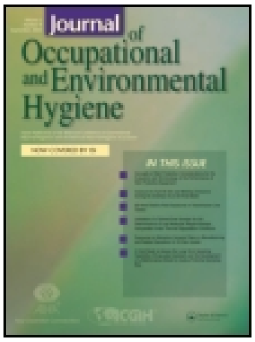

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Laboratory and Field Evaluation of a SAW Microsensor Array for Measuring Perchloroethylene in Breath

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This article describes the laboratory and field performance evaluation of a small prototype instrument employing an array of six polymer-coated surface acoustic wave (SAW) sensors and a thermal desorption preconcentration unit for rapid analysis of perchloroethylene in breath. Laboratory calibrations were performed using breath samples spiked with perchloroethylene to prepare calibration standards spanning a concentration range of 0.1–10 ppm. A sample volume of 250 mL was preconcentrated on 40 mg of Tenax® GR at a flow rate of 100 mL/min, followed by a dry air purge and thermal desorption at a temperature of 200°C. The resulting pulse of vapor was passed over the sensor array at a flow rate of 20 mL/min and sensor responses were recorded and displayed using a laptop computer. The total time per analysis was 4.5 min. SAW sensor responses were linear, and the instrument's limit of detection was estimated to be 50 ppb based on the criterion that four of the six sensors show a detectable response. Field performance was evaluated at a commercial dry-cleaning operation by comparing prototype instrument results for breath samples with those of a portable gas chromatograph (NIOSH 3704). Four breath samples were collected from a single subject over the course of the workday and analyzed using the portable gas chromatograph (GC) and SAW instruments. An additional seven spiked breath samples were prepared and analyzed so that a broader range of perchloroethylene concentrations could be examined. Linear regression analysis showed excellent agreement between prototype instrument and portable GC breath sample results with a correlation coefficient of 0.99 and a slope of 1.04. The average error for the prototype instrument over a perchloroethylene breath concentration range of 0.9–7.2 ppm was 2.6% relative to the portable GC. These results demonstrate the field capabilities of SAW microsensor arrays for rapid analysis of organic vapors in breath.

Keywords breath analysis, microsensor array, perchloroethylene, portable instrumentation, surface acoustic wave sensor

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INTRODUCTION

Biological monitoring is often used by occupational health professionals to evaluate worker exposure to toxic chemicals. Methods involve the collection and analysis of biological media such as blood, urine, or breath, and results can be used to supplement air sampling data in attempting to characterize an individual's exposure dose or body burden.(1,2) Breath analysis has been used to evaluate occupational exposure to volatile organic solvent vapors and offers several advantages including noninvasive sample collection, direct measurement of the parent compound rather than a metabolite, and a relatively "clean" sample matrix compared to blood or urine.

When a worker inhales a volatile organic solvent vapor, a portion will be absorbed by the pulmonary blood supply and distributed throughout the body. Following exposure, alveolar air is enriched by the chemical contained within the pulmonary blood to an extent determined by the concentration of the chemical in the blood and the blood-gas partition coefficient. For stable, hydrophobic chemicals that are poorly metabolized, such as 1,1,1-trichloroethane and perchloroethylene, breath analysis is the preferred biological method for evaluating body burden and the risk of developing adverse health effects.(1–4)

Current approaches to breath analysis typically rely on the collection of a breath sample in some type of inert container or on an adsorbent tube followed by laboratory analysis.(2,5–8) Direct analysis using conventional laboratory instrumentation has also been reported,(9–14) but the cost and complexity of these methods have resulted in limited application to occupational exposure assessment. The noninvasive nature of breath sampling and analysis makes it more convenient than monitoring blood or urine; however, several factors, including the high concentration of water vapor, the potential presence of multiple endogenous compounds, and the short biological half-lives of many absorbed vapors, all serve to make field analysis of breath samples difficult and have limited its use.

Arrays of partially selective microsensors have been used for analysis of gases and vapors, including those based on chemiresistors and surface acoustic wave (SAW) devices.(15–22) SAW sensors detect changes in the mass and viscoelastic properties of thin polymer coatings that occur as a result of interactions with gases and vapors.(23–25) SAW devices offer a number of potential advantages for analysis of organic solvent vapors, including rapid and reversible responses that are typically linear over a broad range of concentrations, and mixture responses that are generally additive, which greatly simplifies interpretation.(26–28) Previous work has shown that an array of 3–6 SAW sensors coated with a set of polymers selected to provide a broad range of solubility interactions can yield characteristic response patterns allowing for the identification and quantification of a large number of individual vapors and components of simple mixtures.(17,26–33,37) Laboratory application of SAW-based instrumentation has been described for personal exposure monitoring and chemical protective clothing permeation testing.(26,34)

The current study extends previous work that focused on the development and laboratory testing of SAW-based instrumentation for the analysis of organic vapors in breath.(35–37) This article describes an evaluation of SAW instrument performance in the laboratory and in the field for the measurement of perchloroethylene in breath. The instrument examined employs a thermally desorbed preconcentration tube for sample collection and an array of six polymer-coated SAW sensors for vapor detection. Sample preconcentration is required to achieve the low- and sub-part-per-million (ppm) detection limits needed for breath sample analysis.(4,26,29,38)

