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**ASSESSMENT OF SUBSURFACE VOCs
USING A CHEMICAL MICROSENSOR ARRAY**

Final Report, Contract No. 02112409

By

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PREFACE

Currently available technology is not adequate to assess environmental contamination at Department of Energy (DOE) sites, take permanent remedial action, and eliminate or minimize the environmental impact of future operations. Technical resources to address these shortcomings exist within the DOE community and the private sector, but the involvement of the private sector in attaining permanent and cost-effective solutions has been limited.

During 1990, on behalf of DOE's Office of Technology Development, Argonne National Laboratory (ANL) conducted a competitive procurement of research and development projects addressing soil remediation, groundwater remediation, site characterization, and contaminant containment. Fifteen contracts were negotiated in these areas.

This report documents work performed as part of the Private Sector Research and Development Program sponsored by the DOE's Office of Technology Development within the Environmental Restoration and Waste Management Program. The research and development work described herein was conducted under contract to ANL.

On behalf of DOE and ANL, I wish to thank the performing contractor and especially the report authors for their cooperation and their contribution to development of new processes for characterization and remediation of DOE's environmental problems. We anticipate that the R&D investment described here will be repaid many-fold in the application of better, faster, safer, and cheaper technologies.

Details of the procurement process and status reports for all 15 of the contractors performing under this program can be found in "Applied Research and Development Private Sector Accomplishments - Interim Report" (Report No. DOE/CH-9216) by Nicholas J. Beskid, Jas S. Devgun, Mitchell D. Erickson and Margaret M. Zielke.

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ABSTRACT

This report describes the results of laboratory investigations of several performance parameters relevant to the deployment of instrumentation employing microfabricated surface-acoustic-wave (SAW) chemical sensor arrays for the measurement of volatile organic compounds (VOCs) in contaminated soil and groundwater. Instruments employing SAW sensor arrays have the potential to provide rapid identification and quantification of vapor phase contaminants. The small size, low cost, sensitivity and selectivity of such instruments promise improvements in the quality and quantity of data used to guide site assessment and restoration efforts.

In this investigation, calibrations were performed for 15 different coated SAW sensors. Each sensor was exposed to six VOCs selected to represent three chemical classes of contaminants that are commonly found at waste sites (i.e., aliphatic, aromatic and chlorinated hydrocarbons). A new pattern recognition method was developed for determining which coated sensors would maximize the selectivity and accuracy of quantitation for a given set of vapor contaminants. Using this method, an optimal subset of four coated sensors was selected for testing in a prototype microsensor instrument. Additional laboratory experiments were performed with this optimized array to assess the limits of detection and linear response ranges for the representative vapors, as well as the additivity of responses to vapors in binary mixtures, temperature and humidity effects, aging effects, and other performance parameters related to the application of this technology to soil and groundwater VOC monitoring.

Results demonstrate that SAW microsensor arrays can identify and quantify specific VOCs at concentrations in the $\mu\text{g/L}$ to mg/L range when present alone or in simple (e.g., binary) mixtures. Limits of detection, while sufficiently low for monitoring most VOCs in many applications, could be improved. Recent advances in SAW sensor design can apparently provide an order of magnitude reduction in detection limits, which would expand the range of applications. Sensor responses are dependent on temperature and, in certain cases, on relative humidity, indicating that compensation or control for these variables is may be necessary. Given the small size, ruggedness, low power requirements, selectivity, accuracy of quantitation, expected low cost of manufacture, and potential for continuous unattended operation, SAW sensor technology offers a potentially effective alternative to existing field instrumentation for headspace analysis, soil vapor monitoring, and vacuum extraction process monitoring of VOCs in subsurface media. Present configurations of SAW microsensor arrays may have several limitations which restrict their application in subsurface VOC monitoring. These include a lack of sensitivity for trace level contaminants, and uncertain ability to identify some components of complex mixtures.

EXECUTIVE SUMMARY

The analysis of volatile organic compounds (VOCs) in soil and groundwater at contaminated DOE sites is currently impeded by cost and performance issues of field monitoring instrumentation. Microfabricated surface-acoustic-wave (SAW) chemical sensor arrays have the potential to provide rapid identification and quantification of VOCs found in contaminated subsurface media. Incorporation of these sensor arrays into small, inexpensive instruments for continuous selective measurement of VOC concentrations would lead to considerable improvements in the quality and quantity of analytical data used to guide assessment and restoration efforts at contaminated sites.

This report describes laboratory investigations of several performance parameters relevant to the deployment of SAW-sensor based instrumentation for VOC-contaminated soil and groundwater monitoring applications.

Technology Description

The SAW sensors used in this investigation consisted of 158-MHz quartz delay-line oscillators having approximate dimensions 0.7 cm x 0.7 cm. The SAW device functions by generating mechanical (acoustic) waves along the surface of the piezoelectric quartz substrate. Oscillation occurs when the device is used as the frequency controlling element in a feedback circuit. Small changes of mass or elastic modulus at the surface of the device result in measurable changes in the oscillation frequency. Sensitivity to organic vapors is achieved by coating the SAW device with a polymer or high-boiling liquid into which the vapor will reversibly partition: vapor sorption increases the mass of the surface coating and causes a proportional shift in the oscillation frequency.

The response of a given coated sensor will depend on the volatility of the vapor and the strength of the coating-vapor solubility interactions (e.g., hydrogen bonding, dispersion, and dipole-dipole interactions). Using an array of SAW sensors, each with a different coating, will provide a response pattern that is characteristic of a particular vapor or class of vapors. Pattern recognition analysis of the multidimensional sensor array output permits determination of the identity and quantity of the vapor. With proper design, a simple array can identify and quantify a wide range of vapors, when present individually or in simple mixtures.

The prototype instrument tested here included an array of four sensors. The instrument occupied about 8500 cm³ (0.3 ft³) and required about 2 W of power, but was not optimized for field use. While this and several other SAW sensor array instrument designs are commercially available, many aspects of their performance, including their applicability to subsurface VOC monitoring applications, have not been investigated.

Technology Performance

A new pattern recognition method, referred to as extended disjoint principal components regression analysis (EDPCR), was developed to (1) aid in the selection of coated sensors to include in the array, (2) predict the performance of a specified sensor array with respect to sensitivity and selectivity of vapor measurement, and (3) determine the

identity and concentration of unknown vapors and vapor mixture components from the sensor array response patterns. EDPCR represents an effective alternative to more commonly used pattern recognition methods for analyzing array responses.

Initial screening tests entailed measuring the responses of 15 different coated SAW sensors to each of six VOCs using controlled test atmospheres of the individual vapors at 25 °C and 50% relative humidity. Two vapors from each of three chemical classes were selected as being representative of fuels and solvents commonly found as soil contaminants, namely hexane and isooctane (aliphatics), benzene and xylene (aromatics), and chloroform and trichloroethylene (chlorinated aliphatics). These calibrations yielded response factors and limits of detection for each of the 90 coating-vapor combinations.

The first application of EDPCR used this set of individual-vapor calibrations to select the subset of four coated sensors that would provide the best discrimination between the vapors when present alone or in binary mixtures. EDPCR was then used to predict the performance of this optimized four-sensor array. Noise was added to simulate typical variations in environmental conditions and sensor responses. Results indicated that vapors would be correctly identified an average of 95% of the time in single and binary vapor mixtures and that vapors could be distinguished both within and between the three chemical classes.

The selected set of coatings was then applied to the SAW sensors for laboratory investigations of performance parameters relevant to the use of this technology in assessing VOC contamination in soil and groundwater applications. Concentration ranges covered varied from 400 to 40,000 $\mu\text{g/L}$, depending on the vapor and the sensitivity of the coating to that vapor. Results indicated that sensor responses to individual test vapors were linear over the concentration ranges examined. Responses to each of several binary mixtures were linear and additive functions of the component responses, indicating that no significant vapor-vapor interactions were occurring. From experimental data involving exposures to nearly 100 test atmospheres of individual vapors and binary vapor mixtures, correct identifications were obtained in 91% of the cases, and concentrations were accurately determined in blind tests restricted to target compounds. Errors in classification were usually associated with mixtures where one component was present in large excess.

The effect of relative humidity (RH) on the responses to several individual vapors was then examined from 0 to 80% RH at 25 °C. For the sensor coated with the most polar polymer, a decline of from 26-34% was observed in the responses to the selected vapors. For the sensor coated with the least polar polymer, responses decreased by 10-18% at the highest RH level. There were no detectable effects for the two other coatings evaluated. The RH sensitivities of intermediate polarity coatings were smaller than those of the most and least polar coatings. The humidity sensitivity observed must be accounted for during calibration procedures to ensure accurate sensor responses. However, since RH changes will be small in many practical situations, this does not represent a serious problem.

Sensor responses exhibited a negative exponential (Arrhenius) temperature dependence from 15 to 40 °C, the magnitudes of which were slightly different for each

vapor, though similar for a given vapor across the four coated sensors. Temperature effects are well-behaved and could be accounted for via temperature monitoring and calibration.

Sensor responses were quite stable, showing no significant variation over a period of two to three months. For individual coating-vapor pairs, calculated limits of detection (LODs) at 25°C ranged from about 30 to several thousand $\mu\text{g/L}$. While improvements in the limits of detection (approximately 10-fold) could be achieved by using recently developed SAW resonators in place of the SAW oscillators employed here, the LODs obtained in this study were sufficiently low and linear response ranges sufficiently wide for many application in site assessment and restoration.

Technology Application

Results indicate that SAW microsensor arrays can identify and quantify VOCs from chemical classes typically found in contaminated soils and groundwater. Sensor responses are linear and additive over a wide concentration range. Detection limits vary significantly depending on the vapor being considered, the coatings employed in the sensor array, and the operating temperature, however, LODs in the range of 20 to 500 $\mu\text{g/L}$ (or about 5 to 125 ppm) are achievable for many VOCs of concern. Recent improvements in SAW sensor design could reduce these limits by an order of magnitude. Coupled with other advantages of this technology, i.e., ruggedness, low power requirements, expected low cost of manufacture (\approx \$1000 for a four-sensor array and necessary electronics in large scale production), and the capability for continuous unattended operation, these results support the use of SAW sensor instrumentation for applications such as headspace analysis, soil gas monitoring, and vacuum extraction process monitoring. Further, it appears feasible to develop battery powered instruments that could fit into 2 to 4 inch diameter wells and pipes, or be used as handheld instruments for use in screening waste drums, compatibility analyses, and other applications. Applications of microsensors in small (1.5 inch diameter) cone penetrometers that are driven in the ground would require further ruggedization (e.g., high impact and shock resistance) and miniaturization. While inherently rugged, the microsensors require a purge gas for baseline correction that might be difficult to provide in this application.

The tested SAW microsensor array configuration may have several limitations which restrict its application in subsurface VOC monitoring. These include a lack of sensitivity at the trace (ppb or low ppm) levels that may be relevant in some soil environments. However, recent advances in SAW sensor design can apparently provide an order of magnitude reduction in detection limits, which would expand the range of applications. A second limitation is the uncertain performance of the microsensor array in identifying and quantifying components of complex mixtures. For some vapors, SAW microsensor response patterns are very similar. These similarities, in conjunction with potential response shifts of the coatings, due to long-term aging, poisoning, and other features, may cause errors in identifying some vapors.

1.0 INTRODUCTION

1.1 Background

Soil and groundwater at DOE sites may contain various inorganic, organic and radioactive contaminants. Fuels and solvents, which often comprise the major fraction of the organic contaminants, can migrate through both the unsaturated (vadose) and saturated subsurface zones. Measurement of the volatile organic compounds (VOCs) in soil and groundwater is a critical component of site assessment and remediation efforts.

1.1.1 Site Assessment and Remediation

In site assessment, chemical analyses are used to identify the extent of contamination, determine the effects of environmental factors, evaluate and select the remediation options, evaluate risks to the public, and determine the permanence of the remediation action. VOC concentrations in soil are most commonly determined by collecting soil samples or cores, separating phases using head-space or other techniques, and chemically analyzing the separated phases. Most *in situ* or surface flux soil-gas measurements are made by collection of samples on sorbent tubes or in syringes and subsequent analysis with field instrumentation or in a mobile (on-site) or central (off-site) laboratory facility.

VOC analysis is also a critical factor in monitoring and controlling site remediation processes. Many cleanup actions have quite similar monitoring requirements. *In situ* remediation approaches applicable to VOCs include vacuum extraction for the vadose zone; soil vapor extraction augmented with air sparging (also called *in situ* volatilization) for the saturated zone (Loden, 1992); and pump and treat for groundwater. Monitoring of both liquid and gas phases is needed to ensure proper operation of process components, including air and water pollution controls and treatment devices (e.g. air strippers).

VOC analyses are also required for routine waste handling activities, such as screening the contents of drums and testing the compatibility of waste from different sources. Additionally, VOC measurements are collected to determine imminent safety hazards, such as those encountered in confined spaces and potentially explosive environments. In some of these applications, VOC concentrations may approach saturation levels.

1.1.2 Vacuum Extraction

For the purposes of this study, approximate specifications or design goals for VOC monitoring instrumentation are taken from vacuum extraction systems (VES) (also called vapor extraction and soil venting). VES places significant demands on soil gas monitoring.

VESs involve the *in situ* volatilization of VOCs and induction of air flow by the application of a vacuum within the soil matrix. A typical VES uses one or many extraction wells, connecting tubing and manifolds, carbon adsorption towers (or other VOC emission control approaches), fans or vacuum pumps, and an exhaust stack. The vacuum is applied at the extraction well(s) positioned in the contaminated zone, and soil gases are drawn into the extraction well. During the development of the well, soil surrounding the well is dried,

air flow paths are developed, a well's maximum radius of influence is reached, and steady state flows are established (EPA, 1989). A vapor/liquid separator removes contaminated water for treatment; contaminants in the air stream are removed by passage through activated carbon canisters. Purging will eventually remove contaminants which favorably partition into the gas phase at subsurface temperatures. The VES approach is effective for many VOCs over a range of environmental conditions (Hutler et al., 1990). It is applicable to volatile and hydrophobic compounds, including solvents (TCA, TCE, PER, DCE, CH₂Cl₂, Freons, etc.) and fuels (toluene, benzene, ethylbenzene, xylenes, etc.). VESs have been successfully used on various scales, including at very large Superfund sites. Costs are low in comparison to other remediation technologies. The major costs are associated with equipment, energy for pumping, and chemical analysis.

