc.[24] was chosen due to its recognized sensitivity to a wide range of combustible vapors. The MOS device contains a catalytically active semiconducting film of SnO_2 whose electrical resistance is modified by the relative amount of reducing and oxidizing gases in its environment.[25] Reducing gases cause the surface density of the negatively charged oxygen to decrease, reducing the electrical resistance of grain boundaries. When exposed to oxygen, in the air, these grain surfaces are replenished, and the resistance of the film increases. For a given chemical, the concentration (C) dependent resistance (R) can be modelled by a power law: $R = A[C]^{-\alpha}$, where A and α are empirically derived constants. The MOS detector provides higher sensitivity compared to the chemicapacitors, but has multiple constraints as a chromatography detector, including: (1) saturation at concentrations readily attainable by chromatography (ppmV-level), (2) poor chromatographic resolution due to its relatively long recovery time, (3) lesser sensitivity to highly

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Table 1 Polymers tested on chemicapacitors

Polymer	Abbreviation	Properties
Hyperbranched poly{[bis(1,1,1-trifluoro-2-(trifluoromethyl)-pent-(Z/E)-4-ol)silylene]methylene}	HC	hyperbranched difluoroalcohol carbosilane; polar, hydrogen bonding, acidic, viscous liquid, unknown MW, from Seacoast Science, Inc.
Hyperbranched poly{[bis((Z/E)-1,1,1-trifluoro-2-(trifluoromethyl)-pent-4-en-2-ol)silylene]-1,4-phenylene ethylene}	3STH134	Polar, hydrogen bonding, acidic, viscous liquid; unknown MW, from Seacoast Science, Inc.
Polyisobutylene	PIB	Extremely Non-polar, liquid, 1350 MW, from Polysciences
Polyepichlorohydrin	PECH	Polar, mild hydrogen bonding, rubbery solid, 700k MW, from Sigma-Aldrich
Polyethylene (co-) vinylacetate (40% acetate)	PEVA 40%	Non-polar, solid beads, low crystallinity, 100k MW, from Sigma-Aldrich
Polyurethane	PUT	Non-polar, solid, MW unavailable, from Chemika Fluka
Polyvinylacetate	PVAC	Polar, strong hydrogen bonding, solid, 260k MW, from SP2
Cyanopropyl methyl phenylmethyl silicone	OV225	Polar, liquid, siloxane-based commercial chromatography stationary phase; from Supelco

chlorinated compounds, (4) high power draw, and (5) need to operate in uniformly oxygenated atmosphere.

Polymer-filled chemicapacitors perform well in chromatography applications because of their rapid responses and recoveries, and capability to discriminate among target compounds much better than the MOS, which allows for greater certainty to confirm the presence of specific targets. The polymer-filled microcapacitors, or chemicapacitors, were fabricated by Seacoast Science, and their structure has been extensively reported on.[20,23,26,27] The chemicapacitor array chips used in the VIM were 2 x 5 mm and contained 10 capacitors, 8 of which were filled with polymer and measured.[†] Each chemicapacitor was filled with a different polymer. The square-shaped, parallel-plate, chemicapacitors were 285 µm on a side, with a perforated top-plate suspended over a solid bottom plate, and a 0.75µm gap between the plates. The electrodes are microfabricated from polycrystalline silicon. Nominal (air-filled) capacitance of these is 1.1pF at 25°C in room air. The dielectric gap of individual sensing capacitors is filled with a polymer that is infused through holes in the top plate using an ink-jet system.[27] The ink-jet technique allows for unique dielectric polymers in adjacent capacitors, which are ~500 µm apart. Capacitance measurements are accomplished by an Application-Specific Integrated Circuit (ASIC) readout chip connected to microcontroller on a circuit board that also contains a USB transceiver. The microcontroller manages the power, communications, calibrations, and data collection timing.[23,26,27]

In operation, absorption of target analytes by the polymer filling the capacitor gap modifies the dielectric properties of the polymer, resulting in a change in capacitance. Polymers were selected to provide both strong responses at the desired vapor concentrations and orthogonality in capacitance changes to a diverse range of vapors (Table 1). Many factors govern the behaviour of polymer-filled chemicapacitors. When a polymer-filled chemicapacitor sorbs chemical vapors, the polymer swells, forms weak chemical bonds[27] (hydrogen bonds, van der Waals bonds, and dipole-dipole interactions[28]) with the sorbed molecules, and has the capability of rearranging under the influence of the electric field used to measure the capacitor. These effects and the addition of the chemical species, which may have a different dielectric permittivity than the polymer, in the bulk of the polymer causes a measurable capacitance change. Whether a polymer-filled capacitor's capacitance increases or decreases in response to a chemical exposure depends on the balance between these factors.[29] At the low concentrations used in this manuscript, the concentration / response behaviour is linear,[27] since none of the polymers achieve saturation as would be modelled by a Langmuir isotherm.[30]

Although the chemicapacitor arrays contained 8 different polymers, PVAC, 3STH134 and PEVA proved most useful in identifying individual components of the chemical mixtures used in this work, and are central to the data presented in this paper.

Chromatography Column

The EPA method (#502.2) to analyze for VOC's in water specifies use of three possible GC columns, one of which is a 105m long, fused silica capillary column containing RTX 502.2 sorbent phase (Restek Corporation, Bellefonte, PA), using helium carrier gas, and a column temperature ramp from 35 to 200°C, to gain the broadest possible analytical capability. The use of a long chromatography column, helium carrier gas, and temperature ramping during the analysis, all contribute to the high cost encountered in current vapor intrusion instruments.