Perchloroethylene is a colorless liquid with a boiling point of 121°C and a vapor pressure of 19 mmHg at 25°C.(4) It is the primary dry-cleaning solvent used in approximately two-thirds of the facilities in the United States and is also a common contaminant of urban air and drinking water at concentrations as high as 10 ppb, and 1–2 ppb, respectively. The major route of absorption in industrial settings is by inhalation, although extensive dermal exposure to liquid perchloroethylene can significantly increase biological levels. The vast majority of absorbed perchloroethylene (97–99%) is eliminated unchanged via exhaled breath, although a small fraction is oxidized to trichloroacetic acid (1–3%) that is excreted in urine. The concentration of perchloroethylene in end-exhaled air can be determined with less variability than trichloroacetic acid in urine; therefore, breath is the preferred medium for biological exposure monitoring. The American Conference of Governmental Industrial Hygienists (ACGIH®) biological exposure index (BEI) committee has recommended 5 ppm of perchloroethylene in end-exhaled air collected prior to the work shift after at least two consecutive workdays as a BEI for perchloroethylene. This value is believed to represent the level that would be observed in samples collected from an individual with inhalation exposure at the threshold limit value of 25 ppm.(4)

MATERIALS AND METHODS

SAW Microsensor Array—Instrument Description and Operation

The key functional components of the SAW instrument are shown schematically in Figure 1a. The instrument employs six 200-MHz polymer-coated SAW resonators with a matched reference SAW resonator and temperature sensor (Figure 1b), two diaphragm pumps, three Teflon® solenoid valves, and a preconcentration tube (PCT) packed with a solid granular adsorbent. The SAW array was constructed by Femtometrics, Inc. (Irvine, Calif.); the preconcentration unit was developed separately in our laboratory and then interfaced with the SAW array. The preconcentration unit enclosure contains the PCT, a temperature controller, the PCT pump, control valves V2 and V3, and the sample inlet port as well as pneumatic and electrical connections for interfacing with the SAW array. The SAW enclosure includes the sensor array, array pump, control valve V1, microprocessor control circuitry, and the scrubber/clean air

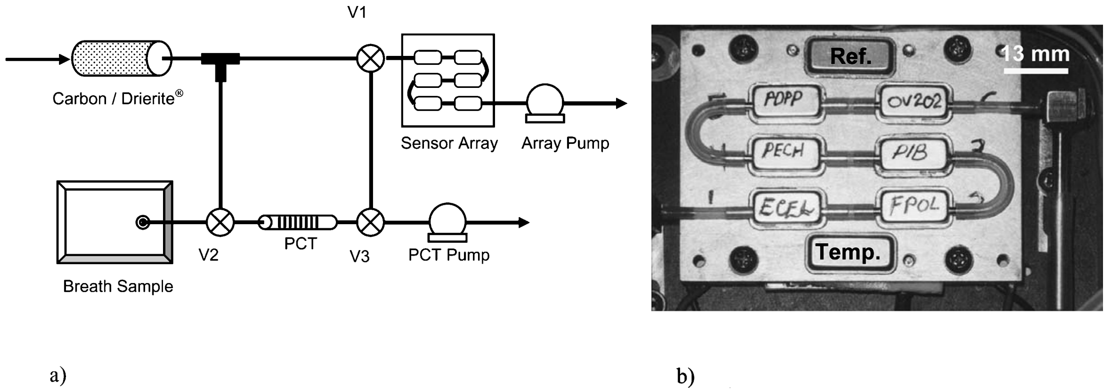


FIGURE 1. (a) Simplified instrument schematic; (b) photograph of microsensor array showing six coated sensors, and reference and temperature sensors mounted in aluminum block

inlet port. The combined volume for the preconcentration unit and SAW array enclosures is less than 0.25 ft^3 and total weight is approximately 3.6 kg.

The polymer coated SAW resonators are sealed using an epoxy adhesive to attach gold-plated lids equipped with inlet and outlet ports consisting of a short length of 3.18 mm o.d. gold-plated tubing. The sensors are connected in a series flow configuration using 3.18 mm i.d. Teflon tubing to pass the sample stream over the array (Figure 1b). Sensors and reference devices are mounted in an aluminum block that employs a Peltier device and temperature controller to maintain a temperature of 15°C to minimize baseline disturbances and improve the reproducibility of sensor responses. The instrument microprocessor controls pneumatic and thermal timing and collects the difference frequencies from the six sensors once per second; the difference frequency is simply the difference between the frequency of the reference SAW device and each of the six sensors. Output signals are passed through an RS-232 port/cable to a laptop computer for display and processing.

