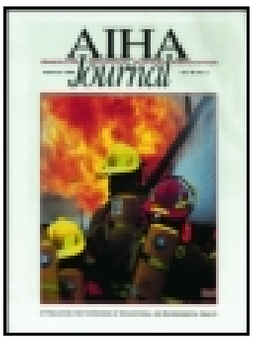

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Personal Monitoring Instrument for the Selective Measurement of Multiple Organic Vapors

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Development and laboratory testing of a small instrument capable of recognizing and quantifying multiple organic vapors at low- and sub-ppm concentrations is described. The instrument is slightly larger than a standard personal sampling pump and employs an array of three polymer-coated surface-acoustic-wave microsensors for vapor detection. Vapors are first trapped on a miniature adsorbent preconcentrator housed within the instrument and then thermally desorbed for analysis by the microsensor array. Each measurement cycle requires 5.5 min. The collective responses from the array are stored and then analyzed using pattern recognition methods to yield the identities and concentrations of collected vapors and vapor mixture components. Following initial optimization of instrument operating parameters, calibrations were performed with 16 organic solvent vapors and selected mixtures to establish a response library for each of two identical instruments. Limits of detection $\leq 0.1 \times$ threshold limit value were obtained for most vapors. In a series of 90 subsequent exposure tests, vapors were recognized with an error of $<6\%$ (individual vapor challenges) and $<16\%$ (binary mixture challenges) and quantified with an average error of $<10\%$. Monte Carlo simulations were coupled with pattern recognition analyses to predict the performance for many possible vapor mixtures and sensor combinations. Predicted recognition errors ranged from <1 to 24%. Performance is shown to depend significantly on the interfacial polymer layers deposited on the sensors in the array and the nature and complexity of the vapor mixtures being analyzed. Results establish the capability of this technology to provide selective multivapor monitoring of personal exposures in workplace environments.

Keywords: gas detector, pattern recognition, personal exposure, sensor array, surface acoustic wave sensor, vapor sensor

Organic vapors rank among the most common contaminants encountered in workplace environments. Although an increasing number of compact industrial hygiene monitoring instruments capable of direct measurement and storage of exposure data have been developed recently,[1–3] none are amenable to selective personal exposure monitoring of multiple organic vapors. For the most part, this is due to limitations associated with the types of sensing components employed. Although portable gas chromatographs are capable of simultaneous measurement of multiple vapors, they are generally too large to be used as routine personal monitors. Furthermore, they provide only a "peak," the retention time of which is used for vapor identification; vapors with overlapping peaks cannot be easily discriminated.

The instrument described here employs an array of surface-acoustic-wave (SAW) sensors each measuring just a few millimeters on a side. In the SAW device, radio-frequency mechanical (i.e., acoustic) waves are generated along the surface of a piezoelectric quartz chip that has been coated with a thin, chemically sensitive interface layer. Small changes in the physical properties of the interfacial coating layer caused by interactions with gases or vapors result in a change of the velocity, and hence frequency, of the SAW, which can be measured with a digital counter.[4–7] Typical

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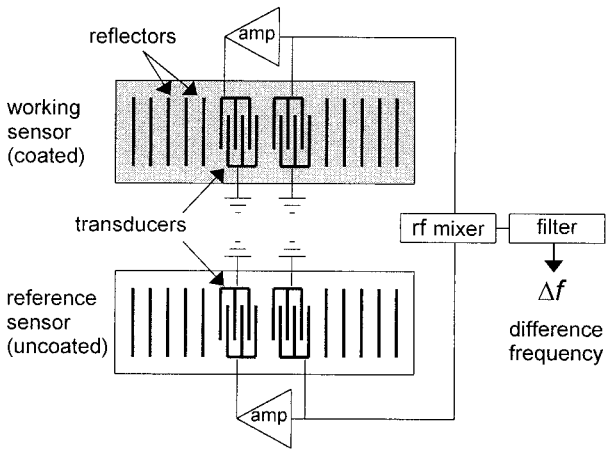

FIGURE 1. Dual SAW resonator configuration used in the sensor array

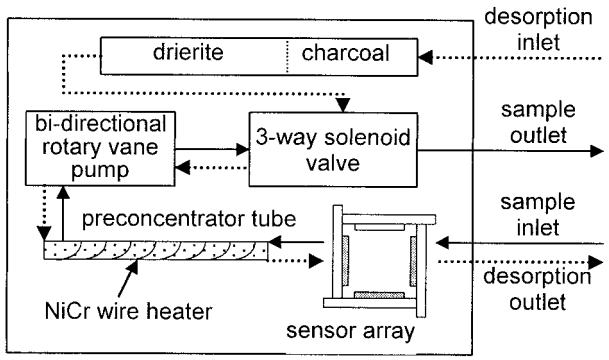

FIGURE 2. Block diagram of the primary sampling and analytical instrument components

operating frequencies for SAW sensors are from 30 to 300 MHz.

Figure 1 shows the basic design features of the quartz SAW resonator structure used in this study. The centrally located input and output transducers each consist of multiple pairs of overlapping electrodes spaced by a few micrometers. The electrodes are deposited by metal evaporation and patterned by photolithography. SAWs launched by these transducers are reflected from similarly patterned metal gratings, which flank the transducers, to produce a resonant cavity that supports a specific frequency and has very low baseline noise.[7] Using a feedback amplifier to complete the circuit results in oscillation at a fixed resonant frequency.

Deposition of the interfacial coating film causes a decrease in the resonant frequency, Δf_c, which is proportional to the mass of the film.[5,7] A new, lower, resonant frequency is then established. Where amorphous polymers are used as interfacial sensor coatings, sensor responses arise from the reversible partitioning of vapors into the coating film. Vapor uptake leads to an increase in the mass of the polymer film as well as swelling and softening due to expansion of the polymer matrix. These effects combine to decrease the resonant frequency, which is the basis for vapor detection.[8,9] Response isotherms are typically linear and responses are rapid and reversible, since very thin coating films are used and vapors desorb spontaneously on removal of the vapor from the atmosphere above the sensor.[8–11]

Equation 1 describes the response of a polymer-coated SAW sensor to a vapor challenge:[11]

$$\Delta f_v/C_v \equiv S = \Delta f_c K_c/\rho \qquad (1)$$

where Δf_v is the sensor response (i.e., frequency shift, in hertz) to a vapor at concentration C_v being sorbed by the coating, S is the sensitivity, ρ is the density of the coating material, and K_c is a factor related to the partition coefficient that is determined by the volatility of the vapor, the strength of the vapor-polymer interaction, and the extent of softening of the polymer by the sorbed vapor.[8,9] In most applications, the output from a coated (i.e., working) sensor is subtracted from that of an identical uncoated reference sensor to improve stability and reduce the frequency of the output signal (see Figure 1).

The selectivity of an individual polymer-coated SAW sensor is limited by the low energy of the vapor-polymer interactions—many vapors will partition into a given polymer coating. However, the use of a multisensor array, where each SAW sensor is coated with a different polymer, provides a means of achieving highly selective multivapor analysis.[12–15] The array of sensors will produce a characteristic response pattern for each vapor that can be decoded using multivariate statistical pattern recognition methods or artificial neural networks.[12–19] Recognition and quantification of a wide range of vapors, present individually or as the components of vapor mixtures, is therefore possible with a single array containing just a few SAW sensors.[12,14–18]

Sensitivity is limited by the amount of coating material deposited on the sensor (see Equation 1). If the film thickness exceeds about 1% of the acoustic wavelength, dampening of the acoustic wave becomes excessive and the resonator may cease to function. For devices operating at 30–300 MHz, acoustic wavelengths range from about 10–100 μm, which limits film thicknesses to $<0.1 - 1$ μm. Although detection limits below American Conference of Governmental Industrial Hygienists threshold limit value (TLV®) values have been reported for a number of vapors using polymer-coated SAW sensors, for many vapors such limits are not achieved.[9,14,18,20,21] This has led to the incorporation of adsorbent preconcentrators into SAW-sensor instrumentation systems.[18,21–24] A measured volume of air is passed through a porous-polymer adsorbent bed and then the bed is flash heated to desorb the trapped vapors into a smaller air volume for analysis. In addition to increasing the effective sensitivity and reducing detection limits, preconcentration also provides some compensation for baseline drift and atmospheric humidity changes. Because sharp vapor pulses are measured on a slowly drifting baseline, the zero point can change without seriously affecting quantification. The effects of fluctuations in atmospheric humidity can be minimized by use of hydrophobic adsorbents that preferentially adsorb organic vapors.[21]

This article describes the development and initial testing of an instrument employing an array of three polymer-coated SAW sensors and an adsorbent preconcentrator, which is small enough to be worn on the belt of a worker and provide selective, simultaneous measurement of multiple organic vapors. Details are provided of the key design and operating features of the instrument as well as performance measures determined from laboratory testing. Methods employed for recognizing and quantifying vapor analytes are demonstrated, and the results of analyses of a test set of vapors are presented. Monte Carlo simulations are then used in conjunction with pattern recognition analyses to illustrate in a more general way the versatility and limitations of this technology for personal exposure assessment.