As a low-cost, low-power alternative to the conventional oven in a gas chromatograph, the VIM was designed with a capillary column constructed of stainless steel and heated directly by applying voltage, resulting in resistive heating to achieve the column temperature. For this work, two lengths (5 and 11m) of the MXT®-502.2 (Crossbond® diphenyl/dimethyl polysiloxane) were compared. The stainless steel columns were connected electrically to a custom circuit that allowed for direct resistive heating. Columns were wrapped helically around a Teflon spool

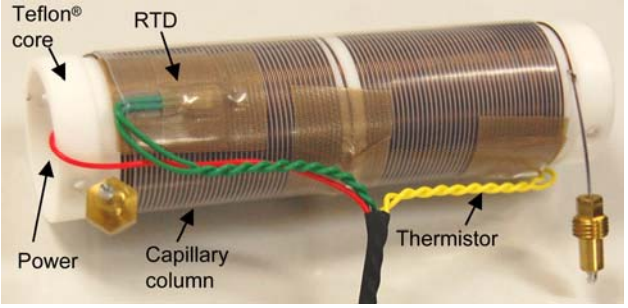

Fig. 1 Chromatography column wound on Teflon® support tube with power wire for heating of the column, RTD for temperature control and thermistor for over-temperature protection.

with a spiraled groove machined to prevent neighboring coils from shorting with each other. A resistance temperature detector (RTD) is mounted at the mid-point of the spool to act as feedback for the circuit's proportional-integral-derivative (PID) control loop. The column is held securely on the spool with heat-shrunk Teflon and mounted in a Garolite shroud to provide thermal isolation and mechanical support. The column assembly (less the Garolite shroud) is pictured in Figure 1.

Shorter columns were chosen as a potential means to achieve a lower-cost system and reduced analytical cycle time. The 5-meter 502.2-column from Restek produced poor separation of the chlorinated compounds using room air as the carrier gas while the 11-meter columns produced satisfactory results; 11m columns were therefore used in all subsequent testing. Using air as the carrier gas and limiting the maximum column temperature 120°C were compromises in instrument design made to obtain suitable performance at low cost. The objective in designing the VIM is to be able to separate individual chemical components of concern in vapor intrusion, and quantitate each. Calibration tests using pure reagents were performed to determine the elution times for each. Multiple column temperatures and carrier air flow rates were tested to evaluate chromatographic resolution.

A custom flow cell was constructed to enclose the sensors to provide a low dead volume interface between the capillary column and the sensors. Standard (1/8 inch) ferruled VICI GC fittings (Valco Instruments Co. Inc.) were used to connect the GC column to the sensor flow cell.

The complete VIM system including all components and power supply is approximately 23 x 20 x 13 cm and was assembled using parts that cost less than $1000US in prototype quantities (excluding an enclosure and computer for data acquisition). All components were commercially available except for certain machined parts, e.g. column support and flow cell, and the custom circuit board, which managed the column, preconcentrator, and various temperature, pressure, and chemical sensor functions.

Preconcentrators

A significant challenge in vapor intrusion is delivering a representative sample of ambient air quantitatively to the detector. In this study, stainless steel packed-tube preconcentrators were constructed from 10cm lengths of (0.88 mm ID x 1.06 mm OD) 316 stainless steel. The stainless steel tube was inserted into a ceramic outer tube, soldered to threaded brass ends, and then filled with absorbent media.[20] The difference between this preconcentrator and our previous device was the replacement of the press-fit connections with threaded tube-end fittings for gas-tight connections. The preconcentrator is resistively heated by applying a controlled voltage between the brass electrodes for short durations. A control circuit was developed to manage the power through the preconcentrator tube. The preconcentrator inlet was designed for 1/8-inch gas-tight compression fitting to connect with the gas delivery system. The outlet was machined for standard #10-32 machine threads to mate with the GC column inlet.

In operation, a large quantity of air to be analyzed is pumped through the preconcentrator, where the sorbent selectively retains the target compounds. Following accumulation of the targets for a predetermined period, the preconcentrator is quickly heated at the beginning of an analysis cycle to introduce the target analytes to the inlet of the chromatography column.

Commercial thermal desorption tubes are available with a number of sorbent packing media. However, earlier work[20] demonstrated that a polymer with intrinsic microporosity[31,32] (PIM-1) provides a higher sorption capacity for the chlorinated hydrocarbons than does Tenax TA, which is commonly used in GC preconcentrators.[33] PIM-1, a yellow powder, was synthesized in-house, and sieved with mesh screens to collect a 60 to 80 mesh fraction. PIM-1 is able to withstand temperatures of up to 300°C without decomposing, and has been shown to sorb a number of industrial solvents and chlorinated vapors from air.[20,34] From 5 to 9 mg of sized sorbent was vacuumed into the preconcentrator tubes and held in place with a small amount of brass wool packed in either end of the inner tube.

To improve sorption and desorption of target vapors by the preconcentrator, 3-way valves (EV Mouse valves, Clippard Instrument Laboratory, Inc., Cincinnati, OH) were used to load and desorb chemicals from the end of the preconcentrator closest to the GC column inlet rather than forcing the analytes to traverse the entire length of the preconcentrator before reporting to the chromatography column (Figure 2). During accumulation of the target analytes, air to be sampled is pumped into the elution end of the preconcentrator, thus filling the sorbent nearest the chromatographic column first. During the analysis step, air flow is reversed and the sample elutes directly from the sorbent immediately into the column. Thus, the vapor sample is collected with air flowing in one direction and but eluted to the column with the air flow in the opposite direction. This arrangement also minimizes retention of target compounds in the preconcentrator after thermal desorption for more precise quantitative measurements.

Optimum preconcentrator performance must balance maximum air flow through the packed sorbent against minimum dilution of analyte slug by the carrier air during thermal desorption. Because of the randomly shaped particles, high pressure drops are observed with the PIM-1 preconcentrators, but in general, air-flows through the preconcentrators were in the range of 100±10 ml/min during the analyte collection step.

Flow Control

Three-way valves were used to control the flow direction of gases in the system. Two pumps were used to allow well controlled air flows over the entire flow ranges. To gain a higher flow during sample collection, a 12V-pump (Airpo part # D028B)