Wellhead concentrations and flows are monitored during VES operation to estimate VOC removal and determine when remediation is complete. Vacuum extraction continues (typically for several months) until wellhead concentrations drop. Intermittent operation may be used if significant increases in vapor concentrations occur after pumping ceases. If so, extraction continues; if not, soil borings are taken to ensure that soils have reached the desired equilibrium concentrations. Intermittent blower operation is probably the most energy efficient approach (Hutler et al., 1990). While initial concentrations may approach vapor saturation, typical VOC levels during pumping are 50 to 25,000 ppm. The VES is typically shutdown when concentrations fall below a few ppm. Appendix I reviews a number of VES applications and VOC concentrations found.

1.1.3 Summary

In summary, instrumentation is needed to identify and quantify VOC concentrations in soil and groundwater in both site assessment and site remediation activities. VOC concentrations requiring quantification range from low-ppm levels to vapor saturation.

1.2 Technology Scope

This research addresses the measurement of VOCs that are found at thousands of sites across the country. This section describes the status of current technologies used to measure VOCs and the anticipated systems that might use microsensors.

1.2.1 Current Baseline Technology

A number of instrumental methods have been explored for monitoring VOCs in soil and groundwater. Unfortunately, their application is limited by their sensing capabilities, expense and/or complexity. For example, photoionization detectors (PID) provide low- or sub-ppm detection of certain organic vapors, but they neither identify individual vapors nor discriminate between components of vapor mixtures. PIDs are also rather expensive, with typical costs of \$4,000 per instrument. Flame ionization detectors (FID) have similar costs and performance limitations as PIDs, and also require supplies of compressed hydrogen and air to support the detector flame. Catalytic filament detectors, while less expensive than PID and FID instruments, are also non-selective, have limited sensitivity and can be poisoned by various reactive gases and vapors. Portable gas chromatographs equipped with PIDs or FIDs provide improved selectivity, but are more expensive (>\$8,000), have lower

through-put, and require a higher level of user training and maintenance than the other instruments mentioned.

To circumvent their limitations, portable instruments are generally used in a screening mode, serving to detect the presence of broad classes of compounds. Identification and quantification is performed by collecting water, soil, gas, or absorbent-based samples, transporting them to an off-site or mobile laboratory, and using conventional analytical laboratory methods. The costs and time associated with collecting, transporting, maintaining and analyzing such samples has historically limited the quantity and quality of data collected.

1.2.2 Anticipated Products and Technology

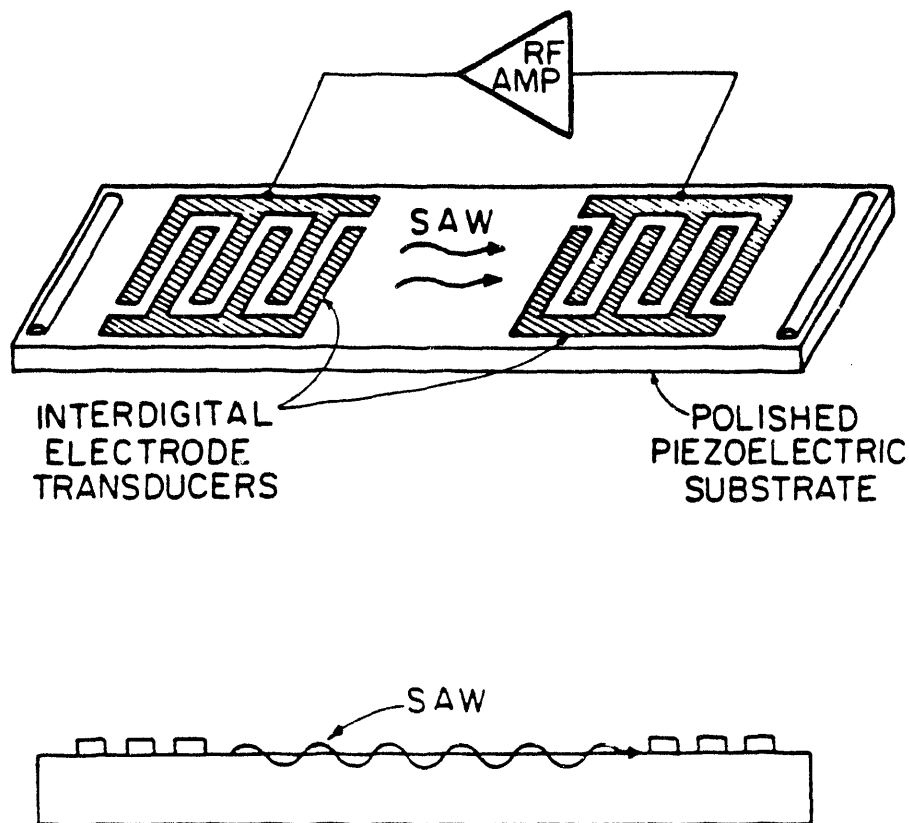
Small, inexpensive, continuous monitoring instruments are needed to allow the collection and analysis of greater numbers of samples, and to improve the quality of data used to guide remediation efforts (DOE, 1989). Such instruments would permit significant increases in the speed and cost-effectiveness of restoration by better utilization and control of resources.

This research has focused on a relatively new sensor technology to determine its suitability for use in monitoring VOCs in assessment and restoration efforts. Ostensibly, this technology has several inherent advantages for this application, including potentially high sensitivity and selectivity, ruggedness, low cost, low power requirements, continuous operation, and the possibility of *in situ* monitoring in penetrometers and wells. However, detailed reports on the capabilities of this technology have not been provided.

1.2.3 SAW Sensor Technology

SAW devices respond with high sensitivity to changes of surface mass and, as a result, can be used for a wide range of potential organic vapor analytes (Nieuwenhuisen et al., 1989). Fig. 1 depicts the basic components of the SAW oscillator. The SAW sensors used in this investigation consisted of 158-MHz quartz delay-line oscillators having approximate dimensions 0.5 cm^2 . The SAW device functions by generating mechanical (acoustic) waves along the surface of the piezoelectric quartz substrate. Oscillation occurs when the device is used as the frequency controlling element in a feedback circuit. Small changes of mass or elastic modulus at the surface of the device results in measurable changes in the oscillation frequency. Sensitivity to VOCs is achieved by coating the SAW device with a polymer or high-boiling liquid into which the vapor will reversibly partition: vapor sorption increases the mass of the surface coating and causes a proportional shift in the oscillation frequency. Advantages of using sorptive polymer coatings include the rapid and reversible sensor responses obtained, and the ability to repeatedly expose the sensor without significant changes in the physical or chemical properties of the coating, thus extending the sensor's service life. The amount of vapor sorbed by the sensor coating is typically a linear function of the vapor concentration over the useful concentration range, and efficient operation is possible at ambient temperatures, reducing power requirements. Since vapor sorption decreases exponentially with increasing temperature (Rogers, 1985), sensitivity increases at lower temperatures.

Fig. 1. Diagram showing SAW delay-line oscillator and surface wave between transducers.



Sensor arrays consist of several SAW sensors, each coated with a different partially-selective polymer (Rose-Pehrsson et al., 1988; Carey et al., 1987; Zellers, et al., 1993). The response of a given coated sensor will depend on the volatility of the vapor and the strength of the coating-vapor solubility interactions (e.g., hydrogen bonding, dispersion, and dipole-dipole interactions). Using an array of SAW sensors, each with a different coating, will provide a response pattern that is characteristic of a given vapor or class of vapors. Since the sensor response to a given vapor depends on the functional groups incorporated into the structure of the polymer, judicious selection of polymers can lead to significant differences in the response patterns for different vapors (Grate and Abraham, 1991; Patrash and Zellers, 1993). With proper design, such an array can measure several different vapors individually or in simple mixtures. However, the problem of identifying and quantifying the components of vapor mixtures using coated SAW sensor arrays has not been extensively studied (Rose-Pehrsson et al., 1988).

The selection of coatings in sensor arrays is based principally on sensitivity and selectivity considerations. Each coating should contribute unique information about the vapor, otherwise, coatings with similar structure will provide redundant or colinear responses. Some qualitative guidance for coating selection can be obtained from coating and vapor physicochemical properties that affect the magnitude of the solubility interactions (Grate and Abraham, 1991), and by using principal components or cluster analyses of sensor calibration data (Carey et al., 1986). However, no general methods for accurately predicting sensor responses and selecting sensor coatings have been developed.

1.2.4 Polymer Coated SAW Sensor Responses

Partitioning phenomena govern responses of polymer-coated SAW sensors. The partition coefficient, K , typically derived from gas-liquid chromatographic (GLC) analysis, represents the equilibrium vapor-polymer solubility at a given temperature (Littlewood, 1970)

$$K = C_c / C_v \quad (1)$$

where C_c is the vapor concentration in the chromatographic stationary phase and C_v is the vapor concentration in air. The predicted sensor response from a vapor sorbed in a polymer-coated SAW oscillator is (Grate et al., 1988 and 1992; Patrash and Zellers, 1993)

$$\Delta f_v = \Delta f_c K_e C_v / \rho_c \quad (2)$$

where Δf_v is the sensor response measured as a frequency shift, Δf_c is the initial frequency shift caused by deposition of the coating, ρ_c is the coating density, and subscript e indicates that K is determined experimentally using sensor responses. Assuming the coating is thin, isotropic and non-conducting, the coating mass is related to Δf_c by

$$\Delta f_c = (k_1 + k_2) f_0 m / a \quad (3)$$

where k_1 and k_2 are substrate constants, f_0 is the oscillator frequency prior to coating, and m/a is the mass per unit area of the coating film (Wohltjen, 1984).

Inherent in Eqs. 2 and 3 is the assumption that the sensor response is dominated by mass-loading effects. Under this condition, K and K_e should be equivalent. However, K_e values determined using Eq. (2) may exceed K values determined using GLC measurements due to changes in the polymer modulus accompanying swelling (Grate et al., 1992, Patrash and Zellers, 1993). To the extent that modulus changes contribute to measured values, K_e is not a true partition coefficient, as defined in Eq. 1. Nonetheless, the prevailing evidence indicates that K_e is proportional to K , and that K_e is a useful summary of the sensitivity. That is, Eq. 2 provides an accurate description of polymer-coated SAW sensor responses to organic vapors over a wide range of concentrations.

1.2.5 Environmental Applications of SAW Sensors

The performance of SAW sensors with respect to humidity, temperature, vapor

mixtures, and other factors has not been well characterized. The effect of these factors must be understood prior to field applications of this technology.

With respect to humidity, VOCs are generally present in soil that is saturated with water vapor. The very high concentration of water vapor may interfere with the sorption of VOCs present at much lower concentrations. The effect of temperature on SAW sensor responses has been mentioned. Temperatures may be quite constant in some proposed applications of the technology, e.g. wells may remain at 15-20 °C for much of the year. However, remediation activities such as vacuum extraction may alter these temperatures. Temperature variations may be quite extreme in certain other applications, e.g., handheld use and placement in above-ground manifolds. Finally, most soil contaminants and many groundwater contaminants are present as mixtures. The response of SAW sensors to vapor mixtures, and in particular, the assumptions of response linearity and additivity to vapor combinations, has not been extensively tested.

In some cases, it may be possible to condition the sensor array and the vapor to achieve constant temperatures and humidities, however, this may significantly increase the complexity, size, weight, and cost of the instrumentation. In cases where responses to factors are well behaved and predictable, it may be possible to use calibrations and mathematical corrections. For example, if sorption processes follow an Arrhenius relationship, a simple temperature measurement could be used to correct SAW responses and determine concentrations.

1.3 Technology Programmatic Requirements

The programmatic requirements for SAW microsensor arrays at DOE sites are basically the development of ruggedized instruments that incorporate automatic processing of sensor output and appropriate interfacing for sampling and user control. No significant programmatic requirements beyond that needed to train users in the use, maintenance, and quality assurance of the technology are needed as the microsensor array would simply replace or augment existing instrumentation.

Some applications would require more significant programmatic requirements. For example, control of vacuum extraction systems based on real-time sensing of VOC levels, would require variable speed fans and pumps that are interfaced to a monitoring and control system.

2.0 METHODOLOGY AND APPROACH

2.1 Facilities and Equipment

Data were collected using a prototype AC-powered instrument supplied by Microsensor Systems Inc. (Bowling Green, KY) which consisted of an array of four 158-MHz SAW oscillators (each with a separate sealed reference oscillator), radio-frequency electronics modules, frequency counters and a microcomputer. Fig. 2 is a photograph of the SAW sensor mounted on its TO-8 header (providing mechanical and electrical connections), showing its small size. Fig. 3 is a photo of the array instrument.

To screen coating materials and examine various operating characteristics, the SAW instrument was incorporated into an exposure and data acquisition system. Fig. 4 shows the experimental setup used in most experiments. Difference frequency measurements between the coated and reference sensors were collected every 2 s and logged on a personal computer. Dynamic (i.e., continuous flow) test atmospheres of the vapors were generated by passing N₂ gas through a fritted bubbler containing the liquid solvent and then into a metered dilution-air stream maintained at a preset temperature and relative humidity. Dilution air was pre-filtered to remove any particulate or organic vapor contamination. For certain experiments, dry N₂ gas was used as the diluent instead of humidified air (see below). After allowing for proper mixing of the vapors in the dilution stream, a portion of the stream was passed through a calibrated infrared gas analyzer (MIRAN 1A, Foxboro, MA). The remainder was diverted to a solenoid valve that directed the flow of contaminated air either to the sensor array or to a vent in the system. A separate humidified clean-air line was directed to the array for the purpose of measuring baseline sensor responses before and after contaminant exposures.

For mixture exposures, an additional bubbler was incorporated into the system. Air concentrations were verified by taking aliquots with a gas-tight syringe and injecting them into a gas chromatograph (GC) (Varian Model 2860, Mountain View, CA) equipped with a packed column (2 ft, 1/8-inch o.d., 1% SP-1000 on acid washed Chromosorb P) and an FID. Peak areas were quantified using an electronic integrator. The GC was calibrated before each experiment using solutions of the analytes in CS₂.

