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Portable Gas Chromatograph with Tunable Retention and Sensor Array Detection for Determination of Complex Vapor Mixtures

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A prototype portable gas chromatograph that combines a multiadsorbent preconcentrator/focuser, a tandem-column separation stage with individual column temperature control and junction point pressure modulation, and a detector consisting of an integrated array of polymer-coated surface acoustic wave microsensors is described. Using scheduled first-column stop-flow intervals and independent temperature programming of the two columns, it is possible to adjust the retention of eluting analyte vapors to maximize vapor recognition with the microsensor array and minimize the time of analysis. A retention window approach is combined with Monte Carlo simulations to guide retention tuning requirements and facilitate pattern recognition analyses. The determination of a 30-vapor mixture of common indoor air contaminants in <10 min is demonstrated using ambient air as the carrier gas. Detection limits of <10 ppb are achieved for the majority of compounds from a 1-L air sample on the basis of the most sensitive sensor in the array. Performance is assessed in the context of near-real-time indoor air quality monitoring applications.

Exposure to air contaminants in nonindustrial indoor workplaces has become a global public health concern. Among the contaminants found in such environments, volatile organic compounds (VOCs) have attracted considerable attention because of their ubiquity and possible etiologic roles in sick building syndrome and chronic disease.[1] Currently, determining the identities and concentrations of VOCs relies on labor- and capital-intensive sample collection and laboratory analytical methods, which limits the quality, quantity, and frequency of data collected. Some indoor-air quality (IAQ) studies have employed nonspecific survey instruments to collect composite indexes of exposure, such as total-VOC (TVOC),[2,3] but the relevance of such measures to health effects is unclear.[4] More sophisticated, transportable instruments have been adapted to workplace studies,[5] but their size, cost, or limited sensitivity preclude their use for routine IAQ monitoring.

This paper describes the design, operation, and laboratory testing of a novel prototype portable gas chromatograph suitable for routine, near-real-time, quantitative determinations of specific components of complex VOC mixtures at the low-parts-per-billion (ppb) concentrations encountered in problem office buildings and residences. Scrubbed ambient air is used as the carrier gas. The key analytical features of the instrument, shown in Figure 1, include a miniature multiadsorbent preconcentrator/focuser (PCF); a tandem-column, high-speed separation module with tunable retention capabilities; and a detector comprising an array of polymer-coated surface acoustic wave (SAW) microsensors that provides a characteristic "fingerprint" of each analyte. The system performance relies on the functional integration of these three instrument components.

The development of the PCF and pressure-tuned chromatographic separation strategies, as well as preliminary sensor array response characterizations, have been described in previous reports.[6−11] Here, we present the first results from the working prototype. The analysis of a set of common indoor air contaminants under controlled laboratory conditions is demonstrated, and the use of flow/pressure modulation and independent temperature programming in the dual-column ensemble to separate compounds that cannot be analyzed as coeluting species by the sensor array is highlighted. Chromatograms are parsed into retention-time windows, and the vapor response patterns within each window

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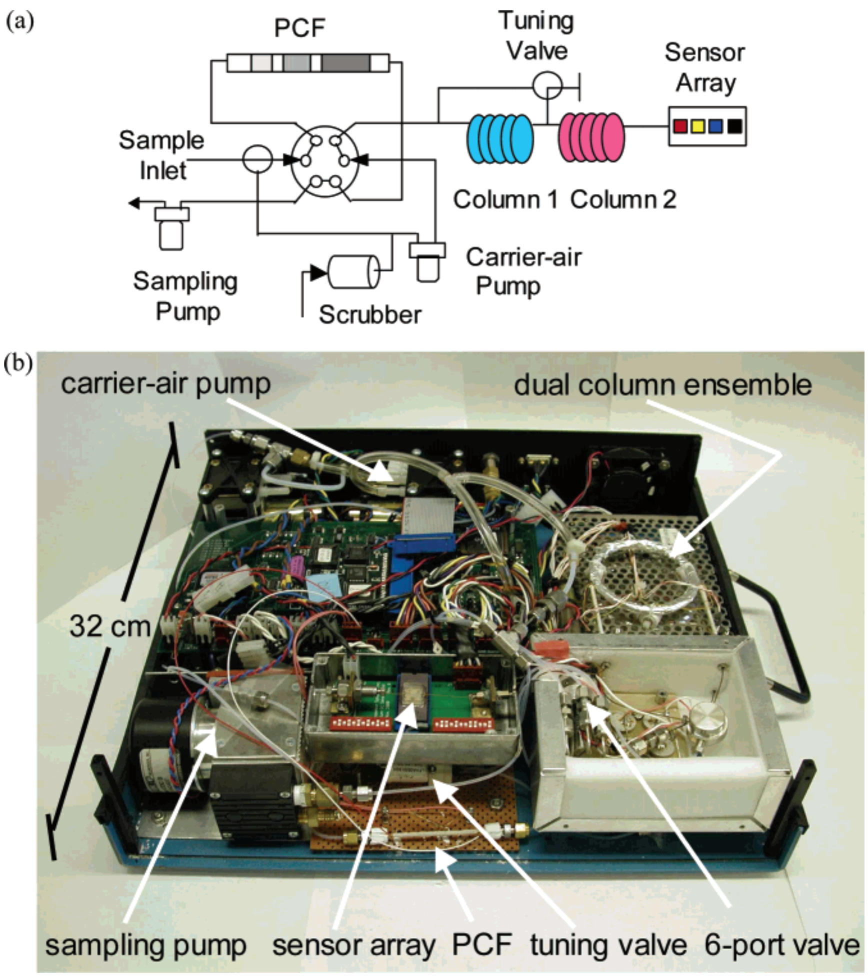

Figure 1. (a) Schematic diagram and (b) photograph of the prototype portable GC containing a multiadsorbent preconcentrator/focuser, a dual-column separation stage with midpoint pressure control and independent temperature control, and an array of four polymer-coated SAW sensors in a low-dead-volume detector cell.

are analyzed by extended disjoint principal components regression (EDPCR). Monte Carlo simulations are used to guide the retention tuning. These data are combined with retention-time values to optimize the recognition and quantification of the mixture components and minimize the time of analysis. Conditions are described for the high-speed analysis of a 30-component mixture spanning a ~6000-fold range of vapor pressures.