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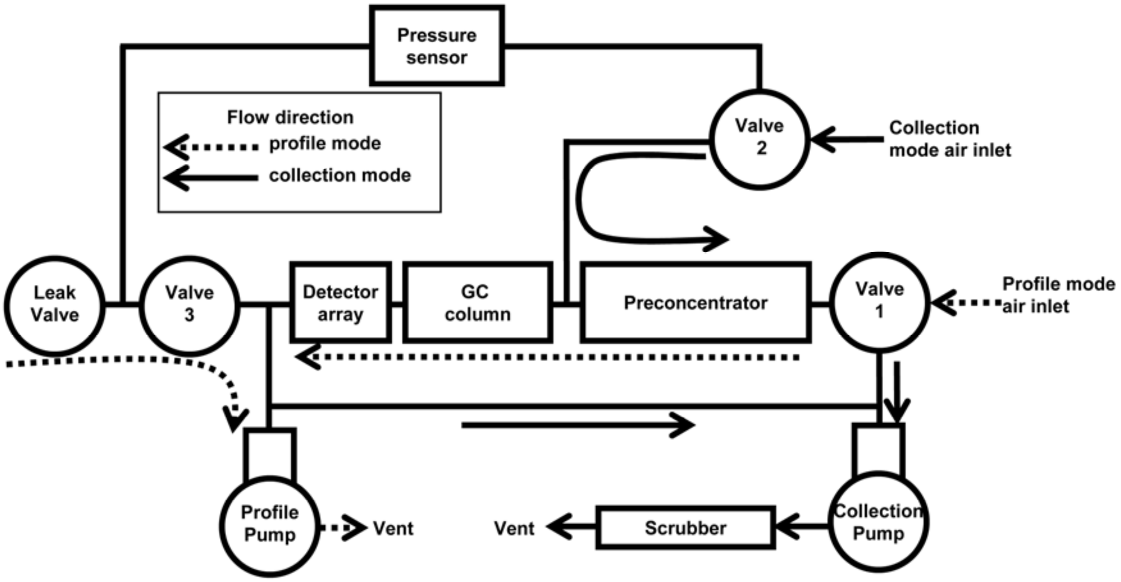

Fig. 2 Schematic of the components and flow paths through the VIM.

was used at full power in vacuum mode to pull ambient air through the preconcentrator. A second 12V-pump (Koge Electronics Co, Ltd., Taipei, part #KPV20C) controlled by pulse-width modulation was used to pull air from the preconcentrator through the GC during the thermal desorption and analysis portion of operation. A pressure sensor (Honeywell # ASDXRRX005PDAA5) measured the pressure drop from the GC column inlet to the sensor enclosure outlet, and provided feedback to the circuit to maintain constant air flow during the profiles. Pressure across the GC column was typically controlled in a range from 7 to 22kPa, with 0.1 kPa resolution, resulting in flow rates of 3 to 15 ml/minute during the detection cycle.

The control circuitry of the VIM manages the column temperature, carrier air pressure and ramping of each as is common in commercial GC systems. In Figure 3, three pressure profiles are shown with resulting chromatograms on two chemicapacitors each filled with a different polymer. As expected, the low (12kPa) constant-pressure chromatograms show broad and well separated peaks, whereas the high (22kPa) constant pressure chromatograms results in tighter spacing between the peaks and the highly volatile DCE is not easily visible. The use of a pressure ramp, in place of a temperature ramp, shows that the DCE can be detected and that the peaks at later times can be compressed to improve the shape and reduce elution time.

Results and Discussion

Thermal Performance of Preconcentrator

Earlier work focused on developing a preconcentrator[20] that absorbs target compounds from the air during the loading (sample collection) portion of the cycle, and thermally desorbs the target chemicals during the analytical portion of the test cycle. The preconcentrator device is heated by briefly passing an electric current through the stainless steel tube containing the sorbent. For proper operation, it is necessary to heat the sorbent uniformly as well as to reach the required desorption temperature to ensure that the target chemicals release rapidly. To achieve long-term operation of the instrument, it is also necessary to avoid thermal decomposition of the sorbent during the desorption step and to avoid oxidation of the sorbent by the carrier gas (ambient air).

To test reproducibility and uniformity of the preconcentrator, a thermocouple was inserted into various locations in the unfilled preconcentrator tubes and the temperature during thermal cycling was recorded electronically (Figure 4). A 6cm segment (~2.5 to 8.5cm) in the middle of the preconcentrator is relatively uniformly heated, with some degree of variance related to the insulation. The uninsulated preconcentrator tube, i.e. without the ceramic sheath, achieves the highest temperatures, whereas the preconcentrators with the ceramic tube and fiberglass wrap remain cooler. The duration of heating, contact resistance and any non-uniformity in the tubing thicknesses affect the temperature and the settings required to achieve a given temperature. The ends of the tube are attached to brass connectors of differing mass and length that act as heat sinks and cause the asymmetric temperature drops at the ends.

For the ceramic-insulated preconcentrators heated for 6s to a set-point of 16.7W, the average temperature of the central segment was approximately 280°C ($\sigma = 21$°C). Sorbent materials were packed in this hot-zone to provide the sharpest possible desorbed vapor pulse while minimizing retention of the targets due to insufficient heating. Some variance from these

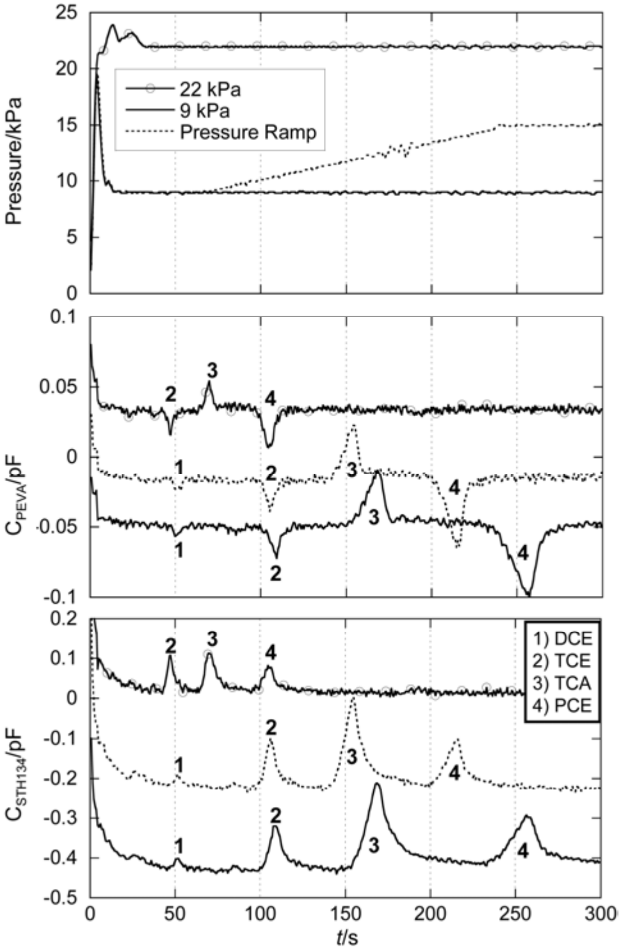

Fig. 3 Pressure profiles and chromatograms from 55minute collection of each chemical at 2.5 ppmV. Traces in each chromatogram correspond to pressure profile in top plot. Chromatograms are offset to ease viewing.

temperature profiles was observed due to the mass of the sorbent and brass wool used to retain the material.