Six different polymers were used to coat the SAW sensors: poly(epichlorohydrin) (PECH), poly(isobutylene) (PIB), poly(diphenoxyphosphazene) (PDPP), trifluoropropyl polysiloxane (OV-202), ethylcellulose (ECEL), and fluoropolyol (FPOL). Polymers were obtained from Scientific Polymer Products, Inc. (Ontario, N.Y.) (PIB, PECH, PDPP) or on precoated sensors obtained directly from Femtometrics, Inc. (ECEL, FPOL, OV-202). Polymers were selected as coatings on the basis of previous studies demonstrating stability and potential selectivity(27,28,37) and on the recommendation of the SAW array manufacturer. Coatings were applied using an airbrush and dilute solutions of each polymer in chloroform. Coating thicknesses of 20–30 nm are achieved as a result of spray application producing a frequency shift of ∼200 kHz.(15)

The PCT was constructed from a 4.8 mm o.d. electropolished stainless steel tube approximately 32 mm long with a thin-film Nichrome resistive heat element attached to the outside producing a heated zone of 19 mm. A fine-wire thermocouple is attached to the PCT to provide feedback to a PID temperature controller (Watlow Series 935A, Winona, Minn.). The PCT is packed with 40 mg of 35/60 mesh Tenax® GR used as received (Alltech Associates, Deerfield, Ill.). Selection of the type and quantity of adsorbent was based on the results of previous studies focusing on breakthrough volumes for a subset of organic vapors.(36) Sample flow-path materials consisted of brass, stainless steel, gold-plated stainless steel, and Teflon, to minimize loss of analyte and potential sample carry-over. Additional details of SAW instruments and PCT construction are provided in previous articles.(35−37)

All calibration and test samples were prepared/collected in 1-L Tedlar® bags (SKC, Inc., Eighty Four, Pa.) that were then connected to the instrument inlet-port via a short length of 3.18 mm o.d. Teflon tubing. When activated, the instrument proceeds through an automated sequence of three operating modes. In preconcentration mode, a 0.25-L sample is drawn through the PCT at a flow rate of 0.1 L/min (PCT pump). In purge mode, solenoid valve V2 is switched to direct 0.10-L of clean dry air over the PCT at 0.1 L/min to purge water vapor prior to sample desorption. The use of a dry-air purge was shown previously to significantly improve limits of detection (LODs) as a result of reductions in magnitude and variability of baseline/blank response.(36,37) During both preconcentration and purge modes, the array pump draws 0.02 L/min of the clean dry air over the sensor array. Following the dry air purge, desorption mode is initiated by deactivating the PCT pump, and switching valves V1 and V3 so that clean dry air is drawn by the array pump through the PCT and over the SAW sensors at 0.02 L/min. The PCT is heated to approximately 200°C at a rate of 15°C/sec to desorb the trapped vapors that are then detected by the sensor array over the course of the 60-s desorption mode cycle.

SAW Microsensor Array—Instrument Calibration

The instrument was calibrated for perchloroethylene in breath over a concentration range of ∼0.1–10 ppm. Test atmospheres were prepared by exhaling a volume of air into a 1-L Tedlar bag (SKC Inc.) and then injecting a known quantity of liquid perchloroethylene. Sample bags were massaged to effect mixing and allowed to cool to room temperature (20–25°C) prior to analysis. The actual concentration of the test-atmospheres was determined by GC-FID using 1-mL injections from a gas-tight syringe and then comparing the resulting peak areas to those of liquid calibration standards. Solvents were all greater than 99% pure and were used as received (Aldrich Chemical, Milwaukee, Wis.). Calibrations consisted of 5–8 concentrations bracketing ACGIH BEI for perchloroethylene in breath, which is 5 ppm. Blank breath samples, i.e., test atmospheres containing only breath, were used to establish the baseline response for the instrument. In previous work,(37) a comparison of instrument responses for blank breath samples and nitrogen samples spiked with water to the point of saturation showed no significant difference, thereby confirming that the instrument's baseline is essentially defined by residual water on the PCT, and further that endogenous vapors in breath are not detectable with this protocol. A minimum of three blank analyses were averaged and subtracted from the responses for calibration standards to yield the net response profile for each sensor for the concentrations examined. Calibration curves were prepared by plotting the response maximum (peak height) in Hz for each coated sensor vs. concentration (ppm).

Portable GC—Instrument Description and Operation

A Photovac 10S Plus portable GC was rented (Response Rentals, Rochester, N.Y.) for the duration of the project to serve as the reference method for the field evaluation of the SAW microsensor array. The portable GC is equipped with an isothermal oven, photoionization detector (PID), a built-in reservoir for zero-air carrier gas, and rechargeable lead-acid batteries allowing for up to 12 hours of operation in the field. The instrument employs wide-bore capillary columns and is equipped with an onboard computer for instrument control, method development, and data display and storage. An integral sample loop and pump can be used to continuously collect and inject air samples; alternatively, an injection port is available for manual injections of vapors using a gas-tight syringe. The instrument is packaged in a suitcase enclosure measuring 46 × 36 × 15 cm and weighs ~14 kg.

Method parameters for breath sample analysis were similar to those specified in NIOSH Method 3704 "Perchloroethylene (portable GC) in exhaled breath and air."(13,14) Sample injections of 0.5 mL were made using a gas-tight syringe with a column temperature of 40°C, a carrier gas flow rate of 15 mL/min, and a PID gain of 1000. A CP-Sil 19 CB column was used (10 m, 0.53 mm i.d.), yielding a retention time of 175 sec for perchloroethylene under these conditions. Peak areas were integrated and displayed by the onboard computer. Calibration of the instrument was accomplished using test atmospheres prepared as described above to yield breath samples containing perchloroethylene concentrations ranging from ~0.1–10 ppm. Calibration curves were prepared by plotting peak area (mV-sec) vs. concentration (ppm).