METHODS AND MATERIALS

Instrumentation

Two identical prototype instruments measuring 13 × 18 × 5.5 cm and weighing 1.2 kg were constructed for this study by Microsensor Systems (Bowling Green, Ky.). Figure 2 shows a block diagram of the primary sampling and analytical subsystem components. Each instrument contains an array of three polymer-coated SAW sensors and a fourth uncoated reference SAW sensor all operating at a resonant frequency of ~250 MHz. A 3.2-cm stainless-steel tube (2.6 mm i.d., 2.8 mm o.d.) packed with a granular adsorbent and wrapped with insulated NiCr wire is used for preconcentration and thermal desorption of vapor samples. A three-way Teflon® solenoid valve (Model AL3306L, Angar Scientific Co., Cedar Knolls, N.J.) and miniature bidirectional rotary-vane pump (Schwarzer Model FZ 135, MRM International, Duluth, Ga.) are used for directing sample flow. An additional adsorbent tube containing 2 g of activated charcoal and 18 g of Drierite® provides "zero air" during thermal desorption and analysis of captured vapor samples. Stainless-steel or Teflon tubing is used to connect all of the components coming into contact with vapor samples.

An on-board microcomputer controls the timing sequences of the pump, valve, and preconcentrator heater, and collects the output signals from the three sensors (i.e., the difference frequency between the working and reference sensors). Measurements from all three sensors are collected every second with 2 Hz resolution. Data are either transmitted via an RS-232 port to an external computer for display and processing or stored in the on-board memory. The instrument can log 1-sec frequency measurements from each sensor, as well as 1-sec sensor-array temperature readings, for about 12 hours. The instrument was not designed for direct display of vapor identities or concentrations; stored short-term measurements are collected and subsequently analyzed by computer to provide exposure-time profiles for each vapor detected. An internal 1.8 amp-hour battery can supply power for several hours; however, for all testing reported here, power was supplied by a regulated DC power supply operated at 7.5 V.

Each sensor is epoxied to a standard three-pin header and inserted into a printed circuit board (2.2 × 2.0 cm). The four printed circuit boards are bolted to the lateral faces of a brass cube (2 × 2 × 2 cm), with the sensor headers fitting snugly into machined ports on the cube. Silicone rubber header gaskets are used to ensure airtight seals of the headers to the ports. The cube is mounted on a larger printed circuit motherboard (5 × 7.5 cm), which carries additional interface and control circuitry. Channels drilled through the cube provide evenly distributed airflow across the exposed surfaces of the sensors. Temperature is monitored with a thermistor affixed to the surface of the cube and recorded by the on-board microcomputer.

The preconcentrator tube (PCT) is packed with 20 mg of a porous polymer adsorbent held in place with glass wool. Teflon tubing is inserted into the ends of the PCT and a sleeve of silicone rubber tubing is clamped around the metal-Teflon junction to prevent leaks. The PCT is wrapped with 52 turns of a polyimide-coated NiCr wire, providing 19-ohm resistance at room temperature and a heated length of ~1.3 cm. A fine-wire type-K thermocouple (Omega Engineering, Stanford, Conn.) affixed beneath the NiCr wire against the outside wall of the PCT monitors the rate of heating and maximum temperature of the PCT during thermal desorption tests.

The adsorbent (XUS43565.01, Dow Chemical, Midland, Mich.), referred to here as XUS565, consists of spherical beads (20/50 mesh) of a methylene bridged copolymer of styrene and divinylbenzene having a specific surface area of 1000 m^2/g according to the manufacturer. This adsorbent was selected from among other common adsorbent materials on the basis of a previous study demonstrating its large adsorption capacity for a range of organic vapors and low affinity for water vapor.[21]

Prior to deposition of polymer coatings, each sensor was cleaned with chloroform followed by methanol and then air dried. The sensor was then further cleaned in an air plasma for 10 min (Model PDC-3XG, Harrick Scientific, Inc., Ossining, N.Y.). The following polymers were used as sensor coatings (see following paragraphs for further discussion): polyisobutylene (PIB), polyepichlorohydrin (PECH), polydiphenoxyphosphazene (PDPP) (Scientific Polymer Products, Ontario, N.Y.), phenylmethyldiphenylsilicone (OV-25), bis-cyanoallyl polysiloxane (OV-275) (Supelco, Bellefonte, Pa.), and fluoropolyol (FPOL). FPOL was graciously provided by Dr. A. Snow of the U.S. Naval Research Laboratory. Each polymer was applied by airbrush as a solution (0.2% w/v) in chloroform (PIB, FPOL), toluene (PDPP, PECH), or acetone (OV-25, OV-275) while the sensor frequency was monitored. Table I lists the frequency shifts for each coating and the approximate mass and thickness calculated by a well-known expression.[5,8] The calculated film thicknesses ranged from 28–65 nm, which correspond to coating masses of 560–720 ng. Sensors coated with PIB, PECH, and FPOL were used in the first instrument, whereas sensors coated with PDPP, OV-25, and OV-275 were used in the second instrument.

TABLE I. Calculated Thickness and Mass of Each Polymeric Sensor Coating

Polymer	Density (g/mL)	Δf_c (kHz)	Thickness (nm)	Mass (ng)
PIB	0.92	470	65	716
PECH	1.36	412	38	628
FPOL	1.65	370	28	564
PDPP	1.20	449	48	684
OV-25	1.15	424	47	646
OV-275	1.00	395	50	602

Operating Modes

A complete analysis requires cycling through four operating modes. In sampling mode ambient air is drawn at 0.120 L/min in through the sampling port and vapors are concentrated on the PCT adsorbent (see Figure 2). In purge mode the direction of the pump is reversed and air is drawn at 0.030 L/min through the charcoal-Drierite cartridge and back through the system to remove residual vapors from above the sensor array and to strip adsorbed water vapor from the PCT adsorbent. In analysis mode the PCT is heated to 180°C and then allowed to stabilize at 160°C. Desorbed vapors are passed across the sensor array at 0.030 L/min on a background of clean dry air. The heater is then deactivated and the PCT is allowed to return to room temperature while the vapors elute through the system (recovery mode). The duration of each operating mode is as follows: sampling mode, 2 min; purge mode, 0.5 min; analytical mode, 1 min; recovery mode, 2 min. Thus, an entire sampling and analytical cycle requires 5.5 min. To minimize power requirements and baseline drift, the sensors are activated for only the first 30 sec of the analytical mode, which is sufficient to monitor the response maxima from all vapors tested.

TABLE II. Calibration Data for the 16 Test Solvents and Six SAW Sensors

Chemical (Abbreviation)	Elution Time[A]	N	TLV[B] (Range)[C]	Sensitivity[D] (LOD)[E]					
				PIB	PECH	FPOL	PDPP	OV-25	OV-275
Dichloromethane (DCL)	15	3	50 (20–400)	2.68 (6.54)	4.73 (8.97)	0.89 (46.8)	2.85 (3.97)	4.70 (6.18)	3.81 (9.99)
Trichloroethylene (TCE)	21	3	50 (10–250)	31.2 (0.52)	18.1 (2.21)	4.88 (5.98)	13.0 (0.84)	22.0 (2.71)	9.11 (5.42)
Perchloroethylene (PCE)	25	1	25 (2.5–125)	95.2 (0.24)	32.4 (1.41)	9.37 (3.89)	27.2 (0.46)	43.3 (1.22)	14.7 (4.12)
Acetone (ACE)	16	1	500 (50–2500)	1.19 (11.7)	4.64 (8.27)	9.80 (3.52)	1.52 (7.44)	3.01 (14.3)	3.06 (11.3)
2-Butanone (MEK)	18	3	200 (20–1000)	4.70 (2.95)	14.1 (2.76)	25.6 (1.03)	5.07 (1.97)	9.18 (4.89)	7.34 (5.89)
2-Methoxyethanol (2ME)	22	1	5 (2–50)	14.3 (1.18)	60.1 (0.70)	206 (0.15)	20.1 (0.61)	29.5 (1.46)	57.1 (0.91)
Isopropanol (IPA)	16	3	400 (40–2000)	2.75 (5.04)	7.09 (5.42)	25.7 (1.35)	2.93 (3.86)	3.73 (11.5)	7.67 (4.53)
1,4-Dioxane (DOX)	24	3	25 (2.5–125)	15.0 (1.32)	41.4 (1.04)	66.2 (0.52)	15.0 (0.89)	23.0 (1.88)	19.7 (2.88)
Tetrahydrofuran (THF)	20	1	200 (20–1000)	6.86 (2.12)	10.1 (3.97)	26.3 (1.01)	4.79 (2.18)	8.93 (5.90)	4.41 (10.7)
n-Hexane (HEX)	18	1	50 (5–400)	10.3 (1.21)	1.63 (22.7)	0.87 (30.7)	1.63 (6.23)	2.69 (18.6)	1.31 (30.2)
Isooctane (IOC)	23	1	300 (30–1500)	23.5 (0.79)	2.72 (15.9)	1.48 (21.4)	2.97 (4.16)	6.35 (7.53)	2.80 (19.5)
Isoamyl acetate (IAA)	29	3	100 (10–500)	104 (0.27)	114 (0.47)	241 (0.17)	48.8 (0.45)	97.4 (0.50)	33.2 (2.03)
n-Butyl acetate (BAC)	24	3	150 (15–750)	58.5 (0.48)	78.6 (0.68)	155 (0.26)	34.3 (0.63)	69.3 (0.71)	24.1 (2.79)
Benzene (BEN)	22	1	0.5 (4–120)	13.5 (1.26)	12.8 (3.27)	3.95 (7.72)	6.79 (1.80)	15.0 (2.87)	5.57 (9.29)
Toluene (TOL)	25	4	50 (10–250)	40.0 (0.52)	31.4 (1.37)	9.25 (3.77)	17.7 (0.75)	34.7 (1.90)	12.4 (4.69)
m-Xylene (XYL)	30	2	100 (10–200)	89.2 (0.32)	54.4 (0.99)	16.2 (2.49)	31.0 (0.70)	59.9 (0.82)	20.9 (3.21)