Figure 4 shows an example of the calibration curve achieved with a preconcentrator measured near the center-point, and heated with different power settings for 7s. In the designed circuit, preconcentrator heating uses pulse-width modulation of the current, which is controlled using a PID feedback loop by monitoring the current and voltage on the tube to reach a “power” set-point. Typically the control circuit requires 2-5s to achieve the power level, therefore the presented power levels are considered set-points, and are not to be considered the actual applied energy.

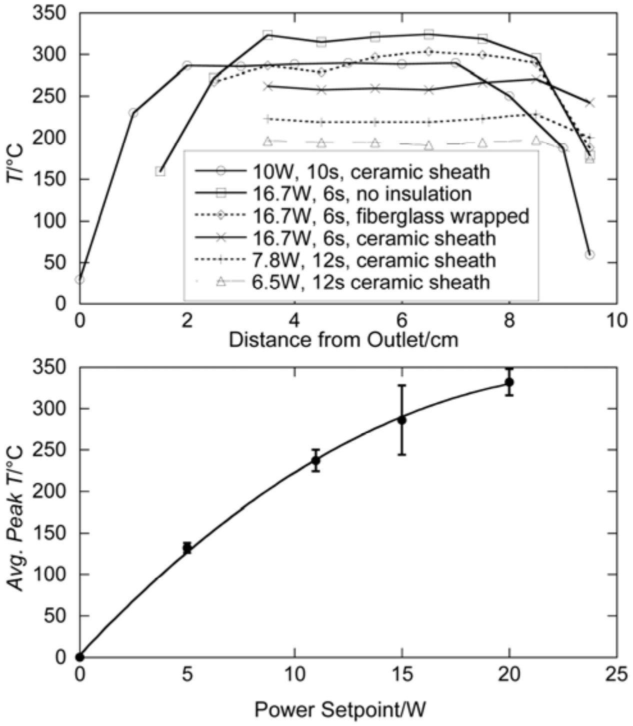

Fig. 4 (upper) Temperature profiles along the length of empty preconcentrators using different power settings and types of insulation, and (lower) Peak temperature achieved in the center of an empty preconcentrator when heated for 7s with various power set-points. Error bars = ±1 standard deviation. The line is a 2nd order polynomial fit with the intercept = 0.

“Clean” Air

The system needs to accurately analyze the extent of vapor intrusion when vapor intrusion chemicals are present, and reliably report the absence of noxious vapors when such is the case. Figure 5 shows chromatograms from the VIM that were connected to the vapor delivery system set to deliver air only. The preconcentrators (9mg of PIM-1) were heated through 10 thermal desorption cycles while purging with air to remove sorbed chemicals to the maximum extent possible. Following this, a single desorption-chromatographic analysis cycle was immediately recorded (i.e. a zero duration collection or “no collect” chromatogram). These analyses show no measurable analyte eluted from the preconcentrator after the multi-step desorption treatment. Dried lab air from the vapor delivery system was then passed through the preconcentrator for up to 21 hours to accumulate any impurities that may be present in the vapor delivery system or in the dried laboratory air from the air compressor. Following these collection cycles, the desorption-chromatographic analysis cycle was triggered. These chromatograms show low levels of contaminants, likely compounds desorbing from polymer-based seals in the mass flow controllers within the vapor delivery system. This is confirmed by sourcing gas from a zero-air compressed gas cylinder. The zero-air is certified to have < 3ppm H_2O and < 1ppm total hydrocarbons. Only the MOS detector shows the possibility of detecting any contaminants in the air.

Chemicapacitor Polymer Selection

Initial screening to select the optimum suite of dielectric polymers for the chemicapacitors was conducted using a VIM system with a 9-mg PIM-1 preconcentrator. The goal was to obtain the greatest response to the five primary targets while rejecting water at the concentrations and conditions tested (Figure 6). The results, normalized to the peak response of STH134, suggest that the polymers could be grouped into five categories: PVAC responded only to water vapor; PIB responded weakly only to TCE and TCA, likely because they are the most polar of the chlorinated vapors tested; PEVA, OV225 and PUT showed decreased capacitance in response to DCE, benzene, TCE and PCE, and increased capacitance in response to water and TCA;

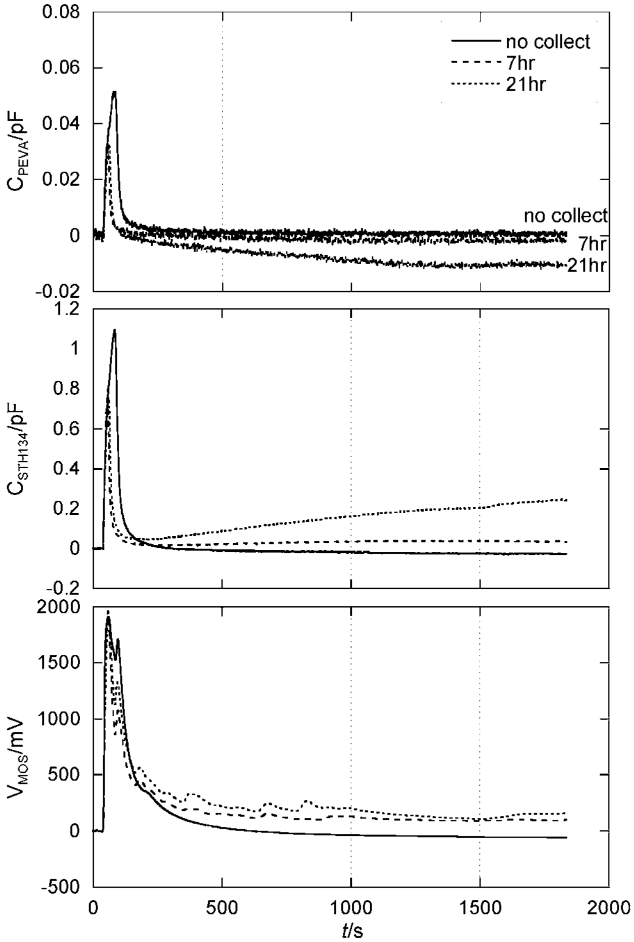

Fig. 5 Chromatograms from three detectors, PEVA-chemicapacitor (top), STH134-chemicapacitor (middle) and MOS (bottom). Each plot contains chromatograms from 0-hr, 7-hr and 21-hr collections of dried lab air.