BACKGROUND

SAW Sensor Arrays for GC Detection. Polymer-coated SAW microsensor arrays possess several potential advantages as GC detectors: they are very small, leading to small detector dead volumes; they require no auxiliary gases; responses typically vary linearly with vapor concentration and responses to mixtures are generally equivalent to the sums of the component responses; they can operate at subambient pressures; they respond to a large number of condensable vapors; and the response patterns from the array can be used to identify eluting compounds or the components of coeluting mixtures by comparison with patterns stored in a calibration library. GC detectors comprising individual SAW sensors or a SAW sensor in tandem with a tin oxide sensor have been reported,[12,13] and the same SAW sensor array as used in this study has been connected to a short micromachined separation column to detect chemical warfare agents and simulants.[14,15]

Previous work on polymer-coated sensor arrays of various types, including SAW sensor arrays, suggests that the patterns generated can allow discrimination among the components of only simple mixtures, regardless of the number of sensors added to the array.[16−18] For the array used in this work, which has only three working sensors, chromatographic conditions must be established to ensure that no more than three coeluting com-

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pounds are presented to the array at one time. In cases where two or three coeluting compounds have similar array response patterns, it may be necessary to reduce further the number of compounds presented simultaneously to the array.

To address this constraint, we have employed an approach whereby the peaks within the chromatogram are analyzed sequentially according to retention-time windows defined during calibration. Peaks within each window are integrated collectively, regardless of the degree of overlap. The integrated area within a window will differ among the partially selective sensors in the array, and the relative integrated areas will be characteristic of the contributing compounds. These can be analyzed by standard pattern recognition algorithms, such as EDPCR, to determine the identities and quantities of all possible species expected in the designated time window. The approach can be summarized by eq 1, where A^i is the integrated peak area from sensor i within

$$A^i = \sum_{x=1}^{n} C_x S_x^i + e^i \qquad (1)$$

the retention window, C_x is the concentration of component x, S_x^i is the sensitivity of sensor i for compound x (from the slope of calibration curve), and e^i is the linear regression residual error of each sensor response. This equation relies on the additivity of peak areas in the composite sensor responses from mixtures, which is well-established in the case of polymer-coated SAW sensors.[16,20]

This approach is analogous to those where peak profiles are fitted to Gaussian functions and the contribution of each component to the total response is allotted accordingly,[19] but avoids any dependence on peak shape, which can vary considerably in portable systems subject to changing environmental conditions, particularly when an adsorbent bed is used for preconcentration and focusing.[7] The more laborious collection of point-by-point measurements over the entire composite peak profile within a given window, followed by pattern recognition analyses of the instantaneous responses at each retention time,[21] was also considered. Although this approach can provide useful qualitative information from the tails of partially resolved peaks, for this initial study, the compounds within a given window were determined during calibration, and since quantitative analysis requires pattern recognition across the entire composite peak profile anyway, there was little justification for the added computational burden.

Tunable/Programmable Retention. Coupling two GC columns in series, each with a different stationary phase, provides retention selectively not achievable with either column alone. Further, the selectivity can be tuned for a specified set of target compounds by programming a schedule of adjustments to the carrier gas pressure at the junction point between the columns.[8,9] The resultant change in carrier gas flow rates in the two columns alters the residence times of eluting compounds and thus the influence of each stationary phase on the ensemble separation. For the prototype instrument used in this study, vapor pairs that are adequately separated by the first column but that coelute from the column ensemble can be addressed by briefly opening the bypass valve connecting the column junction point to the inlet (Figure 1) just after the first component has passed the junction point.[10,11] This stops the flow in the first column while the flow in the second column continues at a slightly higher rate due to the lower pressure drop associated with the bypass. Resumption of the normal flow path by closure of the valve allows the separation to proceed with an increase in resolution of the two previously coeluting compounds and little effect on the other compounds. The duration of the pressure-tuning interval only needs to be a few seconds to be sufficient for separation. Multiple stop-flow intervals, appropriately timed, can be implemented to address additional coelutions.

Independently changing the temperatures of the two columns also allows strategic tuning of retention in the column ensemble.[22] This technique takes advantage of the differential heats of sorption of compounds in the two stationary phases. Compounds with larger heats of sorption (and, consequently, larger retention factors) will be accelerated more by an increase in temperature within a given column, leading to greater absolute decreases in retention. Thus, separation conditions can be optimized for specific regions of the chromatogram by appropriately timed changes in the temperature of one or both columns.

EXPERIMENTAL SECTION

Instrument Description. The prototype GC was constructed by Microsensor Systems Inc. (MSI, Bowling Green, KY) for this project. About the size of a laptop computer, but somewhat thicker, it measures 32 cm (*l*) × 32 cm (*w*) × 10 cm (*h*) and was powered for this study by an external 18-V dc supply. Two minidiaphragm pumps (KNF Neuberger Inc., Trenton, NJ) are used for the preconcentrator sample collection and for the carrier gas, respectively. The low-dead-volume six-port valve switches the preconcentrator between sampling and injection positions and is housed in an insulated enclosure that is heated to 60 °C. Two three-way solenoid valves (Lee Co., Westbrook, CT) are used for the dry-air purge and column pressure tuning (see Figure 1). The cylindrical scrubber was packed with molecular sieves and activated charcoal and was mounted to the outer sidewall of the instrument during testing (note: in normal operation it would be housed inside the instrument chassis).