Laboratory Evaluation of Saw Microsensor Array and Portable GC

Performance of the portable GC and SAW microsensor array instruments was evaluated in the laboratory by comparing the results of analyses for a set of eight test-atmospheres containing perchloroethylene in breath to the results of a reference GC-FID (Varian Star 3400 CX). All instruments were first calibrated with standards corresponding to a concentration range of ~0.1–10 ppm perchloroethylene in breath. The portable GC and SAW instruments were calibrated using standards prepared in Tedlar bags as described previously, whereas the reference GC was calibrated using liquid standards. A series of eight test-atmospheres containing perchloroethylene in breath at concentrations ranging from ~0.5–9 ppm was then prepared and analyzed. A single measurement was taken with each instrument for each of the eight concentrations. Test-atmospheres were connected to the SAW microsensor array and a sampling and analysis cycle was initiated. While the SAW instrument's preconcentration cycle was under way, samples were drawn from the test-atmosphere using a gas-tight syringe and then injected into the portable GC and reference GC for analysis. The Tedlar bags used for the project were equipped with both sampling and septum ports; the sampling port was used for connection to the SAW instrument inlet, and the septum port was used to draw off samples for GC analysis. The resulting peak areas for the GCs, and peak heights for the SAW microsensor array, were compared with the corresponding calibration curves to yield estimates of the concentration of perchloroethylene in the breath samples. Results for the portable GC and SAW instrument were then compared with those of the reference GC.

Field Evaluation of SAW Microsensor Array

The dry-cleaning plant involved in the study was a small family-owned business with approximately 17 employees. When initially approached to participate, the owner declined based on a concern that employees would be disrupted and alarmed. However, after stipulating that he would be the sole experimental subject, agreement to participate was obtained in accordance with University of Iowa Institutional Review Board policies for human subjects. The dry-cleaning plant operations were typical of such establishments and included both laundry and dry-cleaning activities. The building contained a customer-counter section, where clothes are received and returned, and a conveyor system for hanging and sorting finished orders. The production area included two dry-cleaning machines, a table used for pretreating or "spotting" clothes, and four steam presses and irons for pressing garments. The production area also contained an enclosed office for the owner/manager, and storage and maintenance spaces. The owner's activities included bookkeeping and supervisory tasks as well as "spotting" garments, performing maintenance and repairs on equipment, and periodically working in the retail counter area.

Field performance of the SAW microsensor array was evaluated by collecting and analyzing breath samples at the plant and comparing the results for perchloroethylene concentrations with those of the portable GC. Both instruments were set up and calibrated on site: the portable GC was pre- and postcalibrated using three perchloroethylene breath standards spanning a concentration range of ~0.4–7 ppm, whereas the SAW microsensor array was calibrated using a single standard with a perchloroethylene concentration of 7 ppm. Once both instruments were set up and calibrated, breath samples were collected in Tedlar sample bags and analyzed simultaneously using the portable GC and SAW array. The breath sampling protocol employed was similar to that described in NIOSH 3704.(13) The subject was instructed to take several normal breaths followed by a deep inhalation that was held for approximately 10 sec. The first half of the breath was then exhaled into the room, with the remaining portion being collected in the sample bag for analysis. The bag's sample port was then closed and the sample allowed to cool to room temperature prior to analysis. Given that only one subject was available for the field evaluation, additional spiked breath samples were prepared (using investigator's breath) on site and analyzed to ensure that a broader range of perchloroethylene concentrations could be used to compare instrument performance.

Although the SAW instrument(37) and portable GC are capable of measuring perchloroethylene concentrations in both breath and air, the decision was made to compare only breath measurements due to the limited time available for the on-site instrument analysis portion of the study (a half day was initially agreed on). In order to obtain estimates of airborne concentrations of perchloroethylene to aid in characterizing and interpreting the subject's exposure and the measured breath concentrations, personal monitoring was conducted using diffusive badges (cat. no. 575-001, SKC, Inc.). Estimates of the subject's 8-hour time-weighted average (TWA) perchloroethylene exposure for a total of 9 days, including 6 days prior to the day of the field evaluation, the day of the field evaluation, and the subsequent 2 days were obtained. Sample times ranged from 5–8 hours and all nine badges were analyzed at the conclusion of the study using GC-FID.