PECH showed decreasing capacitance to all five targets, but was extremely slow to recover from exposures; the two fluoro-alcohols[35] STH134 and HC showed positive responses to all five targets. However, 3STH134 was notably faster and more responsive than HC. Due to the similarity in responses to PEVA, and the relative ability of PEVA to reject water, data for OV225 and PUT will not be discussed extensively for the balance of this paper.

Sample Collection and Response

Assuming the sorbent in the preconcentrator absorbs target analyte quantitatively, detector response is directly proportional to the volume of sampled air passed through the preconcentrator. Under constant air flow during the collection period, one expects that increasing the collection time directly affects the amount of chemical collected. In practice, the quantity of analyte is limited by the equilibrium sorption of the chemical on the given sorbent. This is exemplified in Figure 7, where progressions of chromatograms resulting from vapors collected for different periods are shown. The MOS device detects the 12.5ppbV (of each) levels sampled by the preconcentrator with as little as 1hr collection period. Given that air flow during collection is approximately 100 mL/min, approximately 6 L of air from the vapor space is needed to elicit a response from the MOS detector.

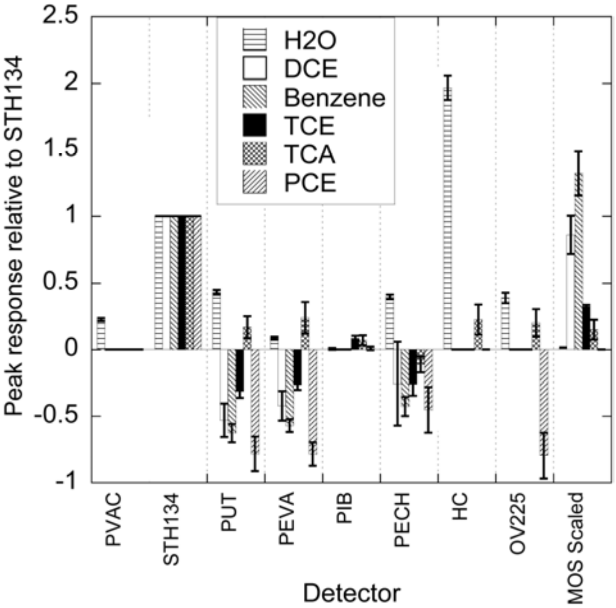

Fig. 6 Relative peak-heights from the polymer-chemicapacitors response chromatograms to chemicals collected on a PIM-1 preconcentrator in dried air. Each detector's peak height response for a given chemical is normalized to the corresponding peak height of the STH134 chemicapacitor. The MOS detector response is scaled by 10^{-5} pF/mV.

The two polymer-filled chemicapacitors require at least a 5 hours collection period to provide measurable response to TCA and PCE at these vapor concentrations. Closer observation of the MOS results shows that the preconcentrator is unable to collect more DCE after 1hr (saturation), whereas it is able to continue collecting the less volatile compounds over the course of the longer collections. This result suggests that it is unlikely that the polymer-filled chemicapacitors will detect 10 ppbV or lower DCE regardless of how long the DCE is collected on the PIM-1 preconcentrator at this temperature (room temp) with the other chemicals present at equal or greater levels.

The high sensitivity of the MOS detector is balanced by its slow recovery, which reduces peak resolution. For example, in Figure 7 the PCE peak (eluting at 800 sec) is well separated from the TCA peak (eluting at 750 sec) using the PEVA chemicapacitor, but is barely noticeable as a shoulder using the MOS detector.

Saturation of the sorbents on the preconcentrators results in decreasing collection efficiency over time (Figure 8). The DCE and TCE quickly saturate the PIM-1 preconcentrator. The DCE responses are from shoulder peaks, as the detector was recovering from the initial water peak, and therefore the absolute heights may be difficult to determine, however the trends and differences between analytes are still obvious. The PCE peak was insufficiently separated for quantification using the MOS detector.

The ability of a preconcentrator material to retain low levels of chemicals is a typical concern in vapor collection applications. Equilibrium is eventually reached with the sampled air, after which, at a given collection temperature the sorbent does not collect more of a particular chemical.

Under ideal conditions, the MOS detector is capable of detecting all target compounds at sub-ppbV concentrations

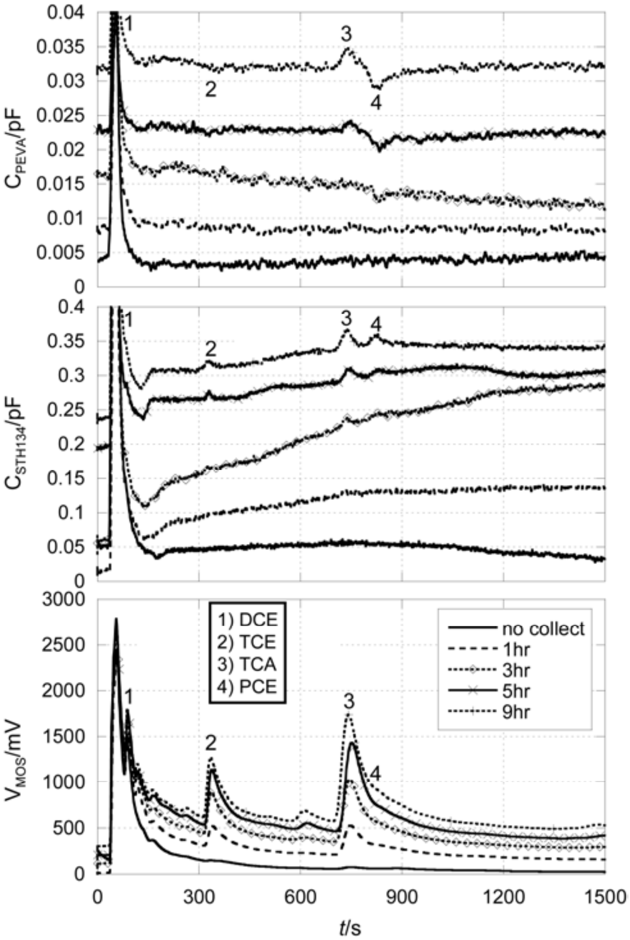

Fig. 7 Chromatograms resulting from three detectors (3STH134 and PEVA chemicapacitors and MOS), collecting four vapors, each at 12.5 ppbV, in dried air. The duration of each collection cycle is noted. Chromatograms are offset (shortest collection to longer collections progressing from bottom to top) to ease viewing.