The miniature PCF consists of a thin-wall stainless steel tube (1.32-mm i.d.) manually packed, in order, with 8 mg of Carbopack B, 2.5 mg of Carbopack X, and 1.8 mg of Carboxen 1000 (Supelco, Bellefonte, PA) and wrapped with a sleeve of polyimide, which holds a minithermocouple against the capillary wall.[7] A coil of Pt wire is used for heating during thermal desorption. The PCF is connected to the six-port valve via $^1/_{32}$-in.-i.d. Teflon tubing, which allows thermal desorption flow in the reverse direction of sampling flow (i.e., back flushing) to avoid band broadening or irreversible trapping of the less volatile compounds on the higher-surface-area downstream adsorbents. The dead volume in the desorption path includes the unpacked space inside preconcentrator and the

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internal volume of the Teflon connection tube, which are estimated to be <20 μL. Heating power is subject to on/off control only, but since the temperature controller responds rapidly to the thermocouple feedback, the temperature overshoot is less than 10 °C above the set point. The time required for the heater to ramp from room temperature to the peak desorption temperature of 300 °C is ~4 s.

The first column consists of a fused-silica capillary, 0.25-mm i.d. and 4.5 m long, having a nonpolar poly(dimethylsiloxane) bonded stationary phase (Rtx-1, 0.5-μm thickness, Restek, Bellefonte, PA). The second column has the same dimensions and a bonded stationary phase of the moderately polar polytrifluoropropylmethylsiloxane (Rtx-200, 0.25-μm thickness, Restek). This combination of stationary phases has been found to provide good separation of compounds similar to those of interest in this study and stable operation with air carrier gas.[8,9] Each column is coiled together with a heater wire and thermocouple in a so-called "at-column heating" configuration. Column assemblies and associated heater control hardware were provided by RVM Scientific, Inc. (Santa Barbara, CA). The two columns can be heated independently at rates of up to 1000 °C/min.

The tuning valve is connected to the junction point of the two columns via a zero-dead-volume union tee. When the valve is closed (off), the column juncture is at its natural pressure, and when it is open, the column juncture is balanced with the pressure at the inlet to the first column (i.e., open to carrier air pump). At the outset of this investigation, the tunable separation module was designed to operate at subatmospheric pressure, with the pump drawing rather than pushing samples through the columns. The primary advantages of subatmospheric chromatography are that diffusion coefficients are increased, which improves the chromatographic efficiency, and the sweep time of the detector cell is reduced, which minimizes extracolumn band broadening. This is important when air is used as the carrier gas because diffusivities of vapors are lower than those in more conventional carrier gases such as He or H_2.[9] However, since the responses of the sensors in the array are inversely proportional to the pressure above the sensors, subatmospheric operation leads to a commensurate reduction in sensitivity.[8] The latter issue was deemed more important so positive pressure operation was selected. Switching the pressure condition in the system is a simple matter of changing the fluidic interconnection to the pump.

The detector is an integrated array of four ST-quartz SAW sensors provided to this study by researchers at Sandia National Laboratories with three coated sensors and one uncoated reference sensor. Each sensor was designed to operate at a nominal frequency of 520 MHz. However, instead of measuring resonance frequency as is typically done, the phase shift of each sensor is measured with on-chip circuitry. Acoustic waves launched by the emitter transducer on the sensor substrate reach the receiver transducer with some degree of phase lag due to interaction with the polymer coating and any sorbed vapors. The phase of each working sensor is individually compared with that of the reference sensor to assess relative phase shift, which is converted to an output voltage in the range of mV. The initial phase position is adjusted by the application of a bias voltage to the point of maximim sensitivity and linear range.[23]

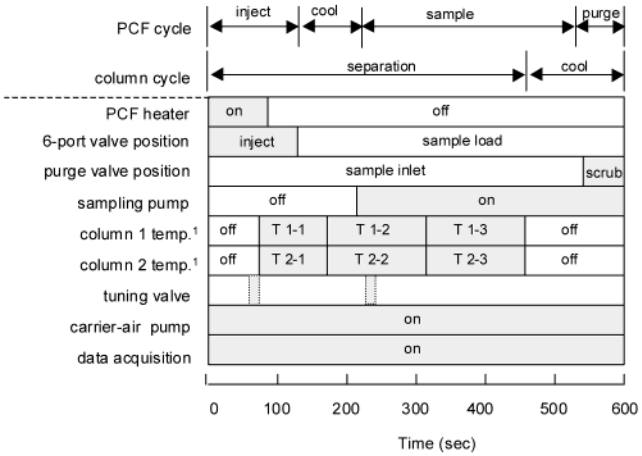

Figure 2. Representative event schedule for tuned analyses with the portable GC.

The four sensors occupy an area of approximately 2 mm × 3 mm and are enclosed beneath a glass cap having two fused-silica capillaries connected to side ports for sample inlet/outlet. The internal volume of the detector cell is <2 μL. Each of the three working sensors was coated with a different polymer from solution by a microcapillary applicator. The polymers used are polyisobutylene (PIB), ethyl cellulose (ECEL), and BSP3, which is a copolymer of poly(dimethylsiloxane) and hexafluorobisphenol A, developed and graciously provided by J. W. Grate of Pacific Northwest National Laboratories.[24] Nominal coating thicknesses were 84, 70, and 78 nm, respectively. PIB is a nonpolar hydrocarbon polymer, ECEL has moderate polarity and hydrogen-bonding properties, and BSP3 exhibits particularly strong hydrogen bonding (i.e., Lewis) acidity. The differences in polymer structure determine their relative selectivity toward different vapors.