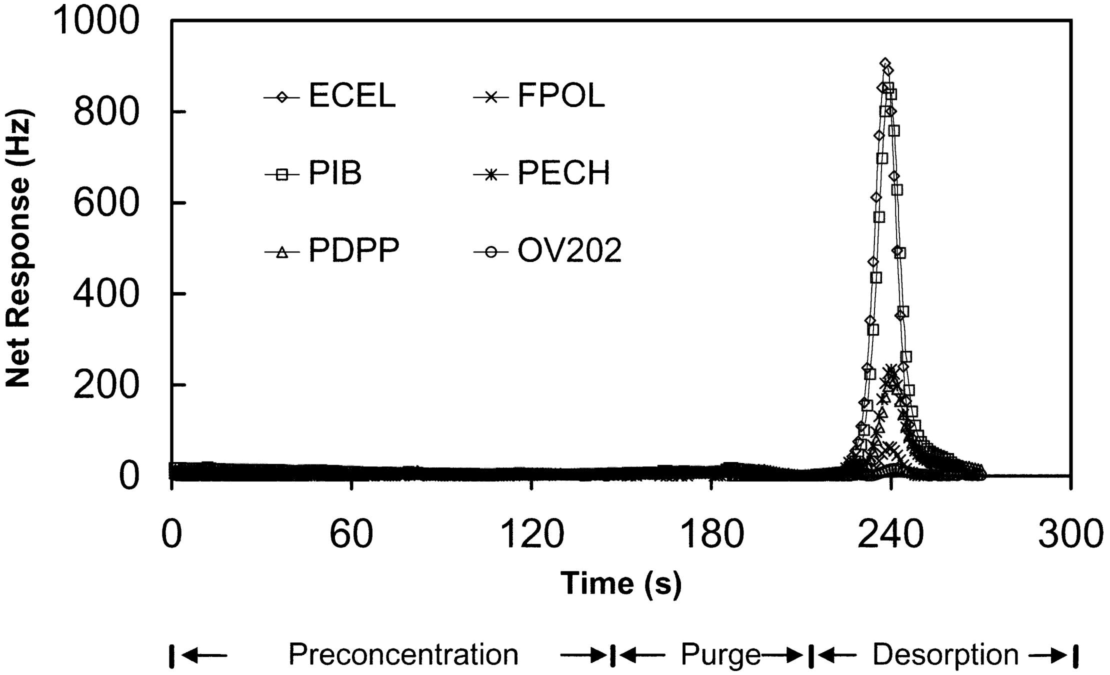


FIGURE 2. Sample analysis timeline for preconcentration (250 mL sample, 100 mL/min, 40 mg Tenax GR), dry air purge (50 mL, 100 mL/min), and thermal desorption (20 mL/min, 200°C). Responses shown for 0.99 ppm perchloroethylene in breath.

RESULTS AND DISCUSSION

SAW Microsensor Array Instrument

Representative net-response profiles for a spiked breath sample containing 0.99 ppm perchloroethylene are shown in Figure 2. Instrument operating modes are indicated below the timeline. As noted previously,(37) response profiles resemble chromatographic peaks—the height or area of the individual peaks is proportional to the concentration of perchloroethylene in the breath sample. The elution time for perchloroethylene was ~240 sec. It has been shown that a crude chromatographic separation based on volatility occurs in the PCT when mixtures of vapors are analyzed and the resulting peak elution times can provide additional information useful in vapor recognition.(37) However, in the present application that focuses on measurement of a single analyte present at concentrations that are orders of magnitude greater than background levels of other chemicals, a more complex mixture analysis is not required.

Calibration curves for the instrument (Figure 3) were linear over the concentration range examined ($r^2 \geq 0.99$) suggesting that the capacity of the PCT was not exceeded. The dynamic range extends for at least two orders of magnitude, which is adequate to span the concentration range of interest of ~0.1–2 × BEI. LODs ranged from 26 ppb for the most sensitive sensor (ECEL) to 280 ppb for the least sensitive sensor (FPOL) in the array and were less than 0.1× BEI in all cases (the LOD was defined as the concentration producing a response equal to three times the standard deviation of the baseline response at the point in time that the vapor elutes). In applications requiring both the recognition and quantification of a given vapor, i.e., mixture analysis, a conservative estimate of the minimum concentration required would be the LOD corresponding to the least sensitive sensor in the array (FPOL, 280 ppb).

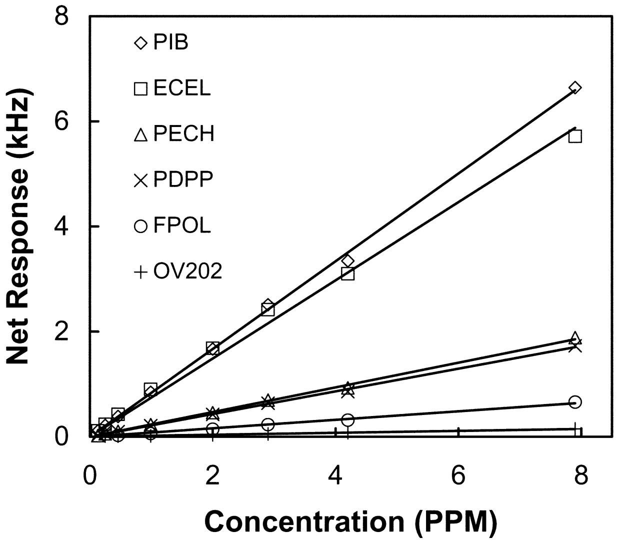


FIGURE 3. Instrument response isotherms for SAW instrument calibration over a concentration range of 0.13–7.9 ppm perchloroethylene