[A]Time (sec) after start of desorption
[B]In ppm from ref. 30
[C]Calibration concentration range in ppm
[D]In Hz/ppm
[E]In ppm

Calibration

Table II lists the 16 solvent vapors tested along with other relevant data. These solvents were selected to span a wide range of volatility and functionality. All solvents were obtained from Aldrich Chemical Co. (Milwaukee, Wis.) at >98% purity and were used as received.

Both instruments were calibrated in a 400-L thermostatted chamber (Psycrotherm G-27, New Brunswick Scientific, New Brunswick, N.J.) controlled to 25 ± 0.2°C. Test atmospheres were prepared in a series of 3-L Tedlar® bags (SKC Inc., Eighty Four, Pa.) connected to the instruments via a manifold of Teflon solenoid valves (Neptune Research, Maplewood, N.J.). A flow-temperature-humidity controller (FTH, Model HCS 301, Miller-Nelson Research, Carmel Valley, Calif.) provided dilution air during test-atmosphere generation.

Test atmospheres were prepared by first injecting a known volume of liquid solvent into a seasoned 1-L Tedlar bag and diluting with air at 25°C and 50% relative humidity (RH) to give a concentration of roughly 500 × TLV or less, depending on the vapor pressure of the solvent. Aliquots were then taken from this bag with a gas-tight syringe, injected into each of five 3-L Tedlar bags, and diluted to cover a 20- to 50-fold concentration range. Dilution air was introduced to each 3-L Tedlar bag from the FTH controller by semiautomated sequencing of the solenoid-valve manifold. Since water vapor permeates rapidly through the walls of the Tedlar bags,[25] they were suspended inside a secondary chamber, within the larger chamber, that was continually purged with air at 50% RH from the FTH controller to avoid changes in the RH of the test atmospheres. The secondary chamber consisted of a metal frame draped with Tedlar sheets that were loosely tethered with adhesive tape.

The two instruments were calibrated alternately at each vapor concentration. Following the 2-min sample collection period (sampling mode), an additional sample was drawn from the same Tedlar bag through the gas sampling loop of a gas chromatograph (GC) and analyzed while the instrument continued through its purge and analysis modes. Valve on/off sequencing within the test system was controlled by a computer equipped with a 16-bit parallel computer interface board (PIO-SSR-24, Keithley Instruments, Taunton, Mass.) using a program written in-house in Visual Basic® 4.0 (Microsoft, Redmond, Wash.). The GC (Model 3700,Varian Associates, Palo Alto, Calif.) was equipped with a 2 ft, 1/8-in i.d., packed column (1% SP-1000 on 60/80 mesh Carbopack B, Supelco, Bellefonte, Pa.) and an FID. GC injections were made using a solenoid valve. The transfer line between the Tedlar bag and the GC sample loop was then purged with clean air at 50% RH for two minutes in preparation for the next sample. Duplicate analyses were performed with each instrument at a given vapor concentration, resulting in four measurements of each test atmosphere by the GC and two measurements by each instrument. Responses were highly reproducible, giving relative standard deviations (RSDs) of ≤2% in all cases. Another computer running ChromPerfect® (Version 3.0, Justice Innovation Inc., Palo Alto, Calif.) software was used to control the GC sample injection valve, import the GC response data, and integrate the sample peaks.

Following calibration of all 16 individual vapors, an additional series of calibrations was performed with the following binary mixtures: toluene + 1,4-dioxane, benzene + isooctane, dichloromethane + m-xylene, butyl acetate + isoamyl acetate, and trichloroethylene + perchloroethylene. These mixtures were selected for several reasons. The mixtures of toluene with 1,4-dioxane and benzene with isooctane were selected because the components have response maxima that elute from the PCT at nearly the same time upon thermal desorption. The mixture of dichloromethane with m-xylene was selected because these vapors have very different elution times. The two additional mixtures were selected to include vapor pairs from the same chemical class. For each mixture pair, nine test atmospheres were prepared covering a range of relative concentrations. Each was tested in duplicate as described above for the individual vapors. Calibrations with the individual mixture components were repeated on the same day that the mixtures were tested.

These data were used as a training set to establish the response patterns and limits of detection (LODs) for each vapor. Several

additional tests were performed subsequently with selected vapors and binary vapor mixtures to establish a test set of response data for evaluating the performance of the instruments in recognizing and quantifying vapors.

Over the course of the 6 months of calibration, the instruments were periodically challenged with ~100 ppm of toluene as a quality control measure. Responses varied randomly around the average of 10 trials, with RSDs of <7% for each sensor. Thus, there is no indication of any loss or degradation of the polymer coatings or the PCT adsorbent over this time. The PCT adsorbent was subsequently replaced and additional testing was performed. Toluene responses before and after PCT adsorbent replacement were also within 7%, demonstrating that the PCT adsorbent can be packed reproducibly and that the heating profile within the PCT does not change appreciably.

Data Analysis

Vapors eluted from the PCT as very broad peaks, making it difficult to determine the integrated peak area. Therefore, the response maxima were used for quantification. For each vapor calibration, a series of at least three blanks containing only clean air at 50% RH was first analyzed. The average time-response profile for the blank was then calculated for each sensor. Invariably, actuation of the PCT heater caused an initial brief decline in the sensor output signal (i.e., the difference frequency) that reached a minimum within a few seconds of the start of heating. This minimum frequency was used as a reference point for all exposures. The peak arising from residual desorbed water vapor in the blank samples occurred about 8 sec after the start of heating and eluted completely within about 20 sec. Subtraction of the reference point frequency from each subsequent 1-sec frequency measurement gave the net response-time profile for the blank. A similar procedure was used to obtain profiles for the test vapors. The maximum response was determined for each test vapor, and the blank response was subtracted from it to yield the final net response for each sensor at a given vapor concentration. Duplicate test-vapor response values were averaged at each exposure concentration. Calibration curves were prepared by plotting the response maximum (Hz) versus concentration (ppm) at five calibrated concentrations over the range specified in Table II. The sensitivity for each vapor-sensor combination was determined from the slope of the calibration curves by linear regression with forced zero.

Pattern recognition analyses were performed using extended disjoint principal components regression (EDPCR), which has been described elsewhere[14,17,18] and is discussed in more detail below in the context of this study. Monte Carlo simulations were performed using an established error model.[26] Both the EDPCR and Monte Carlo software was written in-house in Visual Basic and run on a personal computer. Other pattern recognition analyses were performed in SPSS® (Version 7.0, SPSS Inc., Chicago, Ill.) on a personal computer.

RESULTS AND DISCUSSION

Coating Selection

The ability to discriminate among vapors with a sensor array depends on the use of sensor coatings that can engage in different nonbonding interactions (e.g., dispersion, dipole-dipole, and hydrogen bonding) with each of the target vapors and potential interferences. For this study a set of six polymer coatings was needed for initial testing of the two instruments. Once the coated sensors were calibrated against a series of test vapors, subsets of three sensors could be selected for use in a particular instrument on the basis of performance criteria dictated by the specific exposure scenario.