System Operation. The on-board microprocessor controls all internal modules and communicates with a notebook computer through an RS-232 serial port. Control parameters were first written to a computer text script file and then uploaded to the instrument. The script contains the timetable of every event in the sampling and analytical cycle (i.e., sampling time, preconcentrator heating time, valve switching, column temperature programming, etc.). Sensor output voltages are measured through a multiplexer and a 24-bit A/D converter at an acquisition rate of 16 Hz/channel, transmitted through the RS-232 interface, and treated using software written in LabView 5.0 (National Instrument, Austin, TX).

The column heaters can be adjusted independently stepwise from an initial default (i.e., off, ambient temperature) to each of three additional settings. The carrier gas pressure at the head of column was held constant for all analyses. All events have three possible on/off cycles. A typical timetable of events for an analysis is shown in Figure 2. A sample is injected at $t = 0$ s by heating the PCF for 90 s.[7] Carrier air continues to flow through the PCF for another 30 s and then the six-port valve is switched to the sample load position. The sampling period starts at 220 s and

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Table 1. Target Indoor Air Contaminants, Vapor Pressures, and Instrument Response Parameters

no.	compound	vapor pressure (Torr)	retention time (s)	LOD (ppb) BSP3	LOD (ppb) ECEL	LOD (ppb) PIB	linear range (ppb)
1	acetone	231	38	30	>470	>470	>470
2	2-methylfuran	200	45	41	110	140	>500
3	1,1,1-trichloroethane	124	53	25	44	75	>490
4	ethyl acetate	95	50	9.9	39	>450	>450
5	benzene	95	57	28	33	52	>790
6	2-butanone	91	49	9.9	>410	>410	195
7	1,2-dichloroethane	88	54	32	25	66	>640
8	2,5-dimethylfuran	66	71	23	43	59	>440
9	trichloroethylene	47	65	12	12	20	130
10	2-propanol	43	37	30	>490	>490	>490
11	2,4-dimethylhexane	35	83	13	22	15	155
12	2-methylheptane	30	110	19	27	18	>440
13	toluene	28.5	96	9.5	15	21	130
14	perchloroethylene	18.5	133	5.5	6.8	7.8	>280
15	*n*-octane	14	134	7.4	12	8.4	>310
16	*n*-butyl acetate	12	152	1.0	4.2	8.8	>300
17	chlorobenzene	11.8	156	2.7	3.4	6.5	>250
18	ethylbenzene	10	169	3.6	5.0	6.6	>271
19	*m*-xylene	8	175	2.6	4.0	5.4	>260
20	2-hexanone	11	152	7.2	14	32	>200
21	styrene	6	196	2.0	2.7	4.3	>260
22	α-pinene	5	222	1.7	3.1	2.4	140
23	cumene	5	215	2.1	2.7	3.7	>250
24	*n*-nonane	4.3	206	2.0	3.6	2.2	>242
25	3-heptanone	3.9	211	0.4	2.2	4.3	>260
26	D-limonene	3	305	1.2	1.7	1.5	150
27	D4	3	297	1.5	3.2	2.3	>210
28	mesitylene	2.5	246	0.9	1.4	2.1	>230
29	3-methylbutanol	2.4	88	3.2	7.4	>290	>300
30	*p*-dichlorobenzene	1.76	281	1.1	0.9	1.8	78
31	D5	1.5	367	0.2	1.0	0.5	>110
32	3-octanone	1.4	282	0.6	1.7	2.9	>93
33	1-octen-3-ol	0.2	265	0.5	1.0	6.2	52
34	*n*-dodecane	0.12	382	0.4	0.6	0.3	53
35	naphthalene	0.08	374	0.3	0.4	0.7	>55
36	*n*-tridecane	0.04	437	0.6	0.8	0.4	39

continues for 5.5 min at 0.18 L/min, which is the highest flow rate achievable. After collection of the 1-L sample volume, the PCF is purged with clean, dry air drawn through the scrubber for 50 s (0.15 L) to remove coadsorbed water vapor from the Carboxen 1000 (note: the other adsorbents do not retain water vapor to any significant extent).[7] The six-port valve is switched back to the inject position, and the PCF is heated to inject the next sample. Pressure-tuning segments and column-temperature changes can be inserted at any point in the separation cycle. The maximum column temperature employed for this study was 150 °C.[8] Following collection of an initial sample, the sampling and separation cycles can be synchronized to reduce the total duty cycle.

Calibration Procedure. Test atmospheres were prepared by injecting liquid solvents into a Tedlar bag prefilled with a known volume of clean, dry air. All bags were seasoned by preexposure to low concentrations of the test compounds followed by repeated flushing with clean air until no detectable concentration was observed in samples collected and analyzed by EPA method TO-17 (see below). Target compounds (Table 1) were obtained from Aldrich (Milwaukee, WI) at ≥98% purity except for 2-methylheptane (99%) and octamethylcyclotetrasiloxane, (D4, 98%) (Acros/Fisher, Pittsburgh, PA), 2-methylfuran and 2,5-dimethylfuran (99%, Lancaster, Windham, NH), 4-phenylcyclohexene (98%, Chemsampco, Trenton, NJ), and decamethylcyclopentasiloxane (D5, 98%, Gelest, Tullytown, PA). Concentrations were calculated by assuming complete evaporation for volatile liquids. The concentrations ranged from 20 to 50 ppm for compounds with vapor pressures less than 4 Torr and 200−300 ppm for compounds with vapor pressures higher than 4 Torr. For solid chemicals, such as *p*-dichlorobenzene and naphthalene, several milligrams were placed in a 1-L Tedlar bag, flushed with clean air, filled to ~0.7 L, warmed gently with heat gun, and left at room temperature overnight. Aliquots of the headspace air were then transferred to other Tedlar bags by gastight syringe and diluted as needed.