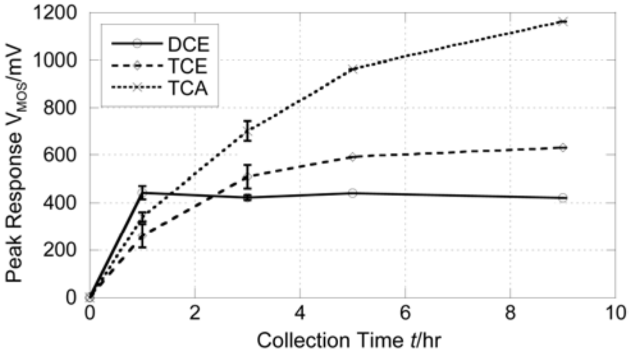

Fig. 8 Peak heights, from Figure 7, achieved from the MOS detector chromatograms vs. collection time on the VIM. Error bars = ±1 standard deviation. Lines are meant to guide the eye.

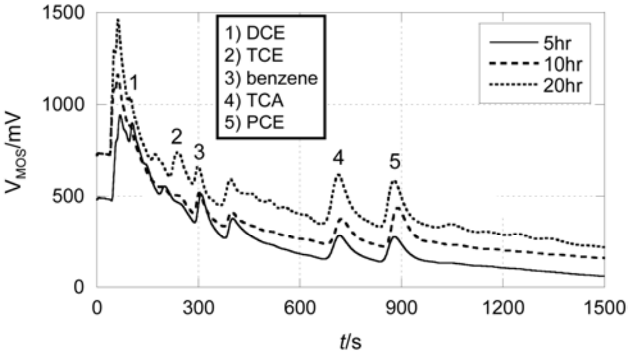

Fig. 9 Chromatograms resulting from the MOS detector for 5, 10, and 20hr collections of the five target chemicals (0.5ppbV each) in dried air. Chromatograms are offset to ease viewing.

(Figure 9) collected on a 9-mg PIM-1 preconcentrator. In contrast to the MOS detector, none of the chemicapacitors responds following vapor collection even with the collection time was extended to 10hrs to ensure saturation of the preconcentrator. Trace contaminants in the test system or lab air are noticeable interferents appearing as peaks at times other than those observed for the 5 targets. This is particularly challenging in that the DCE peak overlaps the water; thus, detection of DCE in the field with the current instrument would be very difficult.

Figure 10 shows chromatograms resulting from a 21hr-collection of 1ppbV each of the 5 target chemicals. At this concentration, despite this extended collection time, no measurable response is seen for DCE on the polymer-chemicapacitors; however the MOS detector is capable of detecting all of the vapors.

By varying the collection time at a fixed concentration, a set of calibration curves was generated that show the equilibrium effect (Figure 11). The resulting plot shows decreasing collection efficiency as the sorbent approaches the point of equilibrium saturation. The same trends are observed on the chemicapacitors; however, the slope of the low concentration regime is shifted due to their lesser sensitivity.

As shown above, the preconcentrator absorbs sufficient benzene, DCE, TCE, TCA, and PCE from 1 ppbV each in dried air to be detected with the MOS detector. The 3STH134- and PEVA-filled chemicapacitors are sufficiently sensitive to detect TCA and PCE at the 1 ppbV level vapor mixture, whereas 3STH134 detects TCE as well (Figure 10). These data appear to be at or near the limits of detection for the polymers using the detector in its current state of development. Chemicapacitors filled with other polymers did not show measurable response to these analytes at these concentrations.

A problem relating to sensitivity of the detector is the capacity limit of the sorbent in the preconcentrator. Increasing the mass of sorbent proportionally increases the capacity of the preconcentrator. However, increasing the mass of sorbent increases the pneumatic resistance of the preconcentrator, which reduces the sample collection rate. Therefore, the preconcentrator must be designed carefully to achieve optimal sample collection.

To confirm the repeatability of the assembled system, it was cycled at least 500 times, with only minimal loss of chromatographic separation and sensitivity. Figure 12 shows chromatograms resulting from 24 consecutive collection (30-min) and analysis cycles. Two issues have been noted: (1) pumps running continuously for several weeks begin to fail due to wear of the brushes against the rotor, and (2) the flow through the preconcentrators changes over time, possibly due to compaction of the irregularly-shaped packing material or gradual failure of the pump. Two of the polymers on the chemicapacitors, 3STH134 and HC, show some aging when heated cyclically or held at elevated temperatures, > 40°C.

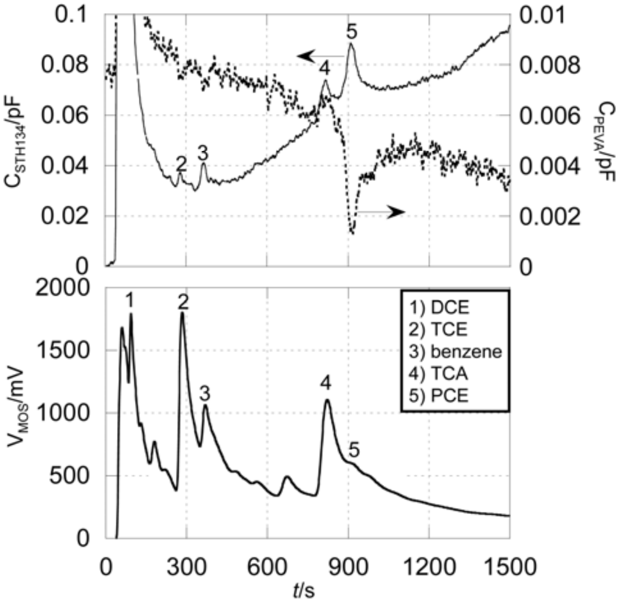

Fig. 10 Chromatograms from 21-hr collection from the VIM, exposed to 1ppbV each of the 5 target chemicals in dried air.