To this end, a previously published data set consisting of the calibrated responses of 10 polymer-coated SAW sensors to 12 organic vapors[9] was evaluated by principal components analysis and hierarchical cluster analysis. This yielded several groups of sensor coatings providing similar response patterns to the vapors in the test set. Complementing that effort, sensor responses from that study and from similar studies of SAW-sensor arrays were also analyzed using linear solvation energy relationship (LSER) concepts.[9,12,14,21,22,27] LSERs provide a semiquantitative basis for considering the collective effects of the various functional groups of the polymers and vapors on the magnitude of vapor partitioning, and have been used successfully in designing arrays and interpreting their responses.[9,20,28,29]

These analyses led to the selection of the six polymers listed in the Methods and Materials section as sensor coatings. Collectively, the coatings span a broad range of structure and functionality, and consequently were expected to provide a diverse set of response patterns to the target vapors. Other criteria used to select coating materials included sensitivity, adhesion to the quartz sensor substrate, long-term stability, and availability. Additional coating materials considered for inclusion in the array were Apiezon L, acrylonitrile/butadiene copolymer, diethylene glycol adipate, polychloroprene, and polyphenyl ether. These were eliminated from consideration either on the basis of redundancy with other polymers or prior evidence of poor stability.

Sampling and Analytical Protocol

Aside from the sensor coating materials, the key parameters affecting instrument performance are the nature and mass of adsorbent used in the PCT, the sample volume, the dry-air purge volume and flow rate, and the desorption flow rate, heating rate, and temperature. A series of preliminary experiments was performed on a subset of solvent vapors to optimize these parameters for this instrument.

The preconcentrator adsorbent ideally should have a high capacity for all target vapors, low capacity for water vapor, and stability in air at the high temperatures needed for repeated thermal desorptions. In a previous study concerned with evaluating different preconcentrator adsorbent materials for breath analysis with a SAW sensor array, the adsorbent XUS565 provided superior performance relative to other common porous polymers (e.g., Tenax GR, Tenax TA, Carbotrap, etc.) with respect to these criteria.[21] Breakthrough tests performed with XUS565 in that study indicated that only 20–40 mg of adsorbent would be required to limit breakthrough to an acceptable level (i.e., <10%) in air at 100% RH for most vapors. Since there was a need to minimize heating power requirements and PCT size in the current instrument, and operation at lower RH levels was anticipated, an adsorbent mass of 20 mg was used, which is at the low end of the range determined from the previous study. Although studies of adsorption capacity per se were not performed in this study, the consistent linearity observed among all sensors for all vapors and vapor mixtures indicates that breakthrough is not occurring to any significant extent under the test conditions.

The sample volume employed in the final protocol was 0.240 L, which represents a compromise between LOD and sampling time, under the constraint posed by the maximum pump flow rate

of ~0.120 L/min. Initial range-finding tests determined that a 0.240-L sample volume provided adequately low LODs for most vapors with no apparent adsorbent breakthrough at higher concentrations. A 2-min sampling period was considered acceptably short for establishing response profiles for the solvent vapors.

Although water vapor is retained on the XUS565, a previous study indicated that passing clean, dry air through the PCT after collection of an air sample, prior to heating, removed most of the water vapor while retaining even the most volatile organic vapors tested.[21] This reduced the water-vapor background in which samples were desorbed and, consequently, improved the reproducibility of responses and the LODs for the vapors. However, those results were obtained with air flowing in the same direction for sample collection, dry-air purge, and analysis steps. To reduce the need for an additional valve in the current instrument, a reversible pump was used: vapors are preconcentrated with the air flowing in one direction and desorbed with the air flowing in the reverse direction.

To determine the feasibility of backflushing to purge water vapor, samples of toluene, 2-butanone (MEK), and dichloromethane at 250, 1000, and 1250 ppm, respectively, in air at 50% RH were collected and then either desorbed immediately or backflushed with clean dry air prior to desorption. Purge times of 0, 10, 30, and 60 sec and purge flow rates of 0.030, 0.060, and 0.120 L/min were tested. Without purging, the water-vapor responses were quite large and overlapped significantly with the response maxima for dichloromethane and MEK on all sensors. With a 10-sec purge the reduction in the water vapor responses was about 50%. Increasing the purge time to 30 sec led to a reduction in responses to water vapor as high as 93% with only minor losses of organic vapors (i.e., <8%). Extending the purge cycle to 60 sec led to only marginal additional water vapor removal and resulted in losses of 40% for dichloromethane. The purge flow rate employed for these tests was 0.030 L/min. Higher purge flow rates resulted in significant losses of organic vapors even at 30 sec. Therefore, a 30-sec purge at 0.030 L/min was adopted for subsequent testing.

The maximum PCT temperature was kept at 180°C because of evidence of decomposition of the XUS565 at higher temperatures.[21] Power constraints in the current instrument limit the heating rate to about 4°C/sec. As a result, vapors elute relatively slowly from the PCT and at slightly different rates. Water vapor elutes prior to all of the organic vapors owing to its weak affinity for the XUS565. The remaining vapors elute within 15–30 sec of the start of heating, and generally elute in order of decreasing vapor pressure (see Table II). Heating rates were highly reproducible from run to run for both instruments, showing an RSD of only 2% for replicate measurements.

Figure 3 shows response profiles for a blank (Figure 3a) and for dichloromethane, trichloroethylene, and m-xylene (Figure 3b). The organic vapor profiles in Figure 3b were obtained separately and have been treated (i.e., blanks subtracted) as described in the Methods and Materials section. A slight overlap of the tail of the water vapor response with the response maxima of the earlier eluting vapors is observed. However, replicate measurements of water vapor responses at 50% RH were highly reproducible across the entire response profile, with standard deviations among all sensors ranging from 2–16 Hz, indicating a minimal effect on organic vapor responses from signal overlap. Note that the water vapor can be determined from its elution time, response pattern, and response magnitude, so that separate measurement of atmospheric humidity is not needed.

Tests with m-xylene and isoamyl acetate revealed that 7–12% of the vapor samples were retained on the adsorbent and carried over to subsequent samples. To remedy this problem the heating time was extended by 60 sec for these vapors. These vapors have the lowest vapor pressures among the 16 test vapors. This result indicates that measuring solvents with still lower vapor pressures may require further extension of the heating cycle time.

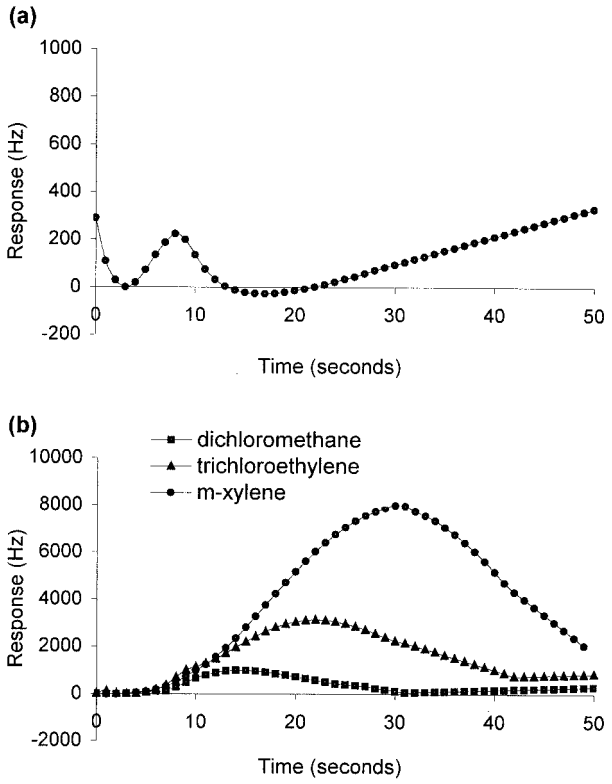

FIGURE 3. Response profiles from the PIB-coated SAW sensor for (a) clean air at 50% RH, and (b) dichloromethane (400 ppm), trichloroethylene (100 ppm), and m-xylene (100 ppm), which have elution maxima at 15, 22, and 30 sec, respectively. Note difference in ordinate scales between (a) and (b).

Sensitivities and LODs

Table II presents the sensitivity of each vapor-sensor pair. Coefficients of determination from linear regression (r^2) were ≥0.98 in all but four of the 96 calibrations, and were >0.93 in all cases. The exceptional cases included vapor-sensor combinations giving lower responses, which are affected more by baseline noise.

The LOD was defined as the concentration producing a response equal to three times the standard deviation of the baseline signal at the time the solvent elutes.[16,18] If the LOD is derived from the most sensitive sensor in an array, there are three-sensor arrays that can be assembled to achieve LODs ≤0.1 × TLV for all vapors except benzene, hexane, and dichloromethane (Table II). However, for vapor recognition the collective response pattern from all three sensors in the array is generally needed,[18] which demands measurable signals from all three sensors. Accordingly, if the LOD is derived from the least sensitive of the sensors, the minimum LOD achievable is >0.1 × TLV for a number of vapors, and for benzene it is ≫TLV. Although the LOD must be considered in decisions about which sensors to include in the array for a particular monitoring problem, situations requiring reductions

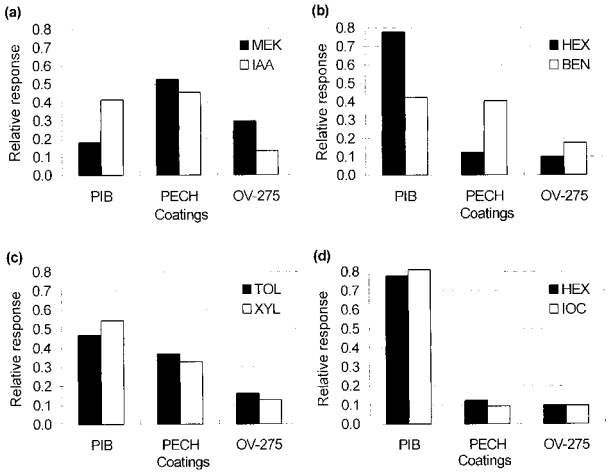

FIGURE 4. Relative response patterns from a three-sensor array coated with PIB, PECH, and OV-275 for (a) 2-butanone and isoamyl acetate, (b) n-hexane and benzene, (c) toluene and m-xylene, and (d) n-hexane and isooctane.