For this testing, the instrument inlet was fitted with a union tee with one end connected to the side-mounted scrubber and the other end sealed with a septum. Calibrations were performed initially with noncoeluting subsets of 12 vapors from Table 1. High-concentration vapor spikes of 0.2, 0.5, 1.0, and 2.0 mL were introduced into the sample stream, which, for a sample volume of 1 L, correspond to equivalent concentrations of 4−600 ppb for spikes of 20−300 ppm. For example, the mass introduced by 1 mL of vapor at 50 ppm is equivalent to 50 ppb in 1 L (i.e., 50 ppb·L). Five replicate analyses were performed at each challenge concentration. The sample volume of 1 L was selected on the basis of a series of preliminary tests performed on two 390-MHz SAW oscillators coated with PIB and BSP3 and sealed in a cell similar to that used for the instrument's sensor array. Results indicated that detection limits in the low- or sub-ppb range could be obtained under similar operating conditions with the current array.[25]

EPA method TO-17 was used to confirm vapor concentrations during the instrument calibration.[26] Stainless steel sampling tubes (Scientific Instrument Service SIS, Inc., Ringoes, NJ) packed with 80 mg of Carbotrap C, 120 mg of Carbopack B, and 60 mg of Carboxen 1000 (Supelco) were preconditioned prior to use. The method was calibrated using solvent spikes prepared in CS_2 and injected into the tubes in volumes that covered an appropriate range of mass (0.8−200 ng) to match that collected from the test atmospheres. Duplicate TO-17 reference samples were collected at 0.1 L/min for 5 min in parallel with those collected by the instrument and analyzed using a short-path thermal desorption module (TD-4, Scientific Instrument Services Inc.) connected to the GC injection port (GC-FID HP6890, Agilent, Santa Clarita, CA). Peak areas from the SAW sensors were integrated using Grams 32 software (Galactic Industries, Salem, NH) following smoothing using a 110-point running average. The average peak areas from the five replicates were regressed onto the average concentrations determined from the reference samples, forcing the regression line through the origin.

EDPCR/Monte Carlo Model. To assist in evaluating the vapor recognition capabilities of the array, Monte Carlo simulations were performed and the data generated were analyzed with EDPCR. The Monte Carlo model employed has been described elsewhere.[16,27] Five hundred simulated (i.e., error-enhanced) sensor responses were generated for each vapor and treated as unknown test samples, each of which was assigned an identity via EDPCR using the library of response patterns established from the calibration data. Average recognition rates were compiled and compared for different separation tuning conditions. The values for the various error terms in the Monte Carlo model were determined experimentally by repeated measurements under controlled conditions. EDPCR and Monte Carlo software routines were written in-house in Visual Basic and run on a personal computer.

RESULTS AND DISCUSSION

Initial Instrument Calibration and Limits of Detection (LODs). Figure 3 shows the three-channel chromatogram for one of the 12-component calibration mixtures, which includes compounds ranging in vapor pressures from 1.5 (D5) to 231 Torr (acetone), using the same temperature program for both columns (see figure caption). Due to the sensitivity differences among the three sensors, the *y*-axis scales for the ECEL and PIB sensors have been enlarged for ease of visualization. Peak shapes are generally good, though some tailing and broadening are evident for the less volatile compounds. Peak widths are somewhat broader than observed in previous tests with this array connected to a bench-scale GC with the same PCF.[7] This is apparently due to a slightly slower PCF heating rate in the instrument, a lower desorption flow rate (2.5 vs 4 mL/min), and additional inlet broadening from the dead volume associated with the PCF−column connection. The less volatile compounds may also suffer broadening from nonspecific adsorption on the postcolumn system surfaces.

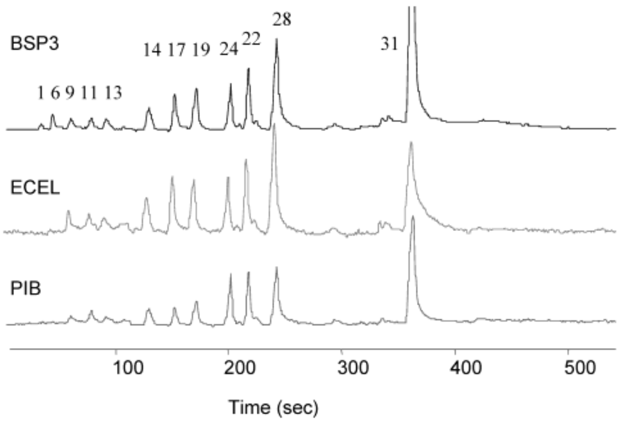

Figure 3. Twelve-compound chromatograms from each sensor in the array using a temperature program (same for both columns) of 35 °C (ambient temperature) for 120 s, 50 °C for 70 s, 70 °C for 120 s, and 130 °C for 140 s.

Calibrations were performed over a range of preconcentrated masses and equivalent vapor concentrations that depended on the vapor. For the more volatile compounds, the concentration range was extended beyond an initially planned maximum of 100 ppb•L in an attempt to address the relatively low sensitivities of the PIB- and ECEL-coated sensors (see below). Plots of peak area versus vapor concentration (from the TO-17 method) were generally linear over the ranges examined (regression r^2 values were >0.98 in most cases and >0.96 in all cases), and the slopes from the three sensors were used to construct response patterns for vapor recognition.

For 10 of the 36 compounds, the response at the highest concentration fell below the linear trend at the lower concentrations. The upper concentration range for each of these cases is given in Table 1. This behavior was not observed for the other compounds over the ranges tested. After probing possible sources of the nonlinearity, it was determined to be due to the sensors rather than other components of the system (e.g., PCF breakthrough, leaks, pump flow rate variations). The precision of responses among the five replicates varied substantially among the different compound−sensor combinations. For example, compounds such as perchloroethylene and *n*-nonane had stable and reproducible responses from all sensors, while compounds such as acetone and mesitylene had large variances at high concentrations. For the least volatile compounds (e.g., *n*-dodecane and *n*-tridecane) extracolumn wall adsorption may have been contributory.