Each sensor was capped with a nickel-plated lid that could be sealed with a Teflon gasket to the TO-8 header on which each sensor was mounted. Exposure to the test atmospheres was achieved through inlet and outlet tubes soldered to the sensor lids. The sensor lids were held in place with machined aluminum blocks (one for each coated-sensor/reference-sensor pair) placed on top of the lids and bolted through the floor of the instrument chassis. The temperature of the sensor array was maintained within 0.1 °C of the preset value by circulating water through the aluminum blocks in contact with the sensor lids using a thermostatted circulator. A 0.001-in diameter type-K thermocouple was fed through the seal of one of the sensor lids and the temperature just above the sensor was monitored with a digital temperature meter (Model HH-71 K1, Omega Engineering, Stamford, CT). All system connections were made using either Teflon or stainless steel tubing and fittings to avoid any losses of vapors.

Fig. 2. Photograph of the SAW sensor mounted on TO-8 header.

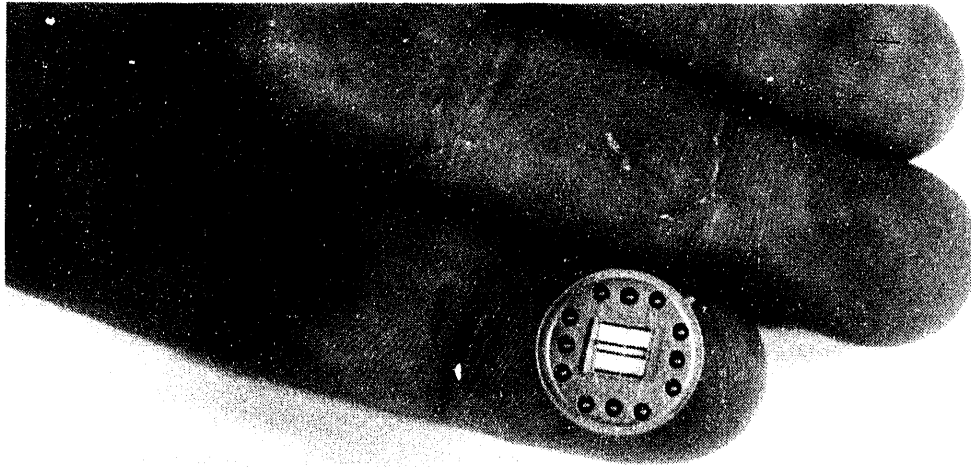


Fig. 3. Photograph of the array instrument. Pen indicates location of SAW sensor.

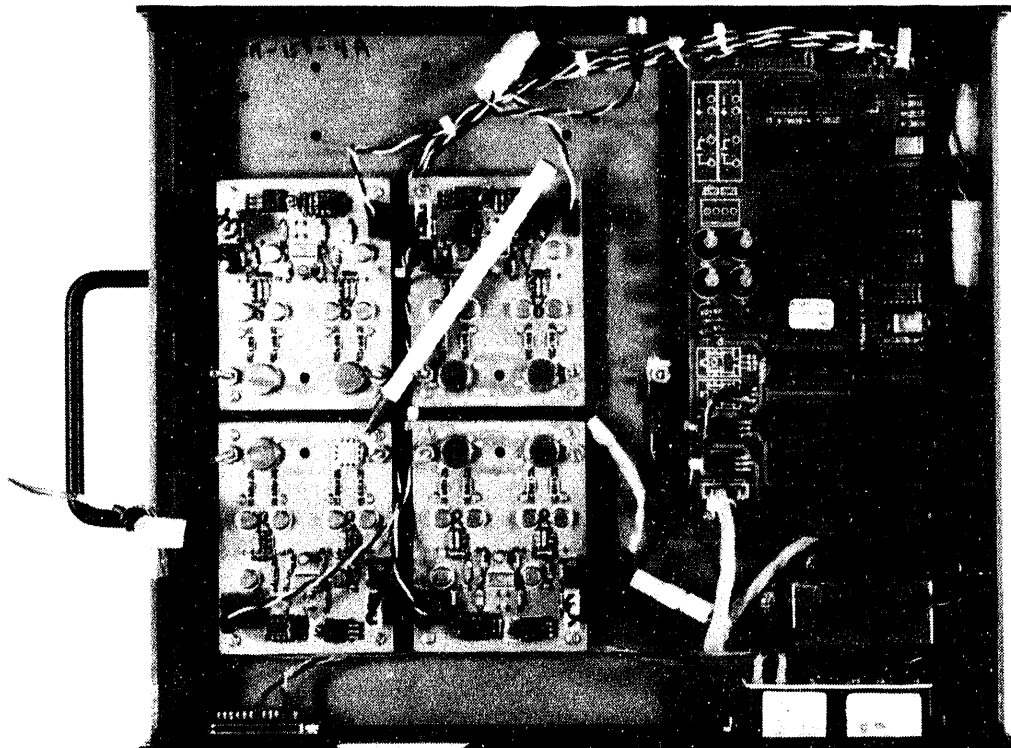
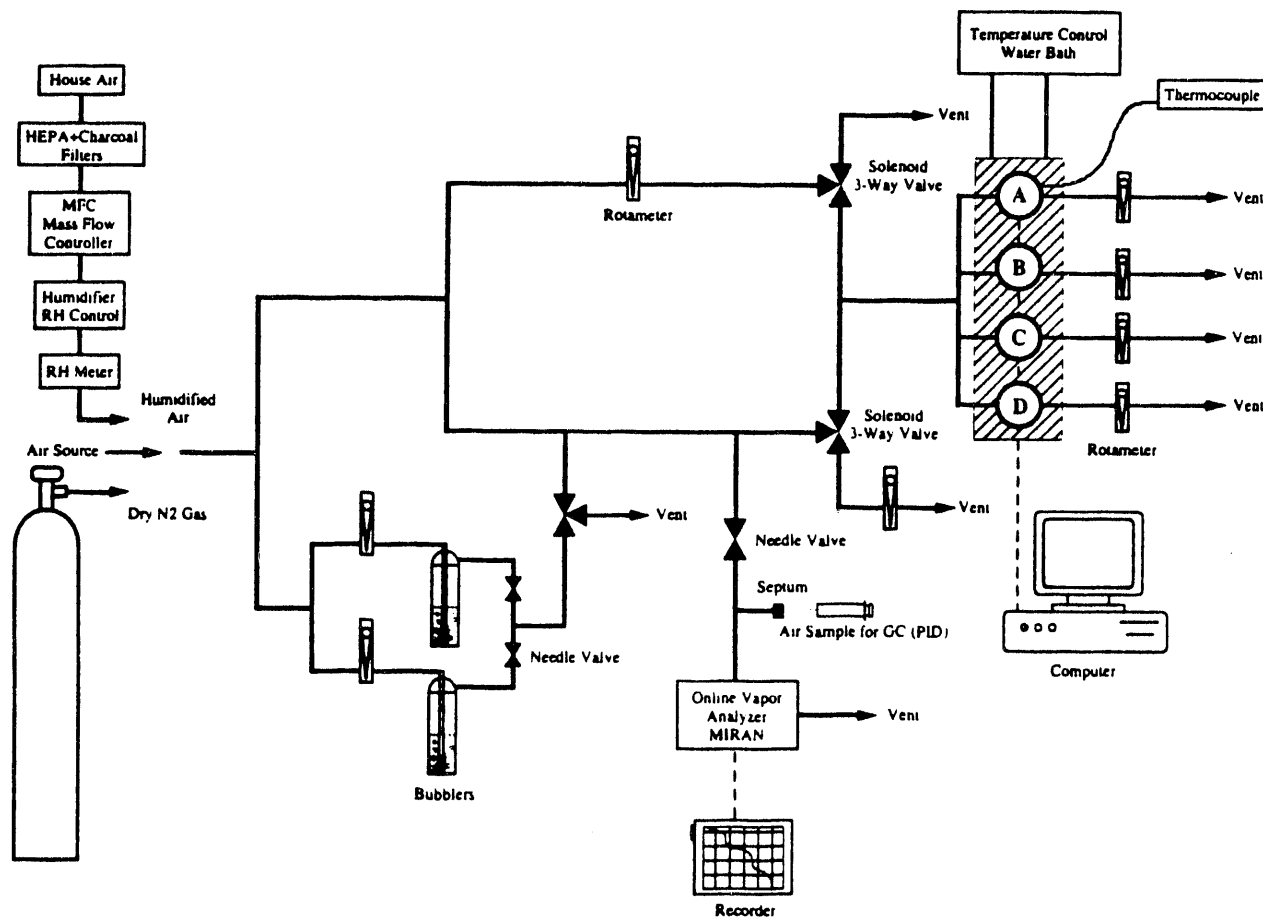


Fig. 4. Test setup used in most experiments.



Flow rates over the sensors were maintained at 0.250 L/min and monitored continuously with four downstream rotameters. For an internal volume of about 0.5 cm³, the theoretical mixing time is well under 1 s. Humidified contaminant-free air (or dry N₂) was continuously passed over the sensors to establish a baseline frequency. The average short-term (i.e., 2-s) noise level of the baseline response was about 10 to 15 Hz. Limits of detection (LOD) for the vapors were calculated using 45 Hz as the minimum detectable sensor response.

2.2 Reagents and Supplies

Sensor coatings examined are listed in Table 1. Several of the coatings were chosen based on an analysis of GC retention data reported by Huber and Reich (1984). Additional coatings were selected based on general considerations of structure and anticipated affinities for the test vapors. Collectively, this set of coating materials span a wide range of polarities and structural features. All coatings were obtained from Scientific Polymer Products (Ontario, NY) with the exception of OV-215 and DEGA which were obtained from Ohio Valley Specialty Chemicals (Marietta, OH). The solvents used and their corresponding boiling points are trichloroethylene (TCE), 87 °C; chloroform, 61 °C; hexane, 69 °C; isooctane, 98 °C; benzene, 80 °C; xylene, 138 °C. Solvents were all > 98% pure (Aldrich, Milwaukee, WI) and were used without further purification.

Table 1. List of coatings, abbreviations, physical forms, and frequency shifts due to coating deposition (Δf_c).

NO.	SYMBOL	COATING	SOLID (S) LIQUID (L)	Δf_c (kHz)
1	PECH	Polyepichlorohydrin	S	201
2	PDPP	Polydiphenoxyphosphazene	S	202
3	OV-215	Vinyl modified trifluoropropylmethyl-silicone	L	228
4	DEGA	Diethylene glycol adipate	L	200
5	PIB	Polyisobutylene	S	195
6	PCP	Polychloroprene	S	179
7	ABC	Acrylonitrile/butadiene copolymer (41% acrylonitrile)	S	199
8	TBEP	Tri-butoxyethyl phosphate	L	222
9	PHA	Poly(hexyl acrylate) 25% solids in toluene	S	162
10	OV-275	Biscyanoallyl polysiloxane	L	196
11	PHOEA	Poly(2-hydroxyethyl acrylate)	S	193
12	OV-25	Phenylmethyldiphenylsilicone (75% phenyl)	L	220
13	ETSA	N-Ethyl o,p-toluenesulfonamide	L	193
14	PMMA	Poly (methyl methacrylate)	S	227
15	PPE	Polyphenylether 6-rings	L	192

2.3 Experimental

Solutions of the coatings (approximately 0.2% by weight) in toluene or a mixture of toluene and acetone were applied by airbrush to the sensors. The amount of coating deposited was inferred from the net frequency shift Δf_c observed after evaporation of the carrier solvent using Eq. 3. Values of Δf_c were all in the range of 190 - 275 kHz. Estimated film thicknesses were in the range of 0.05-0.1 μm . All of the reference sensor frequencies were higher than the coated sensor frequencies prior to coating, thus difference frequencies increased steadily during coating deposition. (Note: If the reference sensor frequencies had been lower initially, then the difference frequency would have passed through a minimum).

In a typical exposure experiment, the array was exposed twice for 60 s to a given concentration of vapor, with each exposure separated by a 60-s purge with clean air (or N_2). The last 15 frequency measurements (30 s) in each exposure period were averaged and compared to the pre- and post-exposure baseline frequencies to determine the sensor response. This procedure was repeated for a minimum of four different concentrations of each test vapor to develop calibration curves covering a 4 to 10-fold concentration range, depending on the vapor. For calibrations performed subsequent to initial screening experiments, concentrations covering a 12 to 30 fold range were used. The minimum vapor concentration used was typically that yielding responses greater than the LOD for at least three of the four sensors. These tests were performed at 25 °C and 50% relative humidity.

Following initial testing, it was found that at the higher N_2 flow rates needed to generate high concentrations of certain vapors, a measurable baseline shift occurred in several sensors, due to changes in RH (typically less than 5%). Therefore, all tests were performed with N_2 gas added to the clean-air stream at a relative flow rate equivalent to that used for vapor introduction into the contaminated-air stream. As a result, the actual exposure RH for these initial tests was somewhat lower than 50%, however, the RH was held constant.

Calibrations were performed for each of the 15 coatings (typically in sets of four) and six vapors. Following exposure to the six vapors, the coating was dissolved from the SAW sensor surface and a new coating applied as described previously. Of the 15 coating materials initially examined, five were eliminated from further analysis because of problems with baseline and/or response instability (OV-25, PPE, and ETSA) or due to extreme water sensitivity to water vapor (PHOEA). A fifth coating, PMMA, was omitted due to its very low response to all vapors. Analyses of the 60 calibration curves from the remaining 10 coatings used techniques presented in the next section. An "optimal" subset of four coatings, selected in order to maximize selectivity, was used for subsequent testing of the effects of temperature, humidity, and vapor mixtures on the array responses.

Temperature effects were examined by exposure to a subset of three vapors at 15, 25, 30 and 40 °C using dry N_2 as the diluent stream. Additional tests were performed at relative humidities (RH) ranging from 0 to 77% RH, while maintaining the sensor array at

25 °C. Sensor responses to VOCs as a function of relative humidity were determined using multipoint calibration curves. Additionally, sensor responses to water vapor alone were determined.

Binary mixture exposures were then performed in an N₂ atmosphere and 25 °C for a subset of vapors. The concentration of each component was varied during these experiments to examine whether the relative concentration of the vapors affected their combined response or the ability to discriminate each component using pattern recognition. From seven to 18 exposures were performed for each binary mixture.