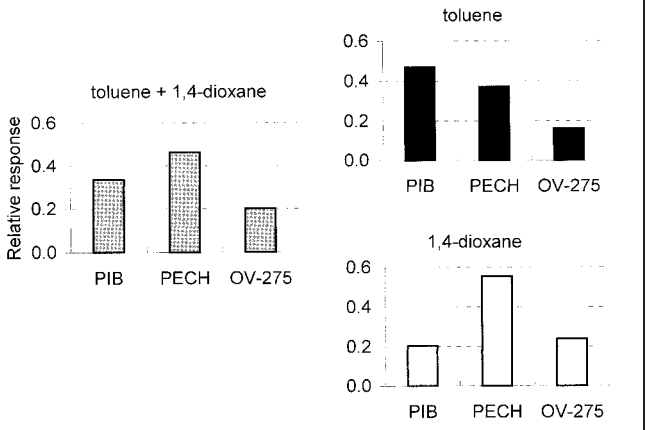

FIGURE 6. Relative response patterns for toluene, 1,4-dioxane, and their 1:1 mixture

in the LOD could be addressed by extending the sampling cycle to permit collection of a larger sample volume.

The partial selectivity for a given vapor among the six sensors is reflected in the range of sensitivity values across each row in Table II. Figure 4 (a–d) shows relative response patterns for four representative vapor pairs using an array of three sensors coated with PIB, PECH, and OV-275. The relative response pattern for each vapor was determined by dividing the sensitivity of each sensor (Table II) by the sum of the sensitivities of all three sensors.

The polar vapors MEK and isoamyl acetate are easily differentiable by their response patterns (Figure 4a), as are the relatively nonpolar hydrocarbons n-hexane and benzene (Figure 4b). The patterns shown in Figures 4c and 4d are for pairs of vapors from the same chemical class, differing in structure by only one or two methyl groups. Thus, they constitute more difficult discrimination problems. Although the response patterns for toluene and m-xylene are similar, there are subtle but significant differences seen in Figure 4c that should permit their differentiation. The responses to n-hexane and isooctane are nearly superimposable. Aliphatic hydrocarbons are typically the most difficult vapors to differentiate because they vary so little in structure and interact with the coatings only by dispersive forces.[14,28]

Figure 5 (a and b) shows response patterns for two additional vapors, trichloroethylene and perchloroethylene, using two different sets of three SAW sensors. With the sensors in Figure 5a, the response patterns for these two vapors are quite different, whereas with the sensors in Figure 5b they are much more similar. This illustrates the importance of selecting the proper set of coated sensors to include in the array.

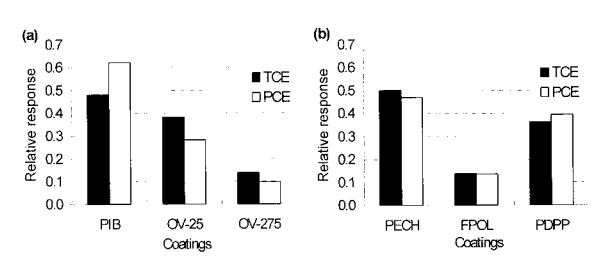

FIGURE 5. Relative response patterns from two different sensor arrays for trichloroethylene and perchloroethylene

Binary Mixtures

It has been shown previously that polymer-coated SAW sensor responses to binary vapor mixtures are equivalent to the sum of the component vapor responses,[14] which greatly simplifies sensor response modeling and pattern recognition analysis. To determine whether multiple vapor responses were additive with the current instrument, calibrations were performed on binary mixtures for a subset of vapors (see Methods and Materials section). Experimental response profiles for the mixtures were compared with those constructed by adding the profiles for the individual vapors over the entire 30-sec measurement period for a range of component concentrations. Differences were <12% in all cases, confirming that responses are indeed additive.

Although the response maxima of certain vapors occur at different times (see elution times in Table II) such that the sum of the responses at a given point in the mixture response profile may not equal the sum of the maxima for the individual components, all of the vapor responses overlap to some extent. The partial resolution of response maxima for certain vapors can aid in discrimination, but the lack of complete resolution of any of the vapor response profiles (see Figure 3b) demands that the pattern recognition analysis alone be capable of differentiating the vapors.

It was observed that certain mixture responses do not yield two distinct "peaks" in the profile, but rather a single broad peak. An initial pattern recognition analysis performed at this apparent response maximum revealed the presence of a mixture. Additional analyses were then performed at the elution times corresponding to the maxima of all identified mixture components to quantify each component (note: peak elution times were known from prior calibration).

Figure 6 shows the composite response pattern for a mixture of 1,4-dioxane and toluene at a 1:1 concentration ratio as well as the extracted relative response patterns attributable to each component vapor. This illustrates the process performed as part of the pattern recognition analysis for mixtures. As discussed below, the pattern recognition problem becomes more difficult as the analysis progresses from the overdetermined case (i.e., where the number

of sensors is greater than the number of vapors) to the fully determined case (i.e., where the number of sensors and vapors are equal).

Evaluating Instrument Performance

Two approaches were used to assess the capabilities of the instrument for vapor recognition, discrimination, and quantification. The first entailed the collection and analysis of an independent set of response data (i.e., data not used to establish calibrations). The second entailed the use of Monte Carlo simulations in conjunction with pattern recognition analysis. With both approaches, responses from one (or more) subset of three sensors out of six were analyzed as if that subset were being used in the instrument (note: there are 20 different 3-sensor subsets out of a total of 6 sensors). Response patterns were then derived and vapor identities and concentrations were determined.

The pattern recognition method employed here is referred to as EDPCR.[14,17,18] With EDPCR the sensor responses to each vapor challenge are first summed to yield a vector in n-dimensional space, where n=3 for a three-sensor array. The set of calibrated responses obtained over a range of concentrations is then modeled using principal components, where each vapor is represented by an individual principal components model determined by regression of the mean-centered response vectors. Responses to vapor mixtures (i.e., binary and ternary) are modeled similarly, assuming additivity of the component vapor responses, and the contribution of each component of the mixture is then extracted from the composite response vector by projection onto the principal components models for the individual vapors. Applying this procedure to the calibration data in Table II establishes a calibration set, or training set, which is then used as the basis for recognizing (i.e., identifying) vapors in subsequent exposures or in Monte Carlo simulations.

Table III shows the results of attempts to recognize and quantify the independent test set of vapors and vapor mixture components using sensors coated with PIB, PECH, and OV-275. As discussed below, this subset of three sensors was expected to provide the best overall performance in recognizing individual vapors from the training set. As shown, 47 of the 50 individual vapor tests (94%) resulted in a correct recognition. Errors in quantification averaged 5%.

For the mixtures the recognition rate depends on the boundaries placed on the problem. If all possible individual vapors and binary mixtures are considered, there are 136 possibilities from the total of 16 vapors. Under these boundary conditions, the binary mixtures were recognized at an overall rate of <50% from the response patterns of the three sensors used above.

If constraints are placed on the number of possible vapors, then the performance improves as expected. For example, if only the 8 vapors actually tested are considered, there are 36 possible individual vapors and binary mixtures. Under these conditions, the array correctly identified both mixture components in 28 of the 40 tests (Table III). For the remaining 12 tests, 1 of the 2 mixture components was correctly recognized. Assigning partial credit to these latter cases, the overall recognition rate is 85%.

Errors in recognition occurred for all of the mixtures of isooctane and benzene. These tests were restricted to relatively high isooctane concentrations and relatively low benzene concentrations in accordance with their respective TLV values.[30] This resulted in all of the benzene concentrations falling below 2.3 × LOD. As has been shown, recognition errors tend to increase, often dramatically, as one approaches the LOD, and the so-called limit of recognition often occurs at a higher concentration than the LOD even when the LOD is based on the least sensitive sensor in the array.[18] The poor results obtained for benzene in this case appear to be due to this factor. The three recognition errors for 1,4-dioxane observed in testing the mixture of toluene with 1,4-dioxane were also confined to cases where its concentration was <2 × LOD, and the sole error for trichloroethylene also fell into this concentration range.