LODs (Table 1) were determined by multiplying the standard deviation of the smoothed baseline for each sensor by a factor of 3 and then dividing by the average slope from calibration. It is recognized that this provides an optimistic estimate of the LOD because it does not take full account of slope variations. The BSP3-coated sensor consistently provides the highest sensitivity and

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Table 2. Recognition Rates from Monte Carlo/EDPCR Analyses of Critical Coeluting or Nearest-Neighbor Compounds in the Chromatograms Shown in Figure 4

window	retention time (s)	compound(s)	recognition rate (%)
A	98−123	*n*-octane/perchloroethylene	93
B	123−153	2-hexanone/butyl acetate	73
C	178−203	nonane	99 (vs butyl acetate) 91 (vs mesitylene)
D	235−270	mesitylene	88 (vs D-limonene)
E	301−324	D-limonene	86 (vs D5)
F	357−430	D5/naphthalene/dodecane	79
		D5/naphthalene	97
		naphthalene/dodecane	99
		D5/dodecane	98

lowest LODs, with LOD values of ≤10 ppb for 26 of the 36 compounds and <1 ppb for 8 of those compounds. Of the remaining 10 compounds, LODs range from 11 to 40 ppb. As expected for a sorption-dependent sensor response, LODs tend to increase with increasing vapor pressure for all sensors.

For the nonpolar PIB-coated sensor, responses for the more volatile and polar compounds, such as the lower ketones and alcohols, are very small. The ECEL-coated sensor also shows low sensitivity to several of the more volatile compounds. As a result, four compounds had responses only from the BSP3-coated sensor over the concentration ranges of interest and an additional three compounds had responses from only the ECEL and BSP3 sensors. The LODs for the PIB-coated sensor are much higher than those obtained for the similarly coated 390-MHz SAW sensor operated as an oscillator and tested in a system of similar configuration (i.e., as a detector for a conventional GC).[25] The reason for the lower sensitivities and relatively high noise levels observed with the current array is not clear but was seen consistently among several arrays during preliminary testing.

Tuned Separations and Pattern Recognition. As expected, vapors from different functional group classes generally yield easily distinguishable response patterns while those from the same functional group classes, particularly the alkanes and aromatics, yield more similar, and often indistinguishable, patterns. However, there are exceptions where intraclass discriminations are possible (e.g., trichloroethylene and perchloroethylene) and where interclass discriminations are not possible (e.g., 2-hexanone and *n*-butyl acetate). Since most homologues are readily separated chromatographically, the problem of similar response patterns among compounds in the same class can be addressed by separating them and using retention time as an added factor in recognition/discrimination. For more complex mixtures, the probability of coelutions increases and the capability of sensor array pattern recognition to identify and discriminate among up to three coeluting vapors can be used to advantage to ease the burden of separation placed on the columns. This highlights the complementary nature of GC and sensor array detection using sorption-dependent sensors.

To illustrate the functional integration of tunable retention and sensor array pattern recognition, a subset of 10 vapors was analyzed under an initial set of conditions that yielded the chromatogram shown in Figure 4a. For brevity, only the BSP3-coated sensor output is presented. Retention time windows containing three or fewer vapors were established by inspection of the chromatogram. Three coelutions occur: *n*-octane with perchloroethylene; 2-hexanone with *n*-butyl acetate; *n*-dodecane with D5 and naphthalene. The normalized response patterns obtained from the calibration slopes for these coeluents are shown above the peaks in Figure 4a. Monte Carlo simulations run on each of these groups and analyzed by EDPCR (a separate analysis for each retention window) yielded predicted recognition rates of 93%, 73%, and 79%, respectively (Table 2) (note: the analyses consider the problem of distinguishing the binary or ternary mixture from all possible component vapors and lower-order mixtures over a simulated concentration range of 3−15 times the LOD of each compound). Using 90% recognition as a threshold for satisfactory performance, these results indicate that it would not be necessary to separate the perchloroethylene/*n*-octane pair but that it would be necessary to separate the other two coeluting mixtures. Results of Monte Carlo/EDPCR analyses of the fully

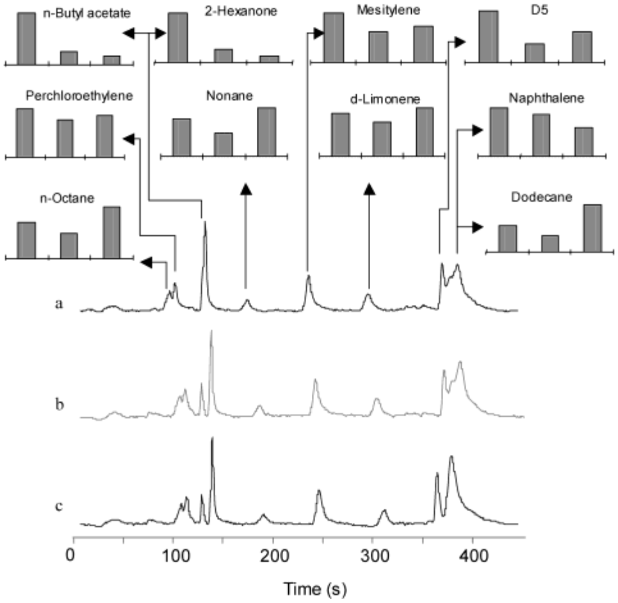

Figure 4. Retention tuning sequence guided by the analyses presented in Table 3. Temperature step durations: step 1, 0−120 s; step 2, 120−190 s; step 3, 190−310 s; step 4, 310−450 s; step 5, 450−600 s. Column temperature sequences: (a) column 1, 50 to 50 to 70 to 130 °C to off; column 2, off to 50 to 70 to 140 °C to off; (b) same as in (a) but with a pressure-tuning segment from $t = 71$ s to $t = 76$ s; (c) column 1: 50 to 50 to 70 to 150 °C to off; column 2, off to 50 to 70 to 130 °C to off, and pressure tuning interval from $t = 71$ s to $t = 76$ s.

resolved compounds are also presented in Table 2 and will be discussed below.