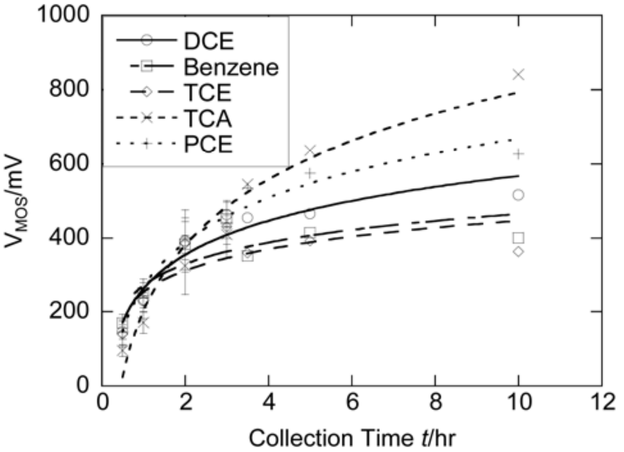

Fig. 11 MOS detector peak heights from chromatograms resulting from 1 ppbV collected using a PIM-1 preconcentrator and varied collection times. Error bars = ±1 standard deviation. Lines are meant to guide the eye.

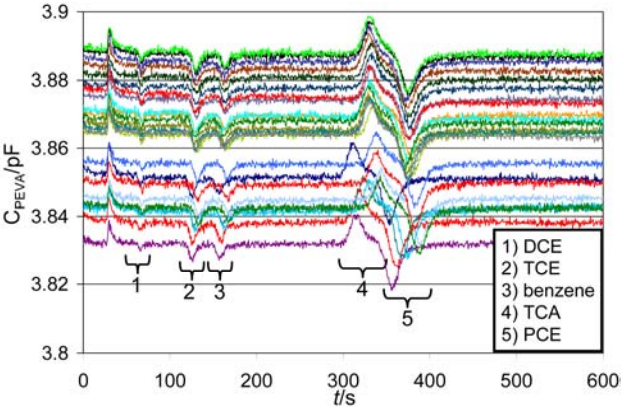

Fig. 12 Chromatograms from the PEVA-chemicapacitor during repeated cycles of the VIM exposed to 500ppbV each, of the 5 target chemicals, for 30 minutes.

Conclusions

This paper discusses the development of an inexpensive system specifically for monitoring vapor intrusion. In its current form, the system has proven capable of detecting 1 ppbV of four chlorocarbon compounds typical of vapor intrusion: dichloroethylene, trichloroethane, trichloroethylene, and perchloroethylene. The system consists of a preconcentrator for vapor collection in conjunction with a compact gas chromatography instrument. The system's detector consists of a sensor array containing MEMS chemicapacitors and a metal-oxide semiconductor combustibles sensor. Both the preconcentrator and the chromatography column are heated by passing an electric current directly through their metal sheathing. A resistance temperature detector is used for feedback control of the GC column temperature. The preconcentrator is heated at a fixed power for a predetermined period. All components are compatible with ambient air, which serves as the carrier gas for the gas chromatography. This combination of heating and carrier gas provides adequate detection capability for minimal cost and instrument footprint and avoids consumables such as carrier gas from compressed gas cylinders. The instrument has proven capable of unattended operation for extended periods, over 500 sample collection and analysis cycles, as would be desirable for monitoring vapor intrusion. The instrument can be manufactured for orders of magnitude less cost than commercial vapor intrusion instrumentation, allowing monitoring of much greater numbers of sites over much longer periods to provide meaningful data to better understand trends in levels of noxious compounds and better documentation of remediation efforts.

PIM-1, a high-porosity sorbent, described in the literature, has shown promise as packing materials for the preconcentrator, however its capability is limited for the highly volatile DCE. Alternative sorbents, such as Carboxen 1000, are likely to fare better for highly volatile compounds.

The lower limit of detection appears to be limited by the amount of air that can be sampled by the preconcentrator in the current instrument. Increasing the amount of sorbent in the preconcentrator would increase the amount of analyte available for each detection cycle. However, increasing the mass of sorbent increases resistance to passage of air through the preconcentrator, which reduces the volume of air that can be pumped through the preconcentrator in a fixed amount of time, thereby directly reducing the quantity of analyte collected for analysis. Increasing the physical size of the preconcentrator introduces greater variability in temperature achieved during thermal desorption of the analyte during the analysis step.

The instrument may still be improved by reducing the heat lost from the column to environment, and making the temperature across the length of the GC column more uniform. This will reduce the drift in the peak elution times and the system's sensitivity to ambient temperature. Extending the column will also improve peak separation but at an increased cost.

Another opportunity to improve the current instrumentation is to increase the sensitivity of the MEMS chemicapacitor. The MOS is much more sensitive to the combustible compounds such as DCE and TCA, but does not detect PCE as easily. The chemicapacitor arrays are better able to distinguish among the various compounds, but are not as sensitive overall to the chlorocarbons. Research to identify dielectric polymers with the ability to form stronger chemical interactions specifically to detect the low-polarity chlorocarbons by chemicapacitors could improve functionality of the vapor intrusion monitor.

Future work will focus on humidity and temperature characterization, as well as identifying methods to improve detector sensitivity. Desiccant or a sample drying tube[36] on the incoming carrier stream can be implemented to remove moisture; however, determining the extent to which moisture competes for sorption sites on preconcentrator sorbent is a priority for further development of the fieldable VIM instrument.

Another weakness of VIM in its current state of development is the need for unattended in-field calibration. Effort currently is underway to achieve suitable calibration methods.

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Notes and references

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† Seacoast uses MEMSCAP, Inc (Durham, NC) to fabricate the basic chips, and performs post-processing, functionality and failure analysis, and coating at Seacoast's labs in Carlsbad, CA.