Preliminary experiments were conducted to examine uses of the sensor array instrument for headspace and in-situ soil characterization studies. Soil column simulators were constructed of 5.4 cm dia. glass cylinders with Teflon endcaps. Each cap contained stainless steel connectors and support screens to contain the soil. After measuring soil density and porosity, soil was uniformly packed into the column. Controlled flows of humidified air and vapor, produced by dynamic dilution, passed through the soil column and also through three different VOC detectors: the SAW sensor array, an FID (Horiba FID-23A, Ann Arbor, MI), and a Fourier transform infrared spectrophotometer (Bomem 100A, Montreal, Canada). Headspace experiments utilized a conventional automated headspace analysis instrument (Tekmar 7010 GT, Youngstown, OH) interfaced to a Varian 3700 GC (Mountain View, CA) equipped with FID and computer data acquisition system. To perform parallel analyses with the SAW sensor array, a manifold was constructed from Teflon tubing that received headspace vapor that had passed through the GC sample loop. This manifold then distributed the vapor to each of the sensors in the array (parallel flow). A multiport valve was used to send clean air to the sensors for baseline measurements.

2.4 Data Reduction and Interpretation

Calculations of average responses, standard deviations and linear regressions were performed using Lotus 123 (Cambridge, MA) on a personal computer. EDPCR analyses were performed on a personal computer using programs written in MATLAB^R (Mathworks, Inc., Natick, MA). Certain additional statistical analyses were performed using SAS^R Version 6.07 (SAS Institute, Cary, NC) on an IBM ES-9000 series mainframe computer, and SYSTAT^R 5.0 (Evanston, IL) on a personal computer.

2.4.1 Calibration Curves

The average sensor response at each concentration for each vapor-coating combination was determined by the net frequency shift of duplicate exposures. Sensor responses were then regressed against vapor concentrations to obtain the sensitivity (slope), standard error, and coefficient of correlation (R^2). K_e values were calculated by Eq. 2 using the Δf_c values for each coating. Limits of detection (LOD) were determined by extrapolating the response curves to a frequency shift of 45 Hz, representing 3 to 4 times the RMS noise observed.

2.4.2 Performance Evaluation

To evaluate the performance of various coated-sensor subsets, and to select an

optimal subset, the individual vapor-coating calibration curves (from linear regression) were used in a Monte Carlo simulation of responses to each vapor and binary vapor mixture. The synthetic responses for each possible subset of four coatings were then processed using EDPCR for identification and quantification. Responses to binary mixtures were generated as linear combinations of sensor responses to the component vapors. For both individual-vapor and binary-mixture simulations, noise was added to the responses to simulate variations in sensor responses expected under normal operating conditions. The following equation was used to generate the responses used in the model:

$$R_j = \sum_i (C_{i,m} + k_1 \sigma_1 \Delta C_i) S_{i,j} (1 + k_2 \sigma_2) + k_3 \sigma_3 \quad (4)$$

where R_j is the sensor response for coating j (Hz), $C_{i,m}$ and ΔC_i respectively are the mean concentration and range of concentrations for vapor i ($\mu\text{g/L}$), $S_{i,j}$ is the slope of the calibration curve for vapor i and coating j ($\text{Hz}/(\mu\text{g/L})$), k_1 adjusts the range of concentrations generated, k_2 specifies the level of slope noise, k_3 specifies the fraction of noise, σ_1 is a uniformly distributed random variable ($-1 \leq \sigma_1 \leq 1$), and σ_2 and σ_3 are independent normally distributed, zero mean, and unit variance random variables. As nominal values, $\Delta C_i =$ concentration range used in the calibration, $C_{i,m}$ is the midpoint of the same range, $k_1 = 0.5$, $k_2 = 0.025$, and $k_3 = 15$ or 22 Hz. The 2.5% Gaussian error was superimposed on individual vapor responses to simulate possible temperature changes that would affect the sensor sensitivity (this number was determined from an unpublished study of calibration slope errors for a PIB-coated SAW sensor exposed to xylene). The additional ± 15 Hz represents a typical level of random noise. Thus, Eq. 4 produces slightly noisy but linear and additive responses at values that span experimental conditions, a range known to be valid. As described later, the additivity assumption was verified experimentally.

The analysis of one set of four coated sensors for each possible vapor combination (either single vapors or binary mixtures) utilized 100 simulations generated using Eq. 4. This number of simulations was found to give stable results. The analysis of a specific coating set for the 6 pure vapors and the 15 binary mixtures, or 21 combinations, required a total of 2100 analyses. The percentage of correct identifications was then determined from EDPCR. Partially correct identifications were scored by the fraction correct, e.g., a correct identification of 1 of 2 compounds yielded 0.5. For those correctly identified, the relative error in the predicted concentration was calculated. There are 210 possible coating sets containing 4 of the 10 coatings in the screening set. Each coating set was ranked according to the percentage of correctly classified vapors and vapor mixture components.

2.5 Quality Assurance

Collected data during the laboratory investigation included temperature, humidity, vapor concentration, air flows, and sensor output frequencies. Measures taken to maintain the quality of collected data included: the use of well-controlled and monitored experimental conditions; replicate exposure measurements at each concentration level; multipoint calibration curves for sensors and analytical instrumentation; continuous measurement of flow rates in the experimental system at all critical points (vapor and

dilution flows, and at each sensor); verification of vapor concentrations in test atmospheres at each concentration level; daily calibrations of IR and GC analyzers; and regular calibration of thermocouples, humidity sensors and other instruments using standard methods.

Results presented below include the outcome of quality assurance measurements. These include the uncertainty of experimental determinations and other statistical measures that indicate data quality, e.g. goodness of fit statistics like R^2 . Additionally, coating stability was repeatedly examined over the course of the data collection period by exposure to either benzene or xylene.

3.0 RESULTS AND DISCUSSION

3.1 Extended Disjoint Principal Components Regression (EDPCR)

Various methods have been developed for correlating the pattern of responses from an array of chemical sensors with the identity or class of a given analyte (Sharaf et al., 1986; Massart et al., 1988; Carey et al., 1986). Typically, principal components analysis (PCA) and cluster analysis (CA) are performed on the concentration-normalized matrix of sensor responses to assess qualitatively the uniqueness of the response pattern for each species. One of several classification methods can then be used to identify an unknown provided that its sensor responses are contained in the calibration set (also referred to as the training set). For an unknown mixture to be correctly identified it is necessary to have previously defined the spatial locations associated with the mixture over the range of component concentrations. Once the identity of an unknown is determined a second analysis, such as multiple linear regression (MLR), partial least squares (PLS) or principal component regression (PCR), is performed to determine the concentration(s) of the analyte(s) (Carey et al., 1987; Carey et al., 1986).

Disjoint principal components modelling (Wold, 1978) and its more familiar derivative SIMCA (soft independent modelling of class analogy) (Sharaf et al. 1986; Massart et al., 1986; Albano et al., 1978) incorporate several features of PCR. In these methods, principal components models are developed for individual groups within a data set. Classification of an unknown is based on the goodness of fit of its response vector to each of the models. This approach differs from standard PCR where principal components are derived from the data matrix as a whole (Dunn, et al. 1989; Vogt et al., 1987; Scott, 1986).

The concepts underlying these methods can be extended to identify both individual vapors and the components of vapor mixtures from sensor response patterns. This extended disjoint principal components regression (EDPCR) method takes advantage of the integration of the qualitative and quantitative aspects of the sensor responses. Since information on the vapor concentrations is retained in the classification models, misclassification can be minimized and estimation of vapor concentrations is facilitated. In addition, by using a single model for the responses to each vapor, the data matrix can be summarized by a series of equations and the computational burden is reduced.

For our initial investigations of the feasibility of using EDPCR for sensor array analysis we used previously reported data from an array of polymer-coated SAW sensors exposed to each of several organic vapors (Rose-Pehrson et al., 1988). The results of these investigations are provided in the publication included as Appendix II of this report. Only the salient features of the EDPCR modeling approach are given here.

The first step in the method is the application of PCA to each group of sensor responses (i.e., the collection of sensor responses to all concentrations of a single vapor). The response vectors for that vapor are then modelled using the most significant principal component(s). Since the only preprocessing that is performed is mean-centering, information about the concentrations of the vapors is accessible during classification.

The model used to classify vapor i is given by

$$r = m_i + \sum_{n=1}^N a_{i,n} m_{i,n} + e \quad (5)$$

where r is the response vector for the vapor at a given concentration, m_i is the mean response vector determined from all of the calibration concentrations measured for that vapor, $a_{i,n}$ is the projection coefficient corresponding to the location of each response vector along the n th principal component represented by the unit vector $m_{i,n}$, e is the residual error vector of the model for the vapor at the measured concentration, and N is the number of principal components. The accuracy of the model can be assessed by inspecting the residual error or by constructing confidence intervals.

Provided that at least one sensors in the array responds differently to a given vapor, each vapor will be represented by a unique response model. The response vector from a given concentration of an unknown vapor (r_u) can be tested for its goodness of fit to each of the models established during calibration by replacing r by r_u in Eq. (5) and solving for a_u to minimize $\|e\|^2$ (see Appendix II). The identity of the unknown is determined from the model for which the smallest $\|e\|^2$ is obtained. Once the identity of the vapor has been established, its concentration is determined by interpolation or linear regression of a_i versus concentration because the projection of the response vector along the line (one-principal-component model) is directly related to its concentration when sensor responses are linearly related to concentration.

For mixtures of two components with additive responses, the response vector can be projected onto the plane bounded by the pure-vapor response vectors. Each binary mixture can then be thought of as an additional group consisting of two pure vapors, i and j , in some combination of concentrations. A classification model for a binary mixture can be established using the following equation (note: a one-principal-component model is assumed and the subscript $n=N=1$ has been omitted for simplicity):

$$r = m_i + m_j + a_i m_i + a_j m_j + e \quad (6)$$

where r represents the response vector for the mixture of i and j and the remaining variables are defined as above for the pure-vapor case. For each combination of vapor concentrations there will be specific values of a_i and a_j . Here again, the smallest residual error obtained by fitting an unknown response vector to all possible models determines the correct class for the unknown vapor.

The response vector for the binary mixture can be projected onto the principal component of each vapor and the concentrations obtained from the calibration data for the individual vapors. The estimated vapor concentrations account for the nonorthogonal components of each vapor. Models analogous to (6) can be used for ternary or more complex mixtures.

Use of the concentration predictions in the classification scheme can aid in minimizing classification errors. Misclassification can arise from the intersection of the vector corresponding to one vapor (or vapor mixture) with those of other vapors. Where the response vectors extend to infinite concentration, there is an increased likelihood of intersection. In practical situations there is a limit to the concentrations encountered. In fact, standard quality control protocols require that an instrument detector be calibrated over a concentration range that brackets the range to be encountered during normal operation. Measurements obtained outside of the calibration range are not strictly valid. If the range of allowable concentrations is rendered finite, the probability of misclassification is reduced. An unknown sample initially classified into this group but falling outside of these concentration limits would be re-classified to the group for which the next lowest residual error is obtained and for which the concentration falls within the permitted range.

As described below, we have found that EDPCR is a useful tool for analyzing sensor responses. Applications of EDPCR to the selection of optimal coatings and the prediction of vapor responses are demonstrated.

3.2 Sensor Calibration and Linearity

Figure 5 shows a series of response profiles for four different coated sensors exposed alternately to a vapor (7670 $\mu\text{g/L}$ of TCE) and then clean air. These responses are typical of those obtained for all of the vapors and vapor mixtures. In all cases, sensor responses and recoveries reached >90% of their equilibrium values within 6-10 s of introduction and removal of the vapor.

Plots of vapor concentration versus Δf_v were generally linear with regression correlation coefficients (R^2) exceeding 0.99. Representative results for four coatings are shown in Figure 6 for exposure to TCE over a concentration range of 300 to 13,000 $\mu\text{g/L}$.

Table 2 provides statistics for all coatings and vapors in the screening set, showing the sensitivity, standard error, and R^2 obtained from linear regression, as well as K_e and the calculated LOD for each vapor-coating combination. In general, the linearity and precision of determinations were excellent. Some variability in sensitivity was observed for vapors giving low responses with a given coated sensor (e.g. hexane and DEGA). This can be attributed to random oscillator noise and errors in concentration measurements. Small differences in relative humidity between the clean and contaminant flow streams may also have contributed to the variability in the DEGA and OV-275 sensor responses since these highly polar coating show the greatest sensitivity to RH fluctuations.

Calculated LODs ranged from about 30 $\mu\text{g/L}$ to several thousand $\mu\text{g/L}$. The general trends are as expected, with higher LODs being associated with the more volatile vapors and/or with coating-vapor combinations where the strengths of the solubility interactions are expected to be low.

Fig. 5. Traces of SAW sensor responses to 7670 $\mu\text{g/L}$ of TCE vapor.