The 2-hexanone/*n*-butyl acetate pair is amenable to pressure-tuned separation because these compounds are resolved on the first column. Figure 4b shows the chromatogram obtained by opening the pressure-tuning valve for 5 s just after the *n*-butyl acetate passes the column ensemble junction point. The 2-hexanone/*n*-butyl acetate pair is now fully separated, and the retention and resolution of each of the remaining compounds remain largely unaffected.

Monte Carlo/EDPCR analyses of the set of three overlapping compounds indicated that any two of those compounds could be allowed to overlap (see Table 2). Unfortunately, these compounds are not resolved on the first column, so pressure tuning was not possible. Figure 4c shows, however, that by accelerating the heating of the second column slightly, the retention of the more polar D5 is shifted sufficiently, relative to the naphthalene and dodecane, to effect the required degree of separation. This can be viewed as a "temperature-tuned" separation, since it amounts to more than just temperature programming. The change in temperature does affect some of the other compound retentions and resolutions but not to any significant extent.

Returning to consider the fully resolved peaks in Figure 4, the question arose as to whether pattern recognition was necessary, since retention time alone could be used to identify the compounds. Obviously, this would reduce the impact of having a sensor array as the detector; if retention time alone were sufficient, then only a single detector would be needed. Certainly, occasions could arise where coelution with an unknown and uncalibrated interference might occur or where such an interference could be present in the absence of the expected (i.e., calibrated) compound in the retention time window. One would want to have the ability to ascertain whether a certain peak were due to the expected compound or not.

Unfortunately, the pattern recognition methods of which we are aware, including artificial neural networks, are all set up to solve problems involving comparisons of a test pattern with a set of possible library patterns and selection of the "best match" according to any of several criteria. With the retention time window approach used here, in cases where there is only a single compound in the window, there are no alternative patterns and therefore no means of assessing whether the pattern obtained for the single compound is sufficiently similar to the calibrated pattern to confirm its identity. To our knowledge, this problem has not yet been addressed in the literature on sensor arrays.

One approach that appears feasible is to establish a statistically derived boundary, or threshold, on the amount of variance from the calibrated pattern beyond which the decision must be made that there is an interference present in the window. This boundary might be derived from some experimentally derived error model similar to that used in the Monte Carlo simulations employed here. This issue is currently under study.

An alternative approach to this problem was used, therefore, which is amenable to implementation via EDPCR. Where there was only a single compound in a window, it was subjected to testing to assess whether the nearest eluting compounds might have been shifted into the window containing the compound under consideration. Thus, a series of analyses was performed to test the recognition of the individual compound against the binary mixtures of that compound with its nearest eluting neighbors. Where there was a neighboring set of overlapping compounds, each of the components of the overlapping set was tested individually with the compound under consideration. Although somewhat contrived, this approach serves to assess the fidelity of the response pattern of each resolved compound.

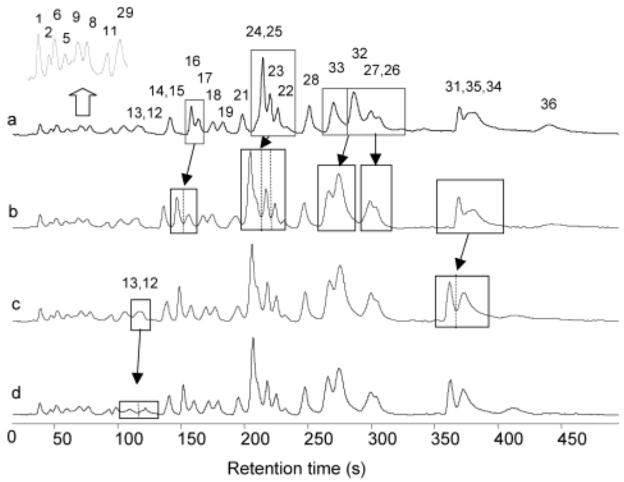

Figure 5. Sequence of temperature and pressure tuning steps for the determination of a 30-component VOC mixture. Refer to Figure 4 for Monte Carlo/EDPCR-determined recognition rates and retention time window assignments. Compound numbers are as indicated in Table 1. Timing of the temperature steps: step 1, 0–120 s; step 2, 120–190 s; step 3, 190–310 s; step 4, 310–450 s; step 5, 450–600 s. Column heaters were off for steps 1 and 5. Settings for steps 2–4: (a) column 1, 50 to 70 to 130 °C; column 2, 50 to 70 to 130 °C; (b) column 1, 50 to 70 to 130 °C; column 2, 70 to 90 to 130 °C; (c) column 1, 50 to 70 to 150 °C; column 2, 70 to 90 to 130 °C; (d) same as in (c) but with a pressure-tuning interval from $t = 82$ s to $t = 85$ s.

Results, summarized in Table 2, show that discrimination of *n*-nonane from its neighbors is relatively facile, while discrimination of D-limonene from binary mixtures with mesitylene or D5 would not be sufficient to meet our threshold of 90% recognition. Thus, coelutions of *n*-nonane with either *n*-butyl acetate or mesitylene could be tolerated, if necessary, but the other compounds would have to be separated. Of course, it is always preferable to separate compounds as completely as possible within the constraints of analysis time.