Laboratory Evaluation of SAW Microsensor Array and Portable GC

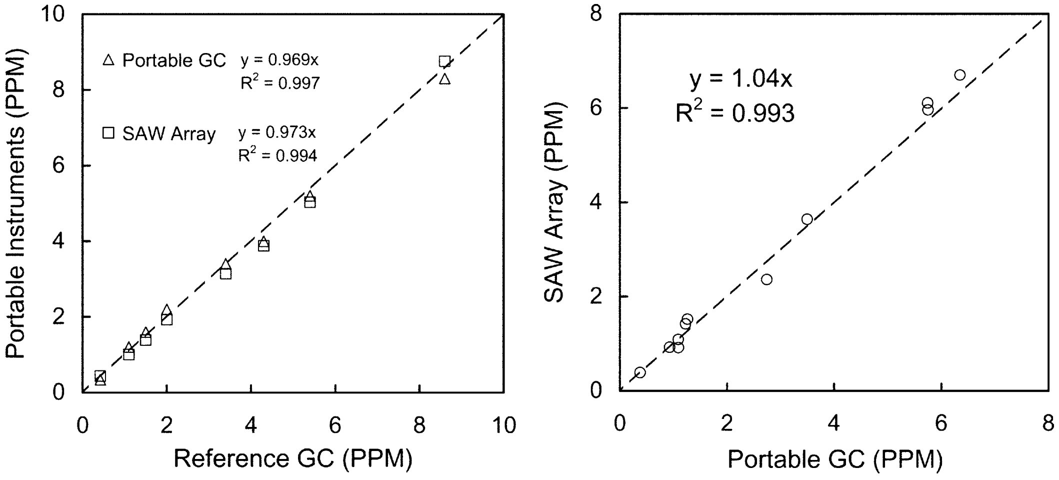
Results for the laboratory comparison of the portable instruments to the reference method are presented in Figure 4a. The concentrations measured for the eight test-atmospheres examined are plotted on the y-axis for the SAW array and portable GC, vs. the results for the reference GC on the x-axis. Each data point represents the result of a single measurement. Results for the SAW array are based on the responses of the four polymer-coated sensors with the highest signal-to-noise ratios: ECEL, PIB, PECH, and PDPP. A multiple linear regression of the calibration data (using forced-zero) was performed to yield a model for predicting vapor concentration as a function of the responses for the four sensors. The FPOL and OV-202 sensors were not included in the model since both had responses below their respective LODs for the lowest concentration of the calibration test-atmospheres. Although the response from a single sensor could be used to estimate perchloroethylene concentrations, the redundancy provided by additional sensors can improve the accuracy of concentration estimates as a result of the cancellation of random error that occurs with signal averaging.(39,40)

Correlations between results for the SAW array and reference GC, and the portable GC and reference GC, were excellent, as demonstrated by the linearity of the plots in Figure 4a and the values of r^2, which exceeded 0.99 for both instruments. Percent errors ranged from −9.8% to 4.2% for the SAW array and from −19% to 10% for the portable GC. The average percent errors were −4.7% and −0.93% for the SAW array and portable GC, respectively. Estimates of the precision of the SAW array and portable GC were obtained by examining the relative standard deviation (RSD) of replicate measurements for test atmospheres spanning a concentration range of approximately 0.5–10 ppm perchloroethylene. In all cases RSDs were less than 10%. These results indicate excellent agreement between the reference analytical method and both the SAW array and portable GC over a concentration range corresponding to ∼0.1–2 × BEI, and served as preparation for the subsequent field study.

Field Evaluation of SAW Microsensor Array

Results for the field evaluation of the SAW microsensor array are presented in Figure 4b. Perchloroethylene concentrations measured using the SAW array are plotted versus the results for the portable GC for 11 breath samples spanning a concentration range of ∼0.5–7 ppm. A total of four breath samples were collected from the subject and analyzed immediately using both the SAW array and portable GC. The first two samples were analyzed at 9:15 a.m. and the second at 10:30 a.m. on the day of the field study. Perchloroethylene concentrations for the subject's four breath samples ranged from 0.93–1.3 ppm, with a mean and SD of 1.1 ppm, and 0.16 ppm, respectively (based on results of portable GC analysis). The remaining seven samples analyzed were spiked breath samples prepared on site to provide a broader range of perchloroethylene concentrations for the comparison of the instruments.

Correlation between SAW array and portable GC results was very good for the 11 breath samples with an r^2 value of 0.993. Regression analysis using a model with forced-zero indicated that the SAW array results showed a slight positive bias with respect to the portable GC: the estimate for the slope of the line was 1.04 with a 95% confidence interval of 1.00–1.08. Errors for the SAW instrument ranged from −16 to 20% with an average of 2.6% and a SD of 11% over a concentration range corresponding to ∼0.1–2 × BEI. These results show excellent agreement between the SAW instrument and the reference portable GC method and demonstrate the



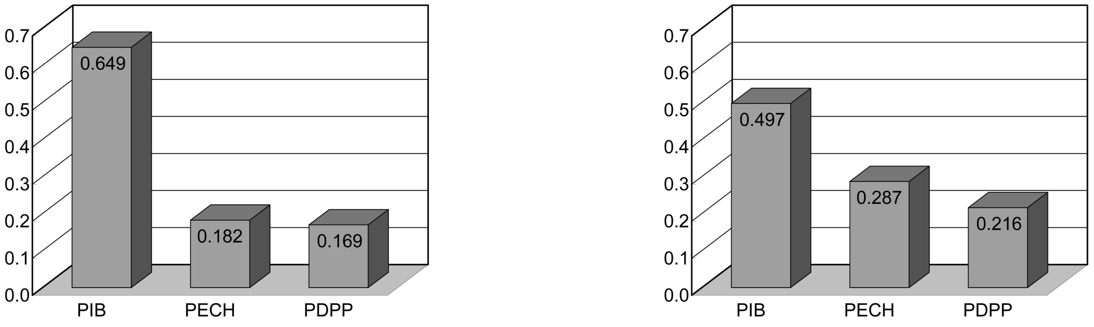
a) b)

FIGURE 4. Comparison of results for the analysis of perchloroethylene in breath: (a) laboratory comparison of portable GC and SAW instruments to reference GC; (b) field comparison of SAW instrument and portable GC

capabilities of this portable technology for rapid and accurate breath measurements in the field.