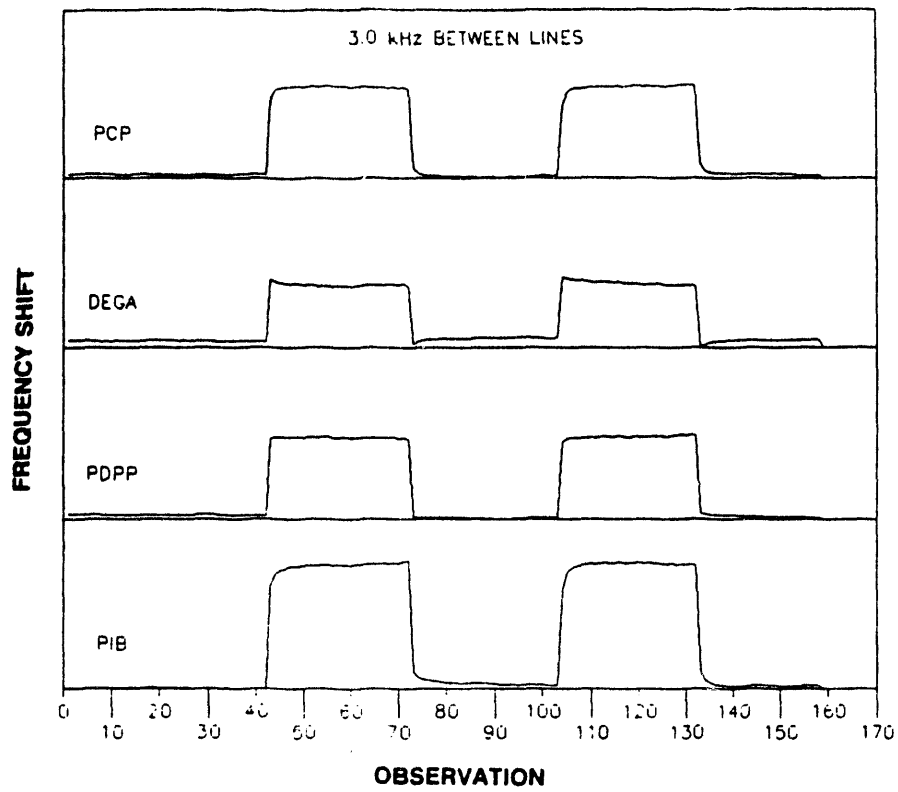
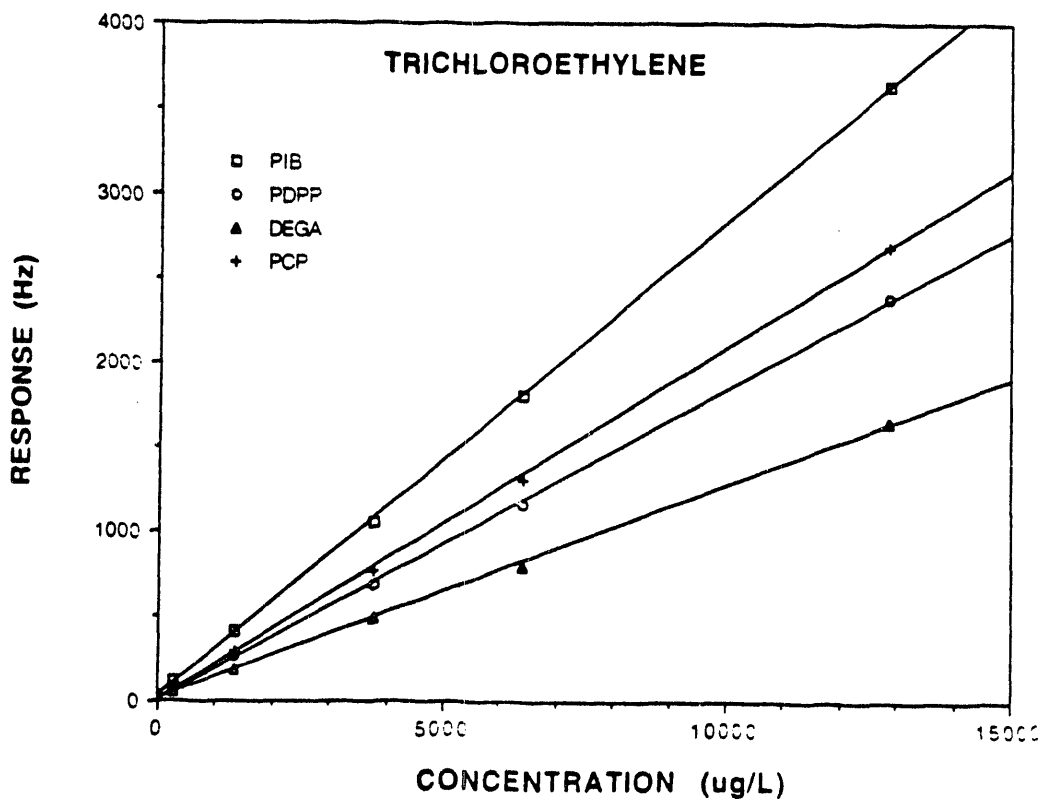


Fig. 6. Plot of SAW sensor responses to 300 to 13,000 $\mu\text{g/L}$ of TCE vapor.



PARAMETER	COATING											
	PECH	PDP	OV 225	DECA	OV275	OV25	PIB	PCP	ABC	PIIOEA	TCEP	PIIA
CHLOROFORM												
Sensitivity (Hz/μg/L)	0.0883	0.0548	0.0213	0.121	0.0878	0.106	0.0684	0.0618	0.194	0.0437	0.199	0.177
Standard Error	0.000592	0.000653	0.000279	0.000649	0.001216	0.000504	0.000781	0.000370	0.000950	0.000799	0.00144	0.000273
R ²	0.998	0.995	0.994	0.999	0.993	0.999	0.995	0.999	0.999	0.985	0.997	1.000
K _s	694	330	102	701	449	547	297	497	986	262	1070	1110
LOD (μg/L)	510	821	1930	371	513	425	658	705	232	1030	226	255
LOD (ppm)	104	168	394	76	105	87	134	144	47	210	46	52
Conc. Range (μg/L)	5700 - 30000	5700 - 30000	5700 - 30000	5700 - 30000	5700 - 30000	5700 - 30000	5700 - 30000	5700 - 30000	5700 - 30000	5700 - 30000	2600 - 26600	2600 - 26600
HEXANE												
Sensitivity (Hz/μg/L)	0.0116	0.0139	0.00451	0.00358	0.00674	0.0400	0.0781	0.0108	0.0163	-0.0124	0.0495	0.0469
Standard Error	0.000174	0.000132	0.000292	0.000287	0.000970	0.000544	0.00103	0.000402	0.000353	0.00161	0.00127	0.000844
R ²	0.984	0.993	0.950	0.908	0.818	0.996	0.996	0.967	0.989	0.728	0.994	0.997
K _s	91	84	20	21	42	210	319	84	83	-74	265	294
LOD (μg/L)	3890	3230	9990	12600	6680	1130	576	4180	2760	3620	909	959
LOD (ppm)	1100	914	2810	3560	1890	319	163	1180	780	1026	257	272
Conc. Range (μg/L)	3401 - 41500	3402 - 41500	3403 - 41500	3404 - 41500	6800 - 21700	6800 - 23700	3400 - 41500	3400 - 41500	3400 - 41500	3400 - 41500	1400 - 18200	1400 - 18200
BENZENE												
Sensitivity (Hz/μg/L)	0.147	0.0946	0.0391	0.0998	0.109	0.213	0.131	0.0798	0.205379	0.016330	0.201222	0.175514
Standard Error	0.00167	0.00271	0.000795	0.000814	0.00114	0.0102	0.00163	0.00164	0.00312	0.000967	0.00400	0.00468
R ²	0.998	0.989	0.994	0.999	0.985	0.965	0.998	0.995	0.997	0.964	0.995	0.991
K _s	1160	570	171	578	561	1080	569	621	1040	98	1080	1100
LOD (μg/L)	306	476	1150	451	413	211	143	564	219	2756	224	256
LOD (ppm)	95	149	360	141	129	66	107	176	68	861	70	80
Conc. Range (μg/L)	2100 - 22700	2100 - 22700	2100 - 22700	2100 - 22700	1800 - 6800	1800 - 6800	2100 - 22700	2100 - 22700	2100 - 22700	2100 - 22700	1500 - 8100	1500 - 8100
TRICHLOROETHYLENE												
Sensitivity (Hz/μg/L)	0.123	0.101	0.0385	0.114	0.0903	0.231	0.186	0.0849	0.206	0.114	0.300	0.261
Standard Error	0.00172	0.001223	0.000953	0.00172	0.00280	0.00403	0.00285	0.00132	0.00293	0.00172	0.00256	0.00262
R ²	0.996	0.997	0.986	0.995	0.982	0.994	0.995	0.995	0.996	0.995	0.999	0.999
K _s	833	397	169	660	451	1200	808	661	1044	683	1604	1637
LOD (μg/L)	365	447	1170	394	498	195	242	530	219	394	150	172
LOD (ppm)	68	83	217	71	92	36	45	98	41	73	28	32
Conc. Range (μg/L)	1400 - 22300	1400 - 22300	1400 - 22300	1400 - 22300	3400 - 12400	3400 - 12400	1400 - 22300	1400 - 22300	1400 - 22300	1400 - 22300	1500 - 18300	1500 - 18300
ISOMTANE												
Sensitivity (Hz/μg/L)	0.02689	0.02259	0.02149	0.0111	0.0120	0.0819	0.193	0.0313	0.0369	0.00970	0.100	0.09218
Standard Error	0.000203	0.000753	0.000346	0.000238	0.00113	0.00133	0.000735	0.000753	0.000306	0.001340	0.00168	0.00108
R ²	0.992	0.882	0.968	0.955	0.928	0.997	0.998	0.913	0.991	0.306	0.998	0.999
K _s	211	136	94	76	47	412	840	244	187	58	537	578
LOD (μg/L)	1680	2000	2100	3440	3750	549	233	1440	1220	4640	440	488
LOD (ppm)	358	427	449	715	801	117	50	307	261	991	103	112
Conc. Range (μg/L)	2700 - 20200	2700 - 20200	2700 - 20200	2700 - 20200	2000 - 14400	2000 - 14400	2700 - 20200	2700 - 20200	2700 - 20200	2700 - 20200	2600 - 10100	2600 - 10100
m-XYLENE												
Sensitivity (Hz/μg/L)	1.01	0.595	0.283	0.576	0.396	1.01	1.35	0.827	1.4225	0.159015	1.515792	1.314023
Standard Error	0.0132	0.0152	0.00627	0.00744	0.0144	0.0297	0.0194	0.0141	0.0155	0.00979	0.00919	0.00659
R ²	0.993	0.977	0.980	0.993	0.996	0.988	0.993	0.990	0.996	0.869	0.999	1.000
K _s	7900	3590	1240	3340	2020	7290	5860	6440	7210	952	8110	8240
LOD (μg/L)	45	76	159	78	114	45	33	54	32	283	30	34
LOD (ppm)	10	17	37	18	26	10	8	12	7	65	7	8
Conc. Range (μg/L)	1600 - 8400	1600 - 8400	1600 - 8400	1600 - 8400	400 - 3300	401 - 3300	1600 - 8400	1600 - 8400	1600 - 8400	1600 - 8400	400 - 1700	400 - 1700

Table 2. Sensitivities, K values, and detection limits for all coatings.

3.3 Coating Selection

As discussed earlier, coated-SAW sensors allow a degree of selectivity that can be exploited using pattern recognition methods that identify and quantify vapors present. The identification and quantification problem increases in difficulty as concentration spans increase; as the possibility of more compounds increases; as exposures move from pure compounds to binary, tertiary, and more complex mixtures; as sensor noise, nonlinearity and compound-compound interactions increase; and if unknown compounds may be encountered. Restrictions on the general pattern recognition problem can improve the ability to identify and quantify unknowns. For example, a four sensor array can not identify more than four compounds simultaneously because the problem is underdetermined mathematically. However, if only individual compounds or binary mixtures are present, the four sensor array may be able to correctly identify and quantify compounds from a large set of possible compounds. Restricting the number of compounds that can be present simultaneously is justified in many applications. In contamination of soil and groundwater, for example, a number of small sets of organic vapors that are frequently observed have been identified from a universe of about 20 compounds (DOE, 1992).

3.3.1 Selection Factors and Criteria

Coatings can be selected using a number of criteria: (1) Coatings must be stable, e.g., resistant to changes over time due to aging, reaction with the gas stream, etc. (2) The LOD achieved with the coating must be acceptable. (3) The sensor output (e.g., frequency shift) must be linear or nearly so with concentration. Transformations made to obtain linear forms can be used, but may be problematic for mixtures. (4) The coatings must maximize selectivity, that is, the ability to discriminate among different compounds. (5) To reduce costs, the smallest number of sensors (coatings) should be employed. (6) The largest number of compounds should be discriminated. (7) Overall results obtained should be robust, that is, not highly influenced by sensor noise and minor miscalibration. These multiple criteria suggest that trade-offs will occur, i.e., no single set of coatings will provide the optimal performance with respect to all goals. For example, selectivity may be achieved at the expense of sensitivity.

Collinearity. To correctly identify compounds, microsensor array responses to each target compound must be unique, i.e., the vector containing frequency shifts for various coatings at a specific concentrations must be linearly independent of the vectors obtained for all other compounds. Collinearity may be caused by pairwise dependencies that involve two compounds. For example, compound A may produce the same response pattern as compound B (at the same or different concentrations). This situation is easily detected by high correlation coefficients between response vectors for the two compounds. Three or more compounds also can cause dependencies that are harder to detect. For example, sensors 1 and 2 may respond to compound A, and sensor 3 to compound B. Compound C may elicit a response in sensors 1, 2 and 3. In this case, while the response for each compound differs, the mixture of three compounds may be difficult to resolve: sensor responses may indicate compound C, compounds A and B, or some combination of the 3 compounds. This situation may escape detection by pairwise measures of dependencies, e.g., correlation coefficients would not indicate an unusual degree of collinearity.

3.3.2 Cluster and K-means Analysis

Several different clustering methods were used as a first approach to coating selection. These methods used a 10x6 data matrix consisting of the sensor sensitivities for all coating/vapor combinations in the screening set. In the matrix, rows (groups) represented sensor coatings, and columns represented vapors.