Analyzing 30 Compounds with Tunable Separation and Pattern Recognition. Figure 5 shows the results of adjusting chromatographic conditions to optimize the analysis of a 30-compound mixture in a minimum amount of time. The initial chromatogram is shown in Figure 5a, and the corresponding retention time window analysis is summarized in Table 3. For brevity, the analyses of windows containing only single compounds have been omitted and their respective windows listed as groups in Table 3. Under these initial GC conditions, there are numerous coelutions. The components of the quaternary mixture cannot be determined with three sensors, and the recognition rates of the components in the two ternary coelutions are below the 90% threshold. Monte Carlo/EDPCR analyses of the various subcomponent combinations of these three- and four-compound groups suggested several possible tuning schemes. The components of all of the two-compound coelutions could be determined by pattern recognition with <10% error over the simulated concentration

Table 3. Recognition Rates from Monte Carlo/EDPCR Analyses of the 30-Compound Chromatograms in Figure 5 before (Figure 5a) and after (Figure 5d) Retention Tuning

window	retention time (s)	compound(s)[a]	recognition rate (%)
initial separation			
A	33−44	1	resolved
B	44−57	2+6	100
C	57−64	5	resolved
D	68−86	8+9	91
E−F	90−111	11, 29	resolved
G	111−131	12+13	98
H	136−153	14+15	93
I	153−170	16+17	99
J−L	170−206	18, 19, 21	resolved
M	206−245	22+23+24+25	indeterminate
N−O	245−281	28, 33	resolved
P	281−319	27+26+32	88
Q	365−409	31+34+35	79
R	429−472	36	resolved
tuned separation			
A	33−44	1	resolved
B	44−57	2+6	100
C	57−64	5	resolved
D	68−86	8+9	91
E−H	88−96	11, 29, 13, 12	resolved
I	136−148	14+15	93
J−N	148−202	16, 17, 18, 19, 21	resolved
O	202−215	24+25	100
P−R	215−259	23, 22, 28	resolved
S	259−291	32+33	99
T	291−320	26+27	97
U	358−367	31	resolved
V	367−400	34+35	99
X	400−430	36	resolved

[a] Compound numbers are listed in Table 1.

ranges (again, 3−15 × LOD). Note, however, that the recognition rates for the 2,5-dimethylfuran/trichloroethylene pair (**8** and **9**) and the perchloroethylene/*n*-octane pair (**14** and **15**) are only 91% and 93%, respectively, and reductions in concentrations result in subthreshold recognition/discrimination. The so-called "limit of recognition" (i.e., the concentration below which recognition becomes unacceptably low)[28] is thus higher than the LOD for these compounds.

The first tuning intervention entailed increasing the second and third temperature steps of the second column by 20 °C each (Figure 5b), which accelerates the polar compounds 2-heptanone (**25**) and 3-octanone (**32**) and results in their separation from cumene (**23**) and D4 (**27**), respectively, leaving D4 and D-limonene as a coeluting pair and shifting the 3-octanone forward onto the 3-octen-1-ol (**33**). Cumene and α-pinene are sufficiently resolved, and the retention of *n*-butyl acetate (**16**) is reduced, leading to a more complete separation from chlorobenzene (**17**). The relatively nonpolar compounds are not retained significantly on the second column and so are affected only slightly, but the 2-heptanone and *n*-nonane peaks (**25** and **24**) still overlap significantly.

Next, the temperature of the first column was raised during the third step of the temperature program. The result is shown in Figure 5c. Originally, D5 and dodecane were well separated, but naphthalene eluted between them creating an unresolved group of three compounds. With this change, all of the later-eluting compounds (i.e., D5, naphthalene, dodecane, tridecane) are accelerated, but naphthalene is accelerated to a lesser degree, resulting in improved separation of D5 and naphthalene.

Finally, a 3-s stop-flow segment was inserted (via the midpoint pressure valve) 82 s into the run to accelerate toluene and separate it from 2-methylheptane (**12** and **13**) (Figure 5d). Although the separation for these two compounds is not critical, given that the pair can be discriminated at a rate of 98% (Table 3), their separation has no significant effect on the other compounds or the analysis time. As shown in the bottom half of Table 3, under these tuned separation conditions, all of the compounds should now be identifiable from their sensor array response patterns, despite the remaining coelutions. The total elution time is under 8 min. Allowing for a 2-min cool down prior to the next separation cycle, and adjusting the sampling cycle to track the separation, an entire analysis can be completed every 10 min.

CONCLUSIONS

As shown here, significant advantages accrue from combining tunable separations with sensor array detection in a portable GC. Pattern recognition analysis of sensor array responses allows for vapor recognition through what might be termed "sorption spectrometry", even for (certain) unresolved components, and retention tuning allows for adjustment of the number and nature of coeluents to take best advantage of the sensor array capabilities while minimizing the time of analysis. Together with the mini-preconcentrator/focuser, which permits collection and focused injection of compounds as well as some degree of humidity rejection,[6,7] this system can determine the components of complex mixtures of common indoor (and ambient) air contaminants at low concentrations with a duty cycle of ∼10 min. At present, the pressure- and temperature-tuning parameters must be determined empirically, in part because of the stepwise nature of the temperature control in this prototype. However, generalized models to guide this process are currently being developed, and revisions to the column temperature control as well as other features of the instrument are being implemented to facilitate such modeling and to improve performance. The low dead volume, rapid response, and unique patterns derived from the integrated SAW sensor array are critical. Increases in linear dynamic range and sensitivity, as well as reductions in noise and slope variance, would be desirable. A preliminary report on an alternative sensor array technology, comprising a chemiresistor array that employs gold thiolate nanoclusters as interfacial layers, that provides higher signal-to-noise ratios also shows promise as a GC detector for this application.[29]

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sensor arrays; and Judy Zhong and Meng-Da Hsieh at the University of Michigan for technical input and data analyses. Funding for this research was provided by Grant R01-OH03692 from the National Institute for Occupational Safety and Health of the Centers for Disease Control and Prevention (NIOSH-CDCP). This work made use of Engineering Research Centers Shared Facilities supported by the National Science Foundation under Award Number EEC-0096866.

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