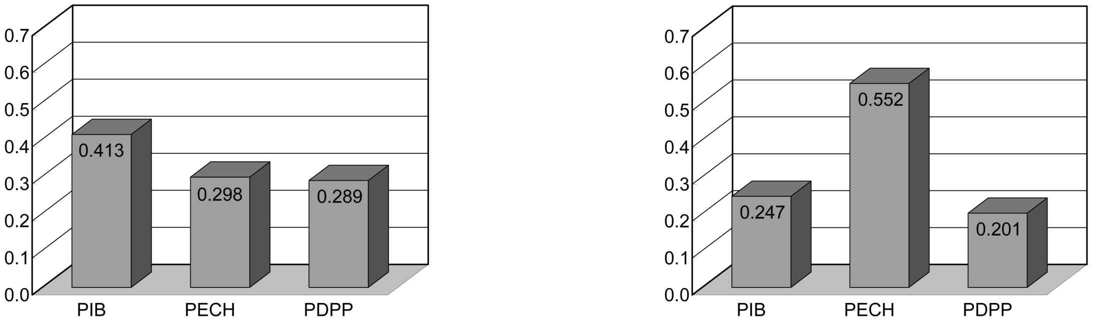
Although a complex mixture analysis was not required for this application, the capability of the sensor array to selectively measure perchloroethylene among common potential interferents was examined. A set of four vapors: perchloroethylene, 1,1,1-trichloroethane, m-xylene, and 2-propanol, was considered as the test set. An array consisting of three (PIB, PECH, PDPP) of the original six sensors was then used to classify the responses for the breath samples analyzed in the field study; it has been shown that arrays of only two to three sensors can selectively discriminate among 16 individual vapors.(29) Relative response patterns based on calibration data for the vapor test set are presented in Figure 5 to demonstrate the contributions of the different polymer coatings to the instrument's ability to discriminate among a set of vapors. The response patterns for each of the 11 breath samples were classified using extended disjoint principal components regression (EDPCR)(32,37) and the top three classifications were recorded. Possible classifications included each of the four individual vapors and their binary mixtures. Referring to the results in Table I, it can be seen that all samples were correctly classified as perchloroethylene. Residual error (ε) can be used as a relative measure of fit or confidence for the EDPCR classifications, and in all cases the ε for perchloroethylene was significantly lower than the next closest match, which was m-xylene for 10 of the 11 samples. The reproducibility of relative responses (RRs) can be seen for the 11 breath samples; the relative standard deviation of the RRs ranged from 4.5–12% for the three sensors despite the large variation in net sensor responses. The results of this analysis demonstrate the potential of the SAW instrument for selective measurement of perchloroethylene among a library set of common vapors and are consistent with more exhaustive studies in which the capabilities of SAW sensor arrays for mixture analysis were characterized.(17,26–33,37)

The calibration protocols employed for the field study were simplified compared with those used in the laboratory evaluation in order to more accurately reflect the way the instruments would likely be used in practice. The portable GC was pre- and postcalibrated on site using three spiked breath standards having concentrations determined immediately prior to the study using the laboratory reference GC. The SAW microsensor array was calibrated against the portable GC using a single breath standard with a perchloroethylene concentration at the upper end of the range to be examined. The subtraction of an average baseline from the response profile for breath samples has the effect of "zeroing" the SAW instrument, making this approach similar to the "two-point" calibration protocols employed for most direct-reading instruments. Ideally, commercially available "span" gases would be used to calibrate the SAW instrument. Although these gases are typically prepared in dry air or nitrogen, a previous study showed that SAW instrument responses were effectively independent of sample humidity as a result of the selection of an appropriately hydrophobic preconcentration adsorbent and the use of a dry-air purge process



a) Perchloroethylene

b) m-Xylene



c) 1,1,1-Trichloroethane

d) 2-Propanol

FIGURE 5. SAW microsensor array relative response patterns for selected vapors

TABLE I. SAW Microsensor Array Results for Field Evaluation—Perchloroethylene in Breath