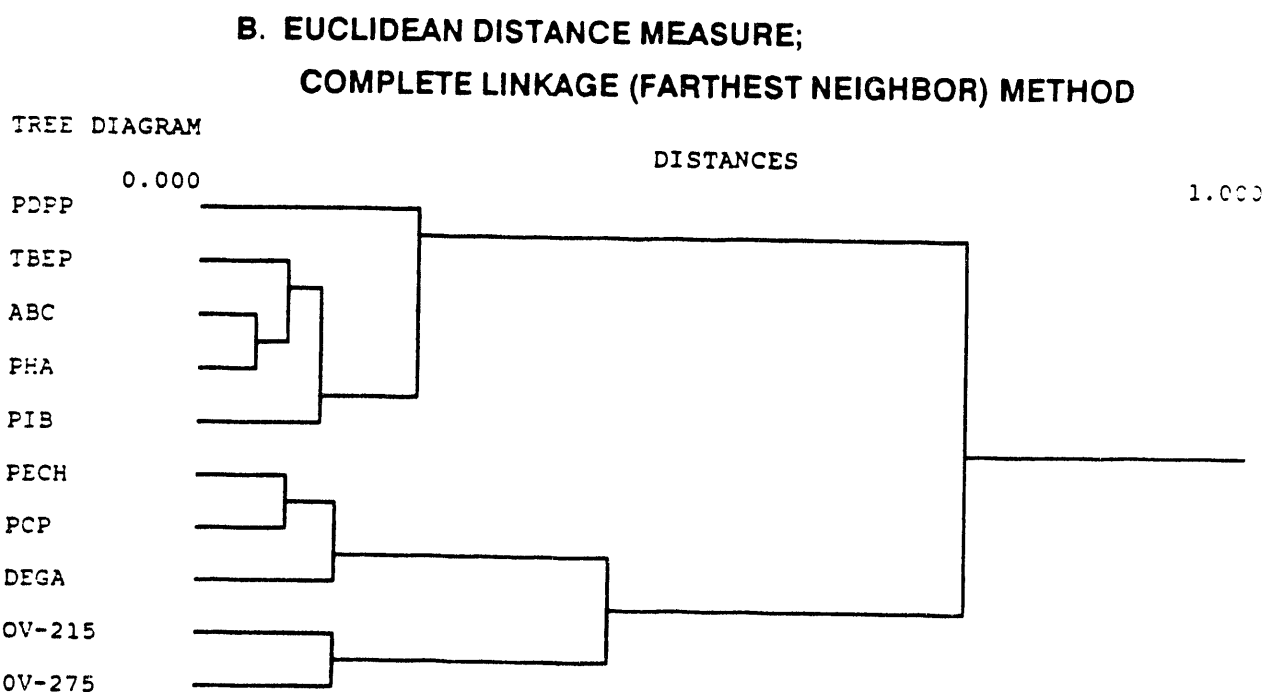
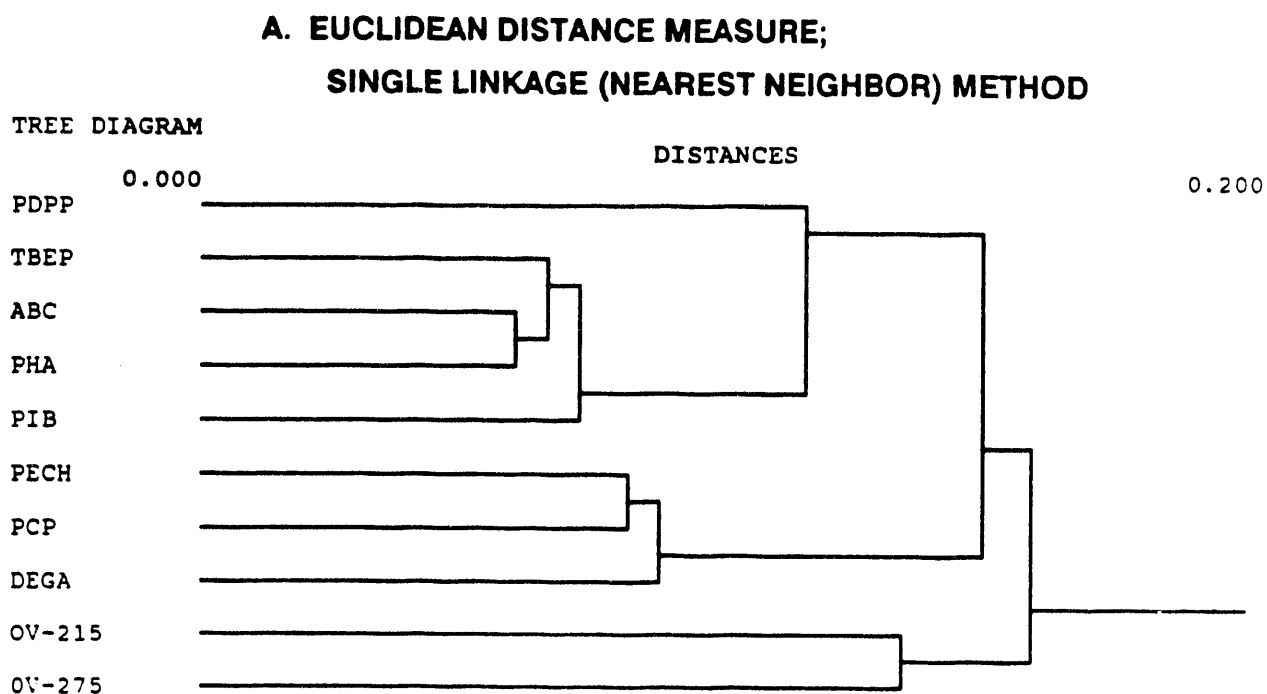
Figs. 7a and b show results from two hierarchical cluster analyses where different metrics were used to assign clusters. The dendrograms group the coatings according to their similarity in response patterns to the six vapors: those connected at a lower point (from the left) are more similar. The choice of which four coatings to include in the final optimal array is equivocal. From Figure 7a, coatings would be chosen from the following four groups: (1) PIB, ABC, TBEP, PHA; (2) DECH, DEGA, PCP; (3) OV-215, OV275; and (4) PDPP. This provides 24 different choices. Groupings in Fig. 7b, which used a different clustering criterion, are somewhat different and thus would provide yet more choices.

The K-means procedure is an alternative to cluster analysis that also provides groupings of similar coatings. Used iteratively, it can obtain groups that satisfy a criterion such as minimum within group variance. This procedure was performed for the screening data set using four groups and a large iteration limit (100). These results are identical to splitting the cluster analysis dendrogram using Euclidian distance and the complete linkage method (Fig. 7b). Again, the final selection of coatings is equivocal.

An assumption implicit in the cluster and K-means analyses is that all coatings within an identified group perform equally well. This assumption, however, has not been tested. In addition, these analyses do not indicate the performance of the various coating sets, such as the identification success rate, the vapors that would be misclassified, and the performance obtained when vapor mixtures are present. Some qualitative insight can be obtained using PCA, but many of these issues would remain unanswered.

In summary, clustering and K-means analyses provide groupings that are equivocal in that many different selections are possible. Groupings depend on the proximity and distance measures used, and little guidance can be given *a priori* concerning the best measures. No quantitative information regarding the success rate of vapor identification is obtained. Finally, results from cluster and K-means analyses do not necessarily ensure that the optimal coating set will be found. Indeed, some differences are found when compared to exhaustive simulation studies using EDPCR, as discussed below.

Fig. 7. Two dendrograms from cluster analysis showing coating classification.



3.3.3 EDPCR

The preceding results show the need for a more rigorous method to select coatings. To this end, a series of simulations using EDPCR was performed to rank all 210 possible combinations of four coatings in the screening set according to the percentage of correctly classified vapors using response data generated for individual vapors and all binary mixtures. The synthetic responses were generated using the error model, Eq. (4), and two levels of random noise (k_3 in Eq. 4).

Table 3 shows results of the numerical analysis for the top 40 coating sets. Not surprisingly, many different combinations provide similar performance: the top 20 coating sets have classification rates from 93 to 95%. Also, the error model affects the classification success rate, and thus the coating set rankings. Coating sets near the middle and bottom of the rankings (omitted from Table 3) had significantly lower classification success rates. The lowest ranked coatings (rankings 200 to 210) had classification success rates from 67 to 75%. The table helps to illustrate the equivocal nature of results obtained using hierarchical clustering and K-means procedures.

The PDPP, PIB, DEGA, and PCP coating set ranked first with the low error model (± 15 Hz), and remained in the top five with the higher error model (± 22 Hz). Overall, this set of coatings provided the best results with respect to vapor classification, so it was chosen as the "optimal" set for further analysis. The results indicate that an average of 5% misclassification is expected with this coating set.

3.4 Optimized Sensor Array

After identification of the optimal coating set, existing coatings on the sensor array were dissolved and the new coatings applied. Calibrations were again performed for the six vapors. Table 4 provides statistics for the optimized array, showing sensitivities, K_e , R^2 , and estimated LODs for the six vapors. As before, excellent linearity was achieved, and sensor sensitivities were determined with a high degree of precision (RSD=1%).

Because the coating selection procedure maximized the ability to discriminate among vapors, the response patterns of the optimized array for the six vapors should be quite different. Fig. 8 shows the relative responses (as sensor sensitivities) for each vapor. In most cases, the response patterns or "signatures" among vapors vary. As expected, vapors within chemical classes, e.g. benzene and m-xylene, show more similar response patterns than vapors between classes, e.g. TCE and isooctane. The chlorinated vapors show both qualitative and quantitative differences, suggesting that chloroform and TCE can be easily distinguished. Pairs of the aromatic and aliphatic compounds, however, have similar patterns. In addition, hexane has very low sensitivity and thus the possibility of higher noise levels. These two factors may make separation more problematic for isooctane and hexane.

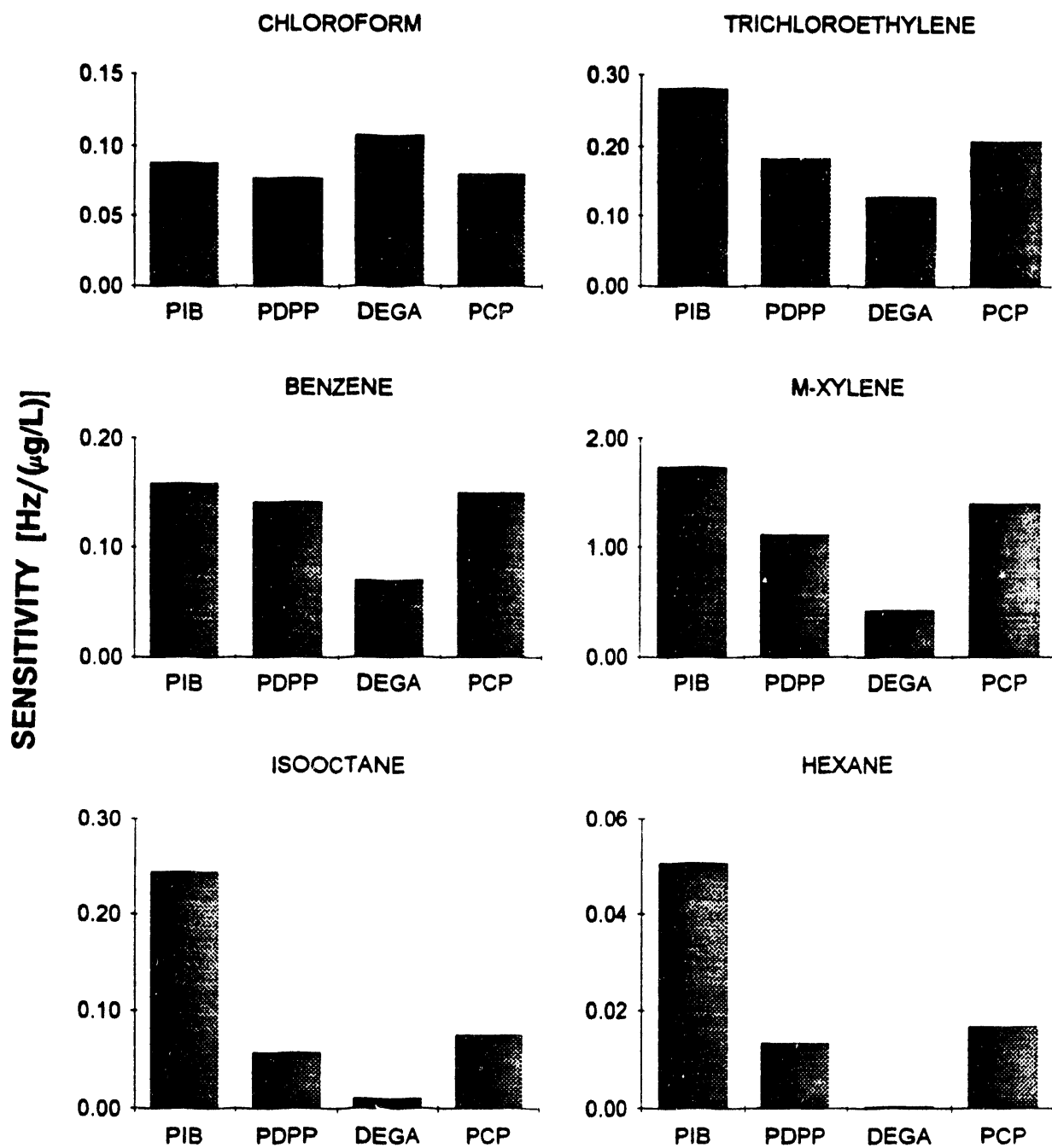
Table 3. Ranking of top 40 coating combinations.

RANKING	COATING SET				CORRECT CLASSIFICATION (%)	STANDARD DEVIATION (%)
1	PDPP	DEGA	PIB	PCP	95.2	3.5
2	PECH	PDPP	DEGA	PIB	94.9	3.9
3	PDPP	DEGA	PIB	OV275	94.7	3.6
4	PECH	OV215	DEGA	PIB	94.7	4.0
5	PDPP	PIB	PHA	OV275	94.6	4.2
6	OV215	DEGA	PIB	OV275	94.5	3.9
7	PDPP	PIB	TBEP	OV275	94.5	3.9
8	OV215	DEGA	PIB	PCP	94.5	4.1
9	PDPP	DEGA	TBEP	OV275	94.2	4.4
10	PDPP	DEGA	PHA	OV275	94.2	3.9
11	PECH	OV215	DEGA	OV275	94.0	4.4
12	PECH	PDPP	TBEP	OV275	94.0	4.3
13	PDPP	DEGA	PCP	TBEP	93.9	4.0
14	PECH	PDPP	DEGA	OV275	93.8	3.8
15	PIB	PCP	PHA	OV275	93.6	4.7
16	PECH	PDPP	PHA	OV275	93.6	4.2
17	PDPP	DEGA	PIB	ABC	93.5	3.9
18	PDPP	PCP	TBEP	OV275	93.4	4.0
19	PECH	DEGA	PIB	PCP	93.4	4.7
20	PDPP	OV215	DEGA	OV275	93.3	4.7
21	PDPP	PIB	PCP	TBEP	93.3	4.5
22	PDPP	DEGA	PCP	PHA	93.3	3.6
23	PECH	PDPP	PIB	OV275	93.2	4.2
24	OV215	DEGA	PCP	OV275	93.0	4.2
25	PDPP	PIB	ABC	OV275	93.0	4.3
26	PDPP	PIB	PCP	PHA	93.0	4.6
27	PECH	OV215	DEGA	TBEP	92.9	4.3
28	PECH	DEGA	PCP	TBEP	92.9	4.0
29	PDPP	PCP	PHA	OV275	92.9	3.8
30	PECH	DEGA	PCP	PHA	92.8	4.3
31	PECH	OV215	DEGA	PCP	92.7	4.2
32	OV215	DEGA	PIB	ABC	92.7	4.7
33	PECH	PDPP	PIB	PHA	92.6	4.1
34	PDPP	ABC	TBEP	OV275	92.5	4.3
35	PECH	PDPP	DEGA	PHA	92.4	4.4
36	PDPP	DEGA	PCP	OV275	92.3	4.9
37	PECH	PIB	PHA	OV275	92.2	4.7
38	DEGA	PIB	PCP	OV275	92.1	4.7
39	OV215	PIB	PCP	OV275	92.0	4.5
40	PDPP	OV215	TBEP	OV275	92.0	5.0

Table 4. Sensitivities, K values, and detection limits for optimized coating set.