Modeling Instrument Performance

To extend the performance evaluation to consider all 20 possible 3-sensor arrays that one could construct out of the total of 6 sensors, a modeling method was used that combines EDPCR with Monte Carlo simulations of vapor responses. The EDPCR-Monte Carlo modeling approach has been used successfully in a number of previous studies.[14,18,24,26,27] Using Monte Carlo methods, random and systematic variations are applied to the calibrated sensor responses of all of the vapors using a Gaussian variance distribution model. By iteratively sampling from the resultant distributions of error-enhanced responses and treating each sample as an ''unknown,'' which is then assigned an identity using the EDPCR models established from the calibration data, the nature and statistical likelihood of recognition errors expected under typical operating conditions can be evaluated. Errors in quantification are determined by comparing the resultant concentration value to what would be expected for the case of no applied error. Thus, instrument performance can be evaluated for any possible exposure scenario and any combination of three (or more) sensors without the need for exhaustive experimental testing.

The Monte Carlo simulations were generated using an error model described elsewhere.[26] The model accounts for variations in pump flow rate (i.e., sample volume), desorption heating rate, baseline noise, baseline drift, residual water vapor in desorbed samples, and calibration procedures. All of these factors were quantified experimentally.

The first case considered was response to an individual vapor that is being analyzed and must be recognized as one of the 16 previously calibrated vapors (i.e., no mixtures were considered). For each 3-sensor array, the procedure of generating synthetic responses and assigning identities was performed 500 times for each of the 16 vapors (total = 8000 simulations) to obtain a stable statistical estimate of the reliability of recognition. Results of each simulation were logged to determine the recognition rate and the identities of any incorrect assignments.

The allowed concentration range was from 0.2–5 × TLV for all vapors except for benzene, n-hexane, and dichloromethane. The LODs of the least sensitive of the six sensors for these three vapors were >0.2 × TLV, so their allowed concentration ranges were adjusted upward. In each case they were tested over a 25-fold concentration range bounded on the left by the LOD. Note that if a response pattern is initially determined to be from a vapor whose concentration is subsequently determined to be outside of the allowed range, it is reassigned as the vapor giving the next closest response pattern whose concentration falls within the allowed range. This, as it turns out, provides an added level of selectivity for cases in which the recognition rate is initially quite low (i.e., <90%). Where the recognition rate is higher, placing bounds on the allowable concentration is not necessary, as results are virtually identical with and without imposing this condition. Although it might be considered unrealistic to employ an upper concentration boundary in the pattern recognition process, since in

TABLE III. Individual-Vapor and Binary-Mixture Test Results Showing Accuracy of Recognition and Quantification Using a Three-Sensor Array with Coatings of PIB, PECH, and OV-275

		Concentration (ppm)		
Chemical	Recognized As	Actual	Measured	% Error
Toluene	TOL	21	21	0
	TOL	21	20	−5
	TOL	50	48	−4
	TOL	50	46	−8
	TOL	100	93	−7
	TOL	100	97	−3
	BEN	10	—	—
Trichloroethylene	TCE	30	31	3
	TCE	30	32	7
	TCE	50	50	0
	TCE	50	52	4
Perchloroethylene	PCE	20	18	−10
	PCE	20	20	0
	PCE	40	40	0
	PCE	40	40	0
	PCE	71	66	−7
	PCE	71	65	−8
Benzene	BEN	27	25	−7
	BEN	27	25	−7
	BEN	19	19	0
	BEN	19	20	5
	BEN	19	17	−11
	TOL	10	—	
2-Methoxyethanol	2ME	50	50	0
	2ME	50	50	0
m-Xylene	XYL	12	10	−17
	XYL	12	10	−17
	XYL	21	20	−5
	XYL	21	20	−5
	XYL	39	37	−5
	XYL	39	37	−5
	XYL	96	91	−5
	XYL	96	94	−2
	IAA	202	—	
1,4-Dioxane	DOX	26	26	0
	DOX	26	26	0
	DOX	50	54	8
	DOX	50	46	−8
	DOX	24	24	0
	DOX	24	25	4
	DOX	50	49	−2
	DOX	50	49	−2
Dichloromethane	DCL	100	100	0
	DCL	100	102	2
	DCL	200	184	−8
	DCL	200	188	−6
Isooctane	IOC	132	117	−11
	IOC	132	125	−5
	IOC	294	281	−4
	IOC	294	284	−3
		recognition rate		94%
		avg. quantification error		5%

field applications it is not possible to ensure such maximum concentration limits are met, one is always required to analyze within the limits of calibration. The concentration limits used here (i.e., 0.2–5TLV) are arbitrary. Extending the range to higher concentrations has no deleterious effect on performance.

Table IV shows the four highest and four lowest ranked three-sensor arrays obtained from the preceding analyses. The recognition rates range from 80–99%. Although there are several arrays that perform quite well, the array with coatings of PIB, PECH, and OV-275 ranked the highest and provided an overall recognition rate of about 99%. Table V presents the recognition matrix obtained from modeling this array. The columns are labeled with the actual vapor identities, and the rows indicate the assigned identities. Errors in recognition are primarily associated with confusion of MEK with 1,4-dioxane (cf. Figures 4 and 6), although additional errors are observed with other vapors at lower rates. For

TABLE III. Continued

		Concentration (ppm)					
		Actual		Measured		% Error	
Chemical	Recognized As	1	2	1	2	1	2
Toluene + Dioxane	TOL+DOX	10	25	11	23	10	−8
	TOL+DOX	10	125	15	111	50	−11
	TOL+DOX	50	25	52	23	4	−8
	TOL+DOX	50	125	44	112	−12	−10
	TOL+DOX	82	50	82	46	0	−8
	TOL+DOX	200	25	182	21	−9	−16
	TOL+DOX	200	125	170	105	−15	−16
	TOL+DOX	90	50	81	46	−10	−8
	TOL+DOX	105	25	108	27	3	8
	TOL+DOX	105	25	96	27	−9	8
	TOL+DOX	118	50	107	49	−9	−2
	TOL+DOX	118	50	133	53	13	6
	TOL+DOX	96	25	98	22	2	−12
	TOL+DOX	96	25	98	22	2	−12
	TOL+DOX	82	50	84	46	2	−8
	TOL	10	5	14	—	40	—
	TOL	50	5	50	—	0	—
	TOL	250	5	180	—	−28	—
Trichloroethylene +	TCE+PCE	10	8	5	9	−20	0
Perchloroethylene	TCE+PCE	10	25	7	17	−10	−24
	TCE+PCE	50	8	45	15	2	50
	TCE+PCE	50	25	48	26	−4	4
	TCE+PCE	25	25	10	29	−36	4
	TCE+PCE	50	125	27	129	−30	3
	TCE+PCE	50	25	53	24	6	−4
	TCE+PCE	50	25	54	24	8	−4
	TCE+PCE	25	25	33	25	32	0
	TCE+PCE	25	25	32	26	28	4
	TCE+PCE	250	8	245	10	−2	25
	PCE	10	125	—	123	—	−2
n-Butyl acetate +	BAC+IAA	150	30	145	33	−3	10
Isoamyl acetate	BAC+IAA	150	100	142	103	−5	3
Isooctane + Benzene	IOC+DOX	161	10	152	—	−6	—
	IOC+DOX	161	10	152	—	−6	—
	IOC+DOX	145	21	146	—	1	—
	IOC+DOX	145	21	146	—	1	—
	IOC+DOX	151	18	162	—	7	—
	IOC+DOX	151	18	150	—	−1	—
	IOC+DOX	293	16	284	—	−3	—
	IOC+DOX	293	16	288	—	−2	—
		recognition rate					85%
		avg. quantification error					10%

the correctly identified vapors, the average error in estimating concentration for the simulated responses was 5%, which is in agreement with the average error observed experimentally (Table III).

Additional analyses of this nature can be performed to screen different arrays for their performance in analyzing individual vapors or mixtures of arbitrary composition. In most occupational environments, however, the identities of the contaminants are determined prior to air sampling by performing an inventory of materials and processes. In many cases, only a few vapors are present at measurable levels.

For the final series of simulations and analyses performed in this study, several ternary vapor subsets were selected from the 16 vapors. Each three-sensor array was then evaluated to determine whether it could recognize and discriminate among the components of the ternary vapor set in any combination. That is, simulations were run for each individual vapor, all binary mixtures, and the ternary mixture. A total of 21 ternary vapor sets was analyzed. Representative results are shown in Table IV, which lists the mixture examined, the recognition rates for the three highest ranked arrays, and the recognition rate obtained for the array coated with PIB, PECH, and OV-275, which gave the best performance when tested against the 16 individual vapors.