			Net Sensor Response (Hz) (Relative Response)		
Sample	**Conc. (ppm)**	**Classification (ε)^A**	**PIB**	**PECH**	**PDPP**
S1	3.6	PCE (9.0) XYL (620) TCA (970)	2222 (0.649)	628 (0.184)	572 (0.167)
S2	6.1	PCE (22) XYL (1000) TCA (1600)	3725 (0.646)	1069 (0.185)	975 (0.169)
S3	6.7	PCE (23) XYL (1100) TCA (1800)	4087 (0.646)	1171 (0.185)	1073 (0.169)
S4	0.92	PCE (33) XYL (180) TCA (270)	559 (0.688)	130 (0.160)	123 (0.151)
S5	2.4	PCE (37) XYL (430) TCA (660)	1440 (0.665)	377 (0.174)	347 (0.160)
S6	0.39	PCE (33) TCA (130) IPA (200)	236 (0.749)	37 (0.117)	42 (0.133)
S7	6.0	PCE (6.8) XYL (1000) TCA (1600)	3630 (0.648)	1025 (0.183)	944 (0.169)
H1	1.4	PCE (14) XYL (250) TCA (390)	866 (0.656)	241 (0.183)	212 (0.161)
H2	1.5	PCE (9.4) XYL (260) TCA (410)	928 (0.652)	263 (0.185)	233 (0.164)
H3	0.92	PCE (32) XYL (180) TCA (270)	564 (0.686)	133 (0.162)	125 (0.152)
H4	1.1	PCE (43) XYL (220) TCA (320)	666 (0.692)	156 (0.162)	140 (0.146)
		Average relative response (SD) =	0.671 (0.03)	0.171 (0.02)	0.158 (0.01)

Notes: S1-7: Spiked breath samples; H1-4: breath samples from subject;PCE: perchloroethylene; XYL: m-xylene; TCA: 1,1,1-trichloroethane; IPA: 2-propanol.
^{A}Residual error from EDPCR assignment.

in the sampling and analytical protocol.(33,37,41) It seems likely that an approach similar to that used to calibrate PIDs, in which correction factors for specific chemicals are applied to adjust results from calibration against a standard test-vapor, could be employed to further simplify field application of the SAW instrument.

Results for air and breath monitoring are summarized in Figure 6. Eight-hour TWA air concentrations reflect the results of monitoring performed using passive samplers for a total of 4 days spanning 1/4–1/7. Breath samples were collected prior to the beginning of the work shift for the 3 days (1/6–1/8) following the day of field study. Air concentrations ranged from 1.7–11 ppm with a mean and SD of 4.2 and 4.8 ppm, respectively. Breath samples ranged from 0.4–1.3 ppm with a mean of 0.75 ppm and SD of 0.48 ppm. All air and breath samples were well below the ACGIH TLV (25 ppm) and BEI (5 ppm–breath) for perchloroethylene. When the results for breath samples collected prior to the work shift are compared with the TWA air concentrations for the previous 2 workdays, it can be seen that ratios of breath and air concentrations are comparable to that expected based on the BEI/TLV (5 ppm/25 ppm = 0.2). Ratios were 0.28 (0.52/1.8), 0.23 (0.42/1.8) and 0.20 (1.3/6.5)

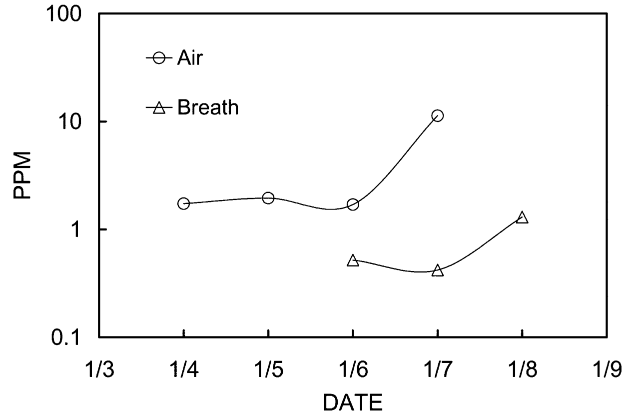


FIGURE 6. Perchloroethylene exposure summary for subject: comparison of 8-hour TWA air concentrations (diffusive samplers) and preshift breath concentrations (SAW instrument) over the time frame of the study

compared with the expected value of 0.20, thus demonstrating reasonable agreement with the perchloroethylene pharmacokinetics on which the BEI is based.

CONCLUSIONS

This study demonstrates that rapid and accurate identification and quantification of perchloroethylene in breath is possible in the field using a SAW microsensor array with preconcentration. The analytical protocol employs a relatively simple process for collection of a 250 mL breath sample in a Tedlar bag. Improvements in sensitivity could be achieved by increasing the sample volume; this could easily be accomplished by collecting several end-exhaled air samples in a bag and then proceeding with the analysis using a slightly modified preconcentration protocol to account for the larger sample volume (longer preconcentration and dry-air purge modes would likely be required). The laboratory evaluation showed excellent agreement between perchloroethylene breath concentrations measured using the SAW and portable-GC instruments, and results from a reference laboratory GC-FID with all errors less than 25% over a concentration range of ∼0.5–9 ppm. The subsequent field evaluation further demonstrated the capabilities of the SAW instrument relative to NIOSH Method 3704 for measuring perchloroethylene in breath using a portable GC. Errors for the SAW array relative to the reference method were less than 25% over a concentration range corresponding to 0.1–2 × BEI. The use of a two-point calibration protocol for the SAW instrument was examined and found to yield good results while greatly simplifying field applications. Although a complex mixture analysis was not required for this application, microsensor arrays have been coupled with gas chromatographic separation to achieve low- and sub-part-per-billion detection limits for multiple analytes.(42)

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