VAPOR	COATING	PIB	PDPP	DEGA	PCP
	ΔF_c (kHz)	185	199	275	198
CHLOROFORM	Sensitivity (Hz/($\mu\text{g/L}$))	0.0883	0.0773	0.108	0.0803
	Standard Error	0.00085	0.00037	0.00066	0.00032
	R ²	0.999	1.000	1.000	1.000
	K _c	440	466	454	499
	LOD ($\mu\text{g/L}$)	509	582	418	560
	LOD (ppm)	104	119	86	115
	Conc. Range ($\mu\text{g/L}$)	300 - 21000			
HEXANE	Sensitivity (Hz/($\mu\text{g/L}$))	0.0506	0.0133	0.0004	0.0166
	Standard Error	0.00041	0.00013	0.00014	0.00027
	R ²	0.999	0.999	0.903	0.999
	K _c	252	80	2	103
	LOD ($\mu\text{g/L}$)	889	3370	108000	2710
	LOD (ppm)	252	955	30627	766
	Conc. Range ($\mu\text{g/L}$)	3800 - 54000			
BENZENE	Sensitivity (Hz/($\mu\text{g/L}$))	0.159	0.142	0.0695	0.150
	Standard Error	0.00296	0.00262	0.00117	0.00300
	R ²	0.996	0.996	0.997	0.995
	K _c	790	854	294	931
	LOD ($\mu\text{g/L}$)	264	318	647	300
	LOD (ppm)	89	99	202	94
	Conc. Range ($\mu\text{g/L}$)	500 - 20000			
TRICHLOROETHYLENE	Sensitivity (Hz/($\mu\text{g/L}$))	0.281	0.183	0.127	0.207
	Standard Error	0.00157	0.00072	0.00113	0.00113
	R ²	0.999	1.000	0.998	0.999
	K _c	1400	1110	537	1290
	LOD ($\mu\text{g/L}$)	160	246	354	217
	LOD (ppm)	30	46	66	40
	Conc. Range ($\mu\text{g/L}$)	300 - 13000			
ISOOCTANE	Sensitivity (Hz/($\mu\text{g/L}$))	0.244	0.0571	0.0100	0.0750
	Standard Error	0.00108	0.00066	0.00045	0.00065
	R ²	1.000	0.999	0.974	0.999
	K _c	1210	344	42	466
	LOD ($\mu\text{g/L}$)	185	789	4490	600
	LOD (ppm)	39	168	959	128
	Conc. Range ($\mu\text{g/L}$)	1200 - 15000			
m-XYLENE	Sensitivity (Hz/($\mu\text{g/L}$))	1.74	1.11	0.424	1.40
	Standard Error	0.01327	0.00795	0.00409	0.00907
	R ²	0.999	1.000	0.999	1.000
	K _c	8670	6710	1790	8670
	LOD ($\mu\text{g/L}$)	26	40	106	32
	LOD (ppm)	6	9	24	7
	Conc. Range ($\mu\text{g/L}$)	50 - 1700			

Fig. 8. Optimized sensor array response patterns for six VOCs.



3.5 Additivity of Sensor Responses

An important assumption in EDPCR and other pattern recognition methods that interpret sensor responses is additivity, meaning that vapor mixtures give a sensor response that is the sum of responses obtained individually from each vapor. Although Rose-Pehrson et al. (1988) report results of binary mixture exposures and claimed additivity of responses in most cases, they also indicated some exceptions. Unfortunately, data were not provided in their report and could not be critically assessed. As mixtures are present in many or most environmental applications, additivity is a critical assumption.

Experiments were performed to evaluate the assumption of additivity using seven binary mixtures of four vapors, namely, benzene + isooctane, benzene + xylene, benzene + chloroform, chloroform + TCE, TCE + isooctane, isooctane + hexane, and isooctane + TCE. Thus, both within and between class combinations were tested. For each mixture, the optimized sensor array was exposed to between seven and 18 different test atmospheres covering all conditions of relative concentration (i.e., high-high, high-low, low-high, low-low, etc.). A total of 62 mixture exposures were performed. The operating temperature for these experiments was 25°C and dry N₂ was used as the diluent stream.

With few exceptions, additivity of sensor responses was found, as demonstrated by several methods, including:

1. Comparison of predicted sensor response based on pure vapor calibrations, to the actual response measured during vapor mixture exposures. Differences between measured and predicted shifts were typically below 10%. Occasionally, larger errors occurred at lower concentrations or where sensor responses were small, owing largely to signal-to-noise problems.
2. Multiple linear regression of vapor concentrations onto sensor responses to obtain sensor sensitivity [(Hz)/(μg/L)]. Here, sensor responses (in Hz) were regressed against the vapor concentrations (in μg/L) for each binary vapor mixture. Several sensitivities may result if several vapor combinations are tested using the same solvent and the same sensor coating. For example, PIB was tested with three mixtures (benzene + TCE, benzene + chloroform, and benzene + isooctane), resulting in three sensitivity factors for benzene with PIB.

Table 5 shows these results and compares them to the pure vapor sensitivities. The R² values for binary mixture regressions typically exceeded 0.98, supporting the additivity (and linearity) assumptions.

3. Multiple linear regression using a global data base consisting of all mixture experiments. Like Method 2 above, sensor responses were regressed against the vapor concentrations. In this case, however, all binary mixture data were used together in the regression. If a vapor was not present in a particular test, its concentration was assigned to be zero.

Table 5. Sensitivities for pure and mixture data for optimized coating set.

VAPOR	TEST	PIB		FDPP		DEGA		PCP	
		Slope	Std.Dev.	Slope	Std.Dev.	Slope	Std.Dev.	Slope	Std.Dev.
BENZENE	PURE	0.1586	0.0030	0.1416	0.0026	0.0695	0.0012	0.1499	0.0030
	ALL MIXTURES	0.1673	0.0020	0.1482	0.0013	0.0749	0.0015	0.1569	0.0016
	BEN ISO	0.1713	0.0056	0.1454	0.0010	0.0699	0.0020	0.1524	0.0015
	BEN m-XYL	0.1580	0.0018	0.1424	0.0022	0.0672	0.0013	0.1496	0.0022
	BEN CHL	0.1729	0.0015	0.1530	0.0018	0.0799	0.0028	0.1626	0.0019
	MEAN	0.1656		0.1461		0.0723		0.1543	
	RSD (%)	3.7694		2.8358		6.3048		3.1861	
CHLOROFORM	PURE	0.0883	0.0009	0.0773	0.0004	0.1076	0.0007	0.0803	0.0003
	ALL MIXTURES	0.0916	0.0011	0.0804	0.0007	0.1153	0.0008	0.0844	0.0009
	CHL BEN	0.0913	0.0009	0.0798	0.0011	0.1171	0.0017	0.0851	0.0012
	CHL TCE	0.0933	0.0013	0.0817	0.0013	0.1147	0.0014	0.0855	0.0013
	MEAN	0.0911		0.0798		0.1137		0.0838	
	RSD (%)	1.9521		2.0196		3.1964		2.4626	
TRICHLORO-ETHYLENE	PURE	0.2814	0.0016	0.1832	0.0007	0.1271	0.0011	0.2072	0.0011
	ALL MIXTURES	0.2698	0.0044	0.1762	0.0030	0.1169	0.0034	0.1970	0.0036
	TCE CHL	0.2597	0.0052	0.1669	0.0053	0.1107	0.0056	0.1874	0.0054
	TCE ISO	0.2814	0.0000	0.1832	0.0000	0.1271	0.0000	0.2072	0.0000
	MEAN	0.2731		0.1774		0.1204		0.1997	
	RSD (%)	3.3113		3.7847		5.8233		4.1232	
ISOOCTANE	PURE	0.2435	0.0011	0.0571	0.0007	0.0100	0.0005	0.0750	0.0007
	ALL MIXTURES	0.2382	0.0031	0.0575	0.0021	0.0112	0.0024	0.0734	0.0025
	ISO BEN	0.2279	0.0045	0.0528	0.0008	0.0075	0.0016	0.0673	0.0012
	ISO HEX	0.2338	0.0049	0.0551	0.0012	0.0087	0.0007	0.0689	0.0017
	ISO TCE	0.2435	0.0000	0.0571	0.0000	0.0100	0.0000	0.0750	0.0000
	MEAN	0.2374		0.0559		0.0095		0.0719	
	RSD (%)	2.5165		3.1531		13.4369		4.4518	
m-XYLENE	PURE	1.7415	0.0133	1.1122	0.0079	0.4244	0.0041	1.3970	0.0091
	ALL MIXTURES	1.8338	0.0336	1.1821	0.0229	0.4333	0.0256	1.5105	0.0277
	m-XYL BEN	1.9201	0.0214	1.2471	0.0253	0.4949	0.0146	1.5810	0.0257
	MEAN	1.8318		1.1805		0.4509		1.4962	
	RSD (%)	3.9792		4.6671		6.9547		5.0666	
HEXANE	PURE	0.0506	0.0004	0.0133	0.0001	0.0004	0.0001	0.0166	0.0003
	ALL MIXTURES	0.0504	0.0011	0.0140	0.0007	0.0005	0.0008	0.0164	0.0009
	HEX ISO	0.0508	0.0014	0.0138	0.0003	0.0006	0.0002	0.0166	0.0005
	MEAN	0.0506		0.0137		0.0005		0.0165	
	RSD (%)	0.3425		1.9670		14.2546		0.5976	

This method is similar to training procedures used in partial least-squares fitting and estimation. It has several advantages. First, it obtains the six sensitivities of one sensor to all vapors in one regression, and thus is simple and fast. Second, it increases the degrees-of-freedom available, thus uncertainties associated with estimated sensitivities may be decreased. Third, the procedure combines results from the different tests. Here, it was used to combine results from various binary mixtures, however, it also could be used to consolidate results from calibrations using individual vapors, as well as binary, tertiary, or more complex mixtures. Finally, it permits calibrations when mixtures can not be generated, or would not be relevant.

Table 5 shows the results using this method and compares them to the individual vapor sensitivities. Again, R^2 values generally exceeded 0.98 and the coating-vapor sensitivities closely match those determined using individual calibrations.

4. Application of fitting algorithms that assume linearity and additivity, such as EDPCR, to identify and quantify vapor mixtures. In this case, a high correct classification rate and high accuracy in quantification shows the validity of the assumptions. This analysis is described below (Section 3.7.1).

The average sensitivity and relative standard deviation (RSD) among sensitivities obtained using Methods 2 and 3 above are listed in Table 5. The RSDs for most coating-solvent pairs are below 5%, which is comparable to the analytical precision of the experiments. Results for the DEGA coating with benzene, isooctane, m-xylene, and hexane, show greater variability largely due to the relative insensitivity of this coating to these vapors. By any measure, these data support the assumptions of linearity and additivity of responses.

3.6 Sensor Stability and Response to Environmental Variables

3.6.1 Temperature

Temperature can affect the sensor performance in two ways. First, a shift in temperature alters the baseline frequency of each sensor due, in part, to the thermal expansion of the quartz substrate: the oscillation frequency generally decreases with increasing temperature. Use of an uncoated reference sensor and collection of the difference frequency can reduce temperature-dependent baseline drift, however, coated and uncoated sensors will generally vary slightly in their temperature responses. Second, temperature changes vapor sorption equilibria. A negative Arrhenius temperature dependence is generally observed for vapors partitioning into organic polymers (Zellers et al., 1990; Brace, et al., 1986; Grate et al., 1992), and is found here, as discussed below.

With respect to baseline frequency drift, the need for thermostating the sensors depends on the temperature stability of the monitored environment. Measurement of baseline frequency as a function of temperature from 15-40 °C gave average temperature coefficients of 680, 130, 70 and 235 Hz/°C for the PIB, PDPP, DEGA, and PCP coated sensors, respectively. If the environmental temperature is reasonably stable it may not be necessary to control the temperature of the sensor, but merely to monitor it, since exposure measurements can be collected over a relatively short period of time.

The effect of temperature on vapor-coating sensitivity was experimentally measured for benzene, isooctane and TCE using the optimal coating set. Multipoint calibrations were performed at 15, 25, 30 and 40 °C for each vapor. Calibration curves were linear in all cases. The sensitivities decreased and LODs increased with increasing temperature, as shown in Table 6. Arrhenius plots of Table 6 data were linear ($R^2 > 0.99$), with slopes ranging from 2.4 to 2.9 for benzene and isooctane on the four coatings, and from 3.2 to 3.6 for TCE (Figure 9).

Table 6. Temperature response of sensors.

VAPOR	TEMPERATURE (°C)		COATING				
			PIB	PDPP	DEGA	PCP	
ISOOCTANE	15	Sensitivity (Hz/(µg/L))	0.313	0.0779	0.0177	0.101	
		LOD (µg/L)	144	578	2540	445	
	25	Sensitivity (Hz/(µg/L))	0.257	0.0566	0.0055	0.0775	
		LOD (µg/L)	175	796	8180	581	
	30	Sensitivity (Hz/(µg/L))	0.216	0.0478	0.0029	0.0650	
		LOD (µg/L)	208	941	15400	692	
	40	Sensitivity (Hz/(µg/L))	0.162	0.0351	0.0049	0.0511	
		LOD (µg/L)	278	1280	9210	881	
	TRICHLOROETHYLENE	15	Sensitivity (Hz/(µg/L))	0.391	0.257	0.200	0.308
			LOD (µg/L)	115	175	225	146
		25	Sensitivity (Hz/(µg/L))	0.283	0.175	0.131	0.216
			LOD (µg/L)	159	257	345	209
30		Sensitivity (Hz/(µg/L))	0.223	0.136	0.102	0.173	
		LOD (µg/L)	202	331	443	261	
40		Sensitivity (Hz/(µg/L))	0.165	0.100	0.0755	0.129	
		LOD (µg/L)	273	450	596	350	
BENZENE		15	Sensitivity (Hz/(µg/L))	0.225	0.202	0.123	0.228
			LOD (µg/L)	200	223	367	198
		25	Sensitivity (Hz/(µg/L))	0.180	0.149	0.0837	0.176
			LOD (µg/L)	250	302	538	256
	30	Sensitivity (Hz/(µg/L))	0.155	0.128	0.0745	0.153	
		LOD (µg/L)	291	351	604	293	
	40	Sensitivity (Hz/(µg/L))	0.113	0.0955	0.0533	0.115	
		LOD (µg/L)	398	471	844	393	

The slope of the Arrhenius plot is proportional, for a given coating, to the molar heat of vapor sorption. Differences in slopes listed in Table 7 suggest that certain vapors might be discriminated from one another on this basis. For example, two identically coated sensors operating at two different temperatures would provide response ratios that are vapor-specific. From Table 7, this would be sufficient to differentiate TCE from either benzene or isooctane, regardless of the coating considered. The slopes for benzene and isooctane are not significantly different, and these vapors could not be differentiated using this approach. Still, the use of sensors operated at different temperatures represents an interesting possibility for enhancing the capabilities of sensor arrays. Higher temperatures decrease sensitivity, and thus may limit the applications of this approach. Water vapor condensation problems may preclude the use of lower temperatures unless the vapor is dried, e.g. using a selectively permeable membrane.