The six mixtures presented in Table IV span the range of performance observed among all 21 mixtures analyzed. Recognition rates of >90% are predicted from the best arrays in 16 of the 21 cases. Overall, recognition rates range from 76–99% for the best arrays, depending on the mixture. For mixtures of similar vapors, rates are lower than for mixtures of vapors from different classes, as expected. Note that although one array can perform well for several mixture analyses, there does not appear to be a universally optimal array, suggesting the need for exchangeable sensors to address different exposure scenarios.

TABLE IV. Ranked Sensor Arrays and Recognition Rates Predicted from EDPCR-Monte Carlo Analyses

Test Set	Rank	Sensor Array			Recognition Rate (%)	95% CI
16 Vapors	1	PIB	PECH	OV-275	99.3	0.6
(individual only)	2	PIB	FPOL	PDPP	99.1	0.5
	3	PIB	FPOL	OV-25	98.8	1.2
	4	PIB	PECH	FPOL	97.9	1.9
	—	—	—	—	—	—
	17	PECH	PDPP	OV-25	86.2	7.2
	18	FPOL	OV-25	OV-275	85.2	7.8
	19	FPOL	PDPP	OV-25	82.7	7.3
	20	PDPP	OV-25	OV-275	80.5	9.8
TCE+HEX+2ME	1	PIB	PECH	FPOL	98.3[A]	0.7
	2	PIB	FPOL	PDPP	97.4	1.3
	3	PIB	FPOL	OV-25	97.4	1.4
	7	PIB	PECH	OV-275	92.6	4.0
TCE+DCL+2ME	1	PIB	FPOL	OV-275	97.6	2.4
	2	PIB	PECH	FPOL	95.6	3.8
	3	FPOL	OV-25	OV-275	95.6	2.7
	17	PIB	PECH	OV-275	81.4	10.6
TOL+DCL+MEK	1	PIB	FPOL	OV-275	93.7	2.4
	2	FPOL	OV-25	OV-275	95.6	3.8
	3	PIB	FPOL	PDPP	95.6	2.7
	8	PIB	PECH	OV-275	81.4	10.6
PCE+DCL+TCE	1	PIB	FPOL	OV-275	86.5	6.2
	2	PIB	PECH	OV-275	85.8	6.5
	3	PIB	OV-25	OV-275	84.8	6.8
DOX+MEK+ACE	1	PIB	OV-25	OV-275	79.7	5.7
	2	PIB	FPOL	OV-25	77.3	7.9
	3	PDPP	OV-25	OV-275	76.5	5.3
	12	PIB	PECH	OV-275	71.3	11.9
XYL+BEN+TOL	1	PIB	PDPP	OV-275	72.6	9.1
	2	PIB	PDPP	OV-25	72.1	9.0
	3	PIB	PECH	OV-25	71.7	9.8
	5	PIB	PECH	OV-275	71.3	11.2

Note: TCE = trichloroethylene; HEX = n-hexane; 2ME= 2-methoxyethanol; DCL = dichloromethane; MEK = 2-butanone; PCE = perchlorethylene; TCE = trichloroethylene; DOX = 1,4-dioxane; ACE = acetone; XYL = m-xylone; BEN = benzene; TOL = toluene.
[A]For the ternary mixtures, partial credit awarded for partially correct recognition

The recognition matrix for the ternary vapor set consisting of toluene, dichloromethane, and MEK presented in Table VI illustrates the types of errors observed in many of the cases considered. Individual vapors are often confused with binary mixtures of the same vapor with a low concentration of another vapor, as observed above (Table III). Interestingly, for this particular vapor set dichloromethane is recognized when present alone, but is overlooked in many of its mixtures and is mistakenly thought to be present in the mixtures of toluene and MEK. The overall recognition rate is about 94%.

Although the Monte Carlo simulations are based on experimentally determined variations in sensor responses, it was of interest to compare the results of the modeling with those for the experimental test set. For the individual vapors, a recognition rate of 94% was obtained, where the Monte Carlo simulations predicted 99%. The difference can be attributed to the limited number of samples collected experimentally. Notably, the errors in recognition observed experimentally between toluene and benzene and between m-xylene and isoamyl acetate are predicted by the simulations to occur in a small percentage of cases. For the eight-vapor binary mixture analyses, the recognition rates observed experimentally are predicted by the Monte Carlo simulations quite accurately for the unconstrained case (i.e., where the tested mixture components must be recognized from among all 136 possibilities out of 16 vapors), but are somewhat better than predicted for the constrained case (i.e., where the tested mixture components must be recognized from among the 36 possibilities out of the subset of 8 vapors). Confusion of benzene for 1,4-dioxane does predominate among the recognition errors in simulations of the benzene-isooctane mixture, however, as observed experimentally. Thus, although the number of experimental trials is small, these results provide further validation of the EDPCR-Monte Carlo approach to sensor array design and characterization.

CONCLUSIONS

This is the first report of an instrument small enough to be worn by a worker that can provide selective, simultaneous measure-

TABLE V. Recognition Matrix Derived from EDPCR-Monte Carlo Analyses for 16 Individual Vapors Using a Three-Sensor Array Coated with PIB, PECH, and OV-275 (Overall Average Recognition Rate = 99.3%)

	TCE[A]	XYL	BEN	TOL	HEX	PCE	DCL	IOC	ACE	IPA	MEK	THF	2ME	DOX	IAA	BAC
Trichloroethylene (TCE)[B]	497	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
m-Xylene (XYL)	3	499	0	3	0	0	0	0	0	0	0	0	0	0	0	0
Benzene (BEN)	0	0	496	3	0	0	0	0	0	0	0	0	0	0	0	0
Toluene (TOL)	0	0	2	494	0	0	0	0	0	0	0	0	0	0	0	0
n-Hexane (HEX)	0	0	0	0	498	0	0	0	0	0	0	0	0	0	0	0
Perchloroethylene (PCE)	0	0	0	0	0	500	0	0	0	0	0	0	0	0	0	0
Dichloromethane (DCL)	0	0	0	0	0	0	500	0	0	0	0	0	0	0	0	0
Isooctane (IOC)	0	0	0	0	2	0	0	500	0	0	0	0	0	0	0	0
Acetone (ACE)	0	0	0	0	0	0	0	0	500	0	0	0	0	0	0	0
Isopropanol (IPA)	0	0	0	0	0	0	0	0	0	498	0	0	0	0	0	0
2-Butanone (MEK)	0	0	0	0	0	0	0	0	0	0	483	0	0	20	0	0
Tetrahydrofuran (THF)	0	0	0	0	0	0	0	0	0	0	0	499	0	0	0	0
2-Methoxyethanol (2ME)	0	0	0	0	0	0	0	0	0	0	0	0	500	0	0	0
1,4-Dioxane (DOX)	0	0	0	0	0	0	0	0	0	0	16	0	0	480	0	0
Isoamyl acetate (IAA)	0	1	2	0	0	0	0	0	0	0	0	0	0	0	497	1
n-Butyl acetate (BAC)	0	0	0	0	0	0	0	0	0	2	1	1	0	0	2	499
Recog. (%)	99.4	99.8	99.2	98.8	99.6	100	100	100	100	99.6	96.6	99.8	100	96.0	99.4	99.8

[a] Actual vapor identities
[B]Assigned vapor identities

TABLE VI. Recognition Matrix Derived from EDPCR-Monte Carlo Analyses of a Mixture of Toluene (TOL), Dichloromethane (DCL), and 2-Butanone (MEK) Using a Three-Sensor Array Coated with PIB, FPOL, and OV-275 (Overall Average Recognition Rate = 93.8%)

	TOL[A]	DCL	MEK	TOL+DCL	TOL+MKE	DCL+MEK	TOL+DCL+MEK
TOL[B]	426	0	0	17	0	0	0
DCL	0	498	0	0	0	0	0
MEK	0	0	381	0	3	21	0
TOL+DCL	74	0	0	483	0	0	1
TOL+MEK	0	0	1	0	296	11	36
DCL+MEK	0	0	118	0	4	453	1
TOL+DCL+MEK	0	0	0	0	197	15	456
Recognition (%)[C]	92.6	99.6	88.1	98.3	86.2	95.8	96.3

[A]Actual vapor identities
[B]Assigned vapor identities
[C]Recognition rate with partial credit awarded for partially correct recognition

ment of multiple organic vapors. With a detector consisting of an array of only three SAW sensors it is possible to identify, differentiate, and quantify at least 16 individual vapors, including many structural homologues, on the basis of their sensor array response patterns. Analyzing the components of binary and ternary vapor mixtures was also demonstrated here experimentally and/or by stochastic modeling. But as the complexity of the mixture increases and the similarity of the vapors in the mixture increases, performance declines.

Two approaches to improving performance for such cases can be considered. The first is to increase the number of sensors in the array, thereby increasing the information content of the response patterns and permitting more complex mixtures to be analyzed.[26] The second is to employ different sensors in the array to optimize selectivity. The latter approach could be implemented in the form of sensor modules that could be rotated in and out of the instrument depending on the situation. The selection of sensors included in the module could be guided by the EDPCR-Monte Carlo modeling procedure presented here.