‡ For this article the following definitions are used: part-per-million = 1 x 10^{-6}, part-per-billion = 1 x 10^{-9}, part-per-trillion = 1 x 10^{-12}, and ppbV indicates a volume basis.

1 US EPA, http://www.epa.gov/OUST/cat/pvi/index.htm, accessed 4/23/14.

2 www.epa.gov/osw/hazard/correctiveaction/eis/vapor/f02052.pdf, accessed 4/23/14.

3 EPA's Brownfields and Land Revitalization page: http://www.epa.gov/brownfields/basic_info.htm#plan, accessed 4/23/14.

4 Groundwater and Soil Cleanup: Improving Management of Persistent Contaminants, Commission on Geosciences, Environment and Resources (CGER), National Research Council, National Academy Press, Washington, D.C., 1999.

5 US EPA National Priorities List: http://www.epa.gov/superfund/sites/npl/ (accessed 1/31/2014)

6 "DOD Vapor Intrusion Handbook," Tri-Service Environmental Risk Assessment Workgroup, Jan. 2009.

7 US EPA, Petroleum Hydrocarbons And Chlorinated Hydrocarbons Differ In Their Potential For Vapor Intrusion, http://www.epa.gov/oust/cat/pvi/pvicvi.pdf, Mar. 2012

8 http://www.epa.gov/region06/6pd/rcra_c/ca/index.html

9 X. Lu, D. H. Kampbell, and J. T. Wilson, "Evaluation of the Role of Dehalococcoides Organisms in the Natural Attenuation of Chlorinated Ethylenes in Ground Water," EPA National Risk Management Laboratory report: EPA/600/R-06/029; July 2006.

10 http://www.epa.gov/reg3hwmd/risk/human/rb-concentration_table/Generic_Tables/docs/resair_sl_table_01run_MAY2013.pdf

11 http://www.cs.cmu.edu/~sensing-sensors/readings/mass_and_optical_spec_brochures/INFICON_portable_GCMS.pdf

12 S. K. Kim, D. R. Burris, H. Chang, J. Bryant-Genevier, and E. T. Zellers, *Environmental Science & Technology,* 2012, 46, 6065.

13 S. K. Kim, D. R. Burris, J. Bryant-Genevier, K. a Gorder, E. M. Dettenmaier, and E. T. Zellers, *Environmental Science & Technology,* 2012, 46, 6073.

14 C. Jin and E. T. Zellers, *Sensors and Actuators B: Chemical,* 2009, 139, 548.

15 P. R. Lewis, R. P. Manginell, D. R. Adkins, R. J. Kottenstette, D. R. Wheeler, S. S. Sokolowski, D. E. Trudell, J. E. Byrnes, M. Okandan, J. M. Bauer, R. G. Manley, C. Frye-Mason, *Sensors Journal, IEEE,* 2006, 6, 784. doi: 10.1109/JSEN.2006.874495

16 J. Yeom, C. R. Field, B. Bae, R. I. Masel, and M. A. Shannon, J. *Micromech. Microeng,* 2008, 18, 12.

17 http://www.defiant-tech.com/products.php

18 http://apixtechnology.com/

19 A. Chou, B. Radi, E. Jaatinen, S. Juodkazis, and P. M. Fredericks, *Analyst*, 2014, 139, 1960–6.

20 S. T. Hobson, S. Cemalovic, and S. V. Patel, *Analyst,* 2012 137(5), 1284. DOI: 10.1039/C2AN16053F. PMID: 22266477

21 W. K. Tolley, T. E. Mlsna, and B. Kunwar, A Low-Cost, Low-Power Gas Chromatograph For Field And Educational Use, International Society for Automation 55th Analytical Division Conference, April 25-28, 2010, New Orleans, LA

22 B. Kunwar, H. Wijaylapala, J. Thieme, S. V. Patel, and T. E. Mlsna, *Journal of Sensors and Instruments*, 2013 1, 1. http://dx.doi.org/10.7726/jsi.2013.1001

23 S. V. Patel , S. T. Hobson, S. Cemalovic, and T. E. Mlsna, *Proceedings of SPIE,* European Symposium Optics and Photonics in Defence and Security, 2005, 5986, 162.

24 Figaro is a Japanese company, with A US distributor. Figaro USA Inc., 121 S. Wilke Rd. Suite 300, Arlington Heights IL 60005 USA; http://www.figarosensor.com/

25 http://www.figarosensor.com/products/general.pdf

26 S. V. Patel, S.T. Hobson, S. Cemalovic, and T. E. Mlsna, *Talanta*, 2008, 76(4), 872.

27 S. V. Patel, T. E. Mlsna, B. Fruhberger, E. Klaassen, S. Cemalovic, and D. R. Baselt, *Sensors and Actuators B,* 2003, 96(3), 541.

28 C. M. Hansen, *Hansen Solubility Parameters*, CRC Press, Boca Raton, FL, 2000.

29 A. Hierlemann, D. Lange, C. Hagleitner, N. Kerness, A. Koll, O. Brand, H. Baltes, *Sensors and Actuators B,* 2000, 70, 2.

30 C. G. Hill, An *Introduction to Chemical Engineering Kinetics & Reactor Design*, John Wiley & Sons, New York, 1977, p. 172-8.

31 P. M. Budd, B. S. Ghanem, S. Makhseed, N. B. McKeown, K. J. Msayib, C. E. and Tattershall, *Chemical Communications*, 2004, 2, 230.

32 N. Du, G. P. Robertson, J. Song, I. Pinnau, S. Thomas, and M. D. Guiver, *Macromolecules*, 2008, 41(24), 9656.

33 Supelco BULLETIN 916, http://www.sigmaaldrich.com/content/dam/sigma-aldrich/docs/Supelco/Bulletin/4542.pdf, 8 pp.

34 D. J. Combes, T. I. Cox, and I. C. Sage, "Preconcentrator device," US patent #08137979, 2012.

35 J. W. Grate. Hydrogen-Bond Acidic Polymers for Chemical Vapor Sensing. *Chem. Rev*. 2008 Jan 26; 108(2):726–45.

36 An example of a Nafion membrane drying tube is the MD series system from Perma Pure, LLC. (Toms River, NJ): http://www.permapure.com/products/gas-sample-dryers/md-gas-dryers/