Beyond the selection of sensor coating materials, the performance of the instrument was shown to rely on several other key design and operating features. These include a reversible sampling pump that permits sample capture and backflushing of the adsorbent preconcentrator at different flow rates; humidity compensation via the use of a novel hydrophobic adsorbent and a dry-air purge step prior to thermal desorption of the target vapors; relatively slow heating that facilitates separation of water vapor from all target vapors; and sufficient heating time to avoid residual vapor accumulation on the preconcentrator adsorbent. The sampling and analytical cycle time of about 6 min represents a reasonable compromise between desired LODs and the resolution of the time-exposure profile obtained.

For several vapors, LODs achieved with the current operating configuration are not low enough to allow measurement at the desired level of 0.1 × TLV. Furthermore, it was shown that vapor recognition often becomes difficult as concentrations extend below about 2 × LOD. In these cases, the concentration that effectively limits performance is defined in terms of "recognition" rather than "detection."[18] With increases in pump flow rates or sampling cycle times, this problem could be addressed easily.

The adsorbent preconcentrator is essential to providing humidity compensation, field zeroing, and enhanced sensitivity. Results obtained in this study confirm previous findings on the utility of the adsorbent referred to here as XUS565 for collecting organic vapors spanning a wide range of volatility,[21] and show further that this adsorbent can be subjected to hundreds of thermal desorption cycles over the course of several months without degradation.

Ongoing work is aimed at characterizing the effects of ambient humidity and temperature on instrument performance and, ultimately, field testing the instrument in several workplace environments.

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REFERENCES

1. **Woebkenberg, M.L., C.S. McCammon:** Direct-reading gas and vapor instruments, In *Air Sampling Instruments*, 8th ed. (B.S. Cohen and S. V. Hering, eds.). Cincinnati, OH: American Conference of Governmental Industrial Hygienists, 1995. pp. 439–510.
2. *Multi RAE Product Specifications.* Sunnyvale, Calif.: RAE Systems, Inc., 1996.
3. **Snyder, A., C. Harden, A. Brittain, M. Kim, N. Arnold, and H. Meuzelaar:** Portable hand-held gas chromatograph/ion-mobility spectrometry device. *Anal. Chem. 65*:299–306 (1993).
4. **Wohltjen, H., and R.E. Dessy:** Surface acoustic wave probe for chemical analysis. I. Introduction and instrument description. *Anal. Chem. 51*:1458–1464 (1979).
5. **Wohltjen, H.:** Mechanism of operation and design considerations for surface acoustic wave device vapor sensors. *Sensors Actuators 5*:307–325 (1984).
6. **Grate, J.W., S.J. Martin, and R.M. White:** Acoustic wave microsensors—Parts I and II. *Anal. Chem. 65*:940–948, 987–996 (1993).
7. **Ballantine, D.S., R.M. White, S.J. Martin, et al.:** *Acoustic Wave Sensors: Theory, Design, and Physicochemical Applications.* Boston, Mass.: Academic Press, 1997.
8. **Grate, J.W., M. Klusty, R.A. McGill, M.H. Abraham, G. Whiting, and J. Andonian-Haftvan:** The predominant role of swelling-induced modulus changes of the sorbent phase in determining the responses of polymer-coated surface acoustic wave vapor sensors. *Anal. Chem. 64*:610–624 (1992).
9. **Patrash, S.J., and E.T. Zellers:** Characterization of polymeric surface-acoustic-wave sensor coatings and semi-empirical models of sensor responses to organic vapors. *Anal. Chem. 65*:2055–2066 (1993).
10. **Martin, S.J., G.C. Frye, and S. Senturia:** Dynamics and response of polymer-coated surface acoustic wave devices: Effect of viscoelastic properties and film resonance. *Anal. Chem. 66*:2201–2219 (1994).
11. **Grate, J.W., A. Snow, D.S. Ballantine Jr., et al:** Determination of

partition coefficients from surface acoustic wave vapor responses and correlation with gas-liquid chromatographic partition coefficients. *Anal. Chem. 60*:869–875 (1988).

12. **Rose-Pehrrson, S.L., J.W. Grate, D.S. Ballantine Jr., and P. Jurs:** Determination of hazardous vapors including mixtures using pattern recognition analysis of responses from surface acoustic wave devices. *Anal. Chem. 60*:2801–2811 (1988).
13. **Hierlemann, A., U. Weimar, G. Kraus, M. Schweizer-Berberich, and W. Gopel:** Polymer-based sensor arrays and multicomponent analysis for the detection of hazardous organic vapors in the environment. *Sensors Actuators B 26–27*:126–134 (1995).
14. **Zellers, E.T., S.A. Batterman, M. Han, and S.J. Patrash:** Optimal coating selection for the analysis of organic vapors with polymer-coated surface acoustic wave sensor arrays. *Anal. Chem. 67*:1092–1106 (1995).
15. **Wohltjen, H., D.S. Ballantine Jr., and N.L. Jarvis:** Vapor detection with surface acoustic wave microsensors. In *Microsensors and Microinstrumentation* (ACS Symposium Series 403; RW. Murray, R.E. Dessy, W.R. Heineman, J. Janata, and W.R. Seitz, eds.). Washington, D.C.: American Chemical Society, 1989. pp. 157–175.
16. **Carey, W.P., and B.R. Kowalski:** Chemical piezoelectric sensor and sensor array characterization. *Anal. Chem. 58*:3077–3084 (1986).
17. **Zellers, E.T., T.S. Pan, S. Patrash, M. Han, and S. Batterman:** Extended disjoint principal components regression analysis of SAW vapor sensor array responses. *Sensors Actuators B 12*:123–133 (1993).
18. **Zellers, E.T., J. Park, T. Hsu, and W. A. Groves:** Establishing a limit of recognition for a vapor sensor array. *Anal. Chem. 70*:4191–4201 (1998).
19. **Sutter, J.M., and P.C. Jurs:** Neural network classification and quantification of organic vapors based on fluorescence data from a fiber-optic sensor array. *Anal. Chem. 69*:856–862 (1997).
20. **Grate, J.W., S.J. Patrash, and M.H. Abraham:** Method for estimating polymer-coated acoustic wave vapor sensor responses. *Anal. Chem. 67*:2162–2169 (1995).
21. **Groves, W.A., E.T. Zellers, and G.C. Frye:** Analyzing organic vapors in exhaled breath using a surface acoustic wave sensor array with preconcentration—selection and characterization of the preconcentrator adsorbent. *Anal. Chim. Acta 371*:131–143 (1998).
22. **Grate, J.W., S.L. Rose-Pehrsson, D.L. Venesky, M. Klusty, and H. Wohltjen:** Smart sensor system for trace organophosphorus and organosulfur vapor detection employing a temperature-controlled array of surface acoustic wave sensors, automated sample preconcentration, and pattern recognition. *Anal. Chem. 65*:1868–1881 (1993).
23. **Frye, G.C., C.W. Colburn, R. Kottenstette, et al:** "Coatings and Sampling Systems for Trace Detection of VOCs Using SAW Sensors." Electrochemical Society Meeting—Symposium on Acoustic-Wave Based Sensors—Extended Abstracts, Abstract No. 946, San Antonio, Texas, Oct. 6–11, 1996. p. 864. Pennington, NJ: Electrochemical Society, Inc.
24. **Groves, W.A., and E.T. Zellers:** Prototype instrument employing an array of surface-acoustic-wave sensors for measuring organic vapors in exhaled breath. *Am. Ind. Hyg. Assoc. J. 57*:1103–1108 (1996).
25. **Groves, W.A., and E.T. Zellers:** Investigation of organic vapor losses to condensed water vapor in Tedlar bags used for exhaled breath sampling. *Am. Ind. Hyg. Assoc. J. 57*:257–263 (1996).
26. **Park, J., W.A. Groves, and E.T. Zellers:** Vapor recognition with small arrays of polymer-coated mircosensors—a comprehensive analysis. *Anal. Chem. 71*:3877–3886 (1999).
27. **Zellers, E.T., and M. Han:** Effects of temperature and ambient humidity on the performance of polymer-coated surface acoustic wave vapor sensor arrays. *Anal. Chem. 68*:2409–2418 (1996).
28. **Grate, J., and M.H. Abraham:** Solubility interactions and the design of chemically selective sorbent coatings for chemical sensors and arrays. *Sensors Actuators B 3*:85–11 (1991).
29. **McGill, R.A., M.H. Abraham, and J.W. Grate:** Choosing polymer coatings for chemical sensors. *CHEMTECH 24*:27–37 (1994).
30. **American Conference of Governmental Industrial Hygienists (ACGIH):** *1997 Threshold Limit Values for Chemical Substances and Physical Agents and Biological Exposure Indices.* Cincinnati, Ohio: American Conference of Governmental Industrial Hygienists, 1997.