The importance of temperature on the sensor performance is evident from the results presented. Although only temperature monitoring may suffice in certain cases, most applications will require precise temperature control. As discussed in the next section, thermostating can also decrease the high relative humidity found in field applications that may interfere with sensor responses. Given the small volume occupied by the array, the use of low-power Peltier-type temperature controllers are feasible for field applications.

3.6.2 *Relative Humidity*

Sorption and desorption of water vapor by the sensor coatings will cause frequency shifts similar to those for the target vapors considered here. Additionally, the amount of water vapor in the coating at a given humidity level may affect the response to other vapors. Although several reports have examined the former issue (Brace et al., 1988; Lee et al., 1982; Randin and Zullig, 1987), the latter has not received much attention. In one recent report, the response to butanol was influenced strongly by humidity with both highly polar and non-polar coatings (Patrash and Zellers, 1993). Therefore, several tests of relative humidity (RH) effects were performed.

Sensor responses to atmospheric humidity changes were determined by exposing the array alternately to dry N_2 and to air at RHs ranging from 20 to 85%. Responses were rapid and reversible in all cases. Fig. 10 shows measured frequency shifts versus RH for the four coatings. Responses for PIB, PDPP and PCP were similar and small. In contrast, DEGA showed considerable water sensitivity, an anticipated effect since water has a greater affinity for more polar coatings. Even PIB, which is a non-polar aliphatic hydrocarbon, still sorbs some water vapor.

Fig. 9. Arrhenius temperature response plots.

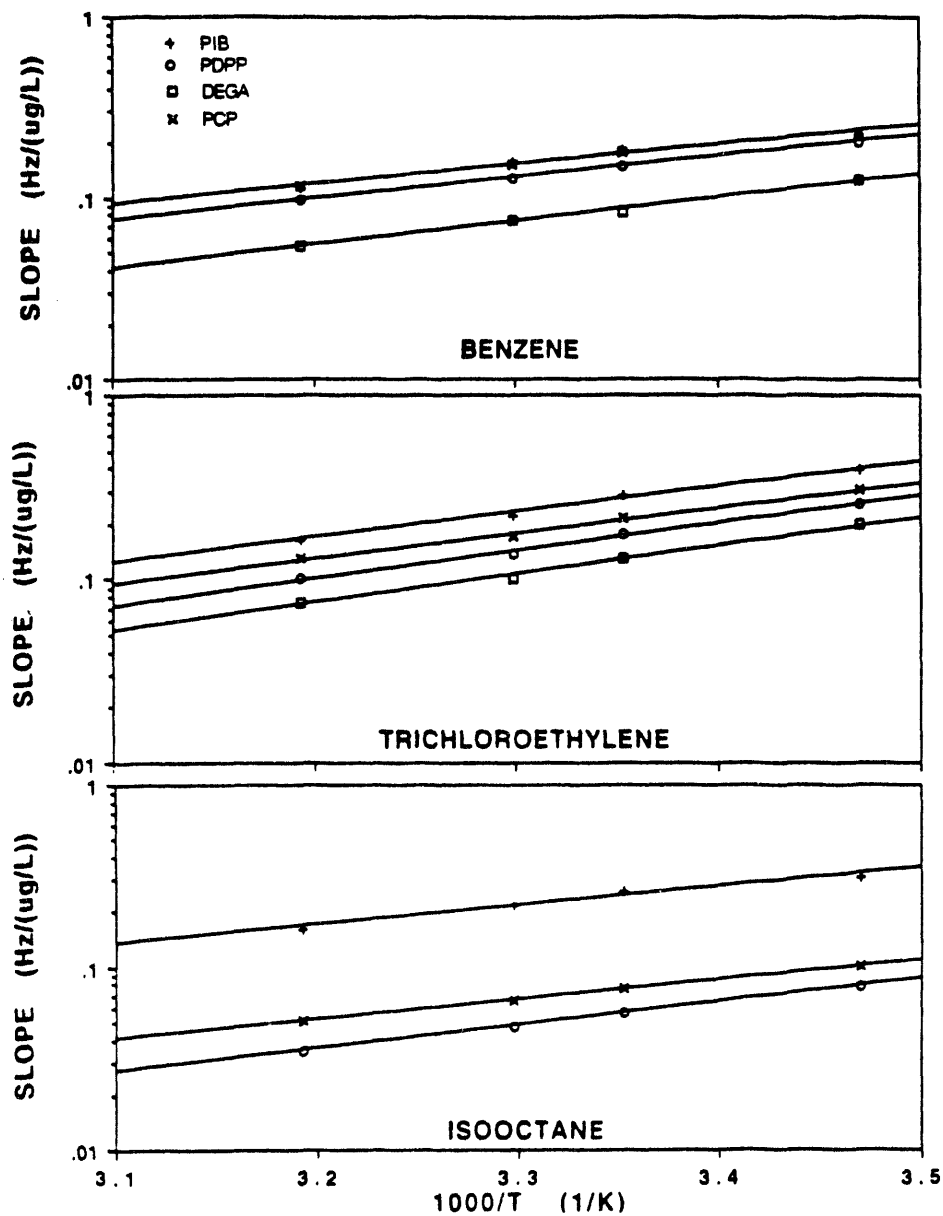
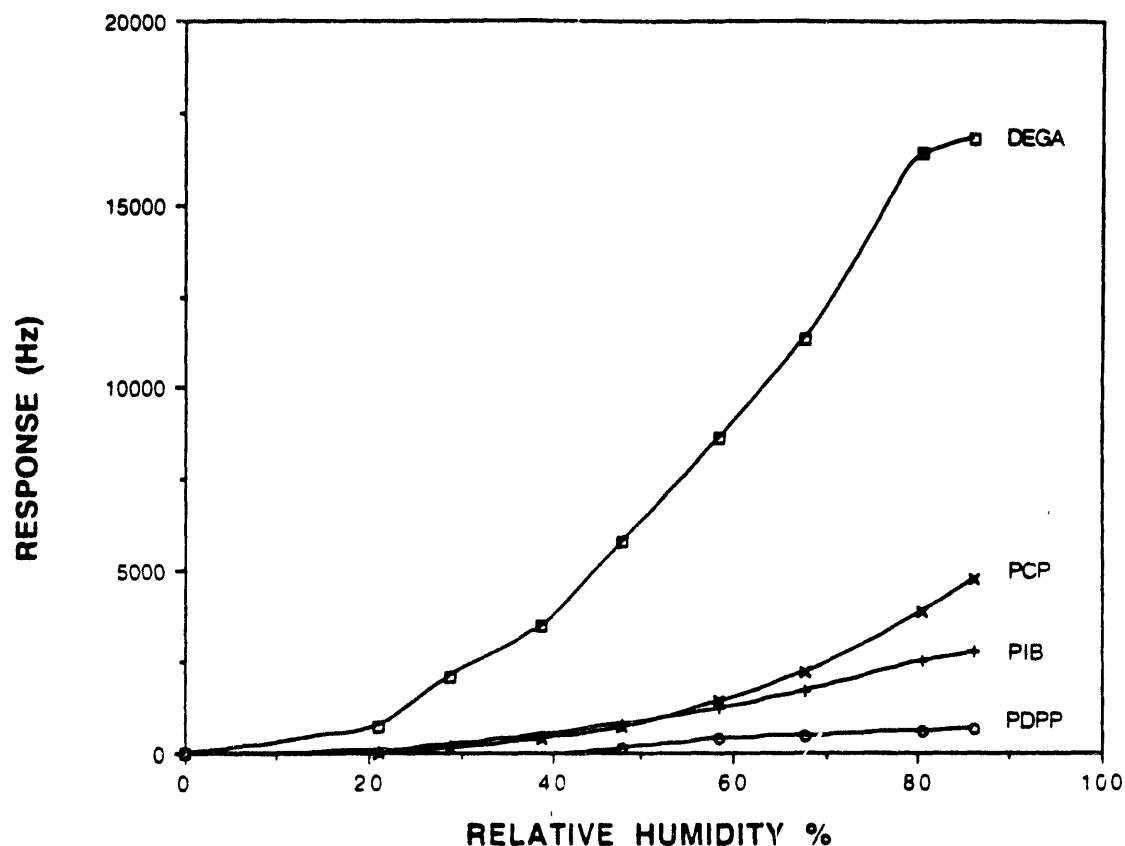


Table 7. Slopes of Arrhenius plots.

VAPOR	SLOPE			
	PIB	PDPP	DEGA	PCP
BENZENE	2480	2700	2980	2470
ISOCTANE	2400	2880	ND	2500
TRICHLOROETHYLENE	3160	3450	3560	3190

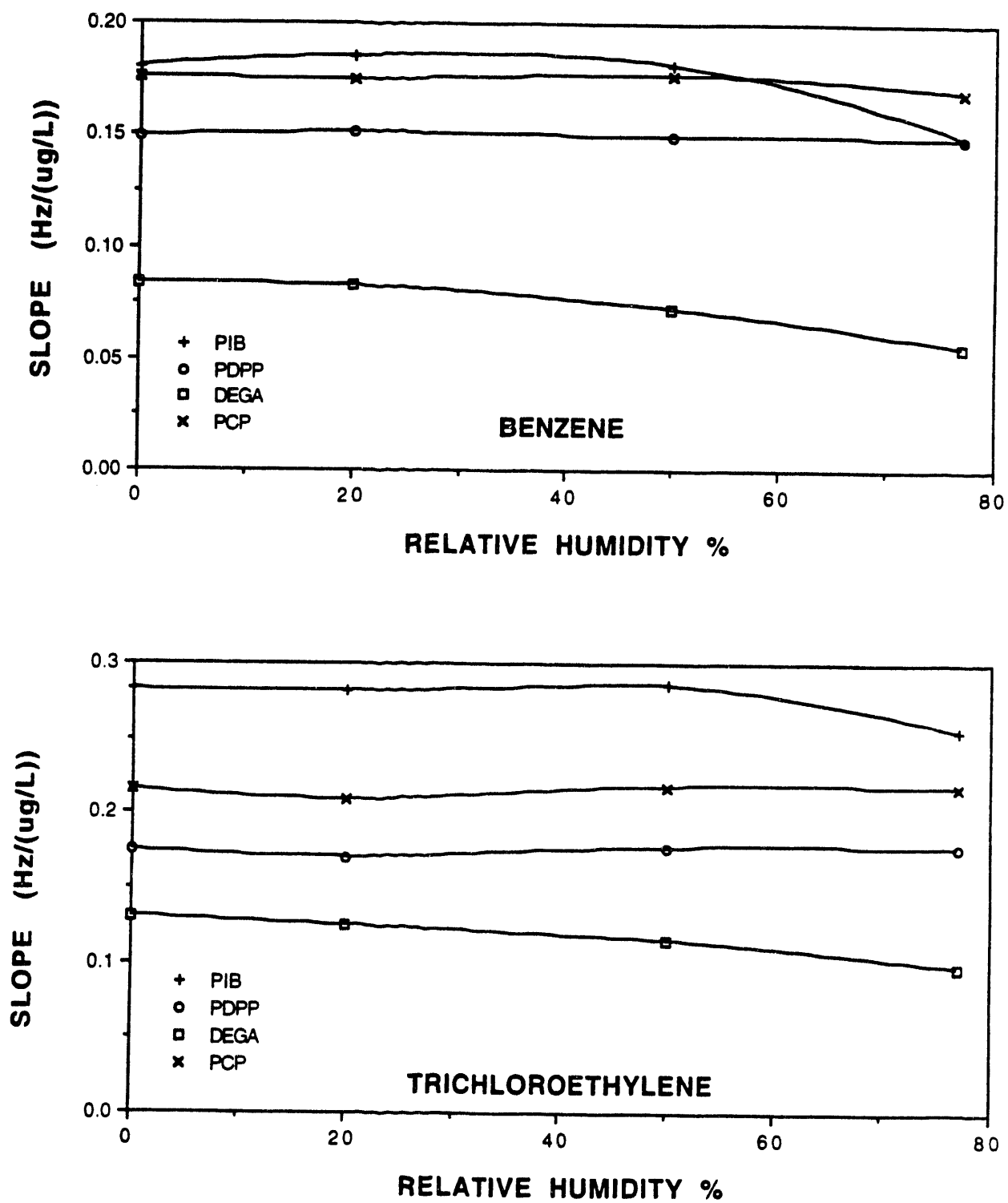
Fig. 10. Sensor responses to water vapor from 0-85% RH.



Effects of water vapor on sensor responses to benzene and trichloroethylene were tested by comparing sensitivities in dry N_2 to those at 20, 50 and 77% RH over a range of vapor concentrations. In the case of the DEGA-coated sensor, a steady decline in response with increasing humidity was observed: the sensitivity decreased by 26% and 34% for TCE and benzene, respectively, over the RH range examined. For the PIB-coated sensor, there was no effect at lower RH levels, but a 10-20% decline in response was observed for these vapors between 50 and 77% RH. Neither the PDPP nor PCP coated sensors were affected by RH.

The decreased responses under highly humid conditions for the PIB coated sensor is most likely due to competition between water and the test vapors for polar sorption sites at the surface of the underlying quartz substrate. A similar explanation was given by Grate et al. (1992) to account for variations in the responses of coated SAW devices whose substrates had been cleaned by different methods.

Fig. 11. Sensitivities as a function of relative humidity.



For the polar DEGA coating, the amount of water vapor present in the coating increases significantly with increasing RH. In this case, interfacial adsorption at the substrate probably contributes relatively little to the overall response. The observed decrease in the vapor responses is consistent with a gradual increase in the net polarity of the water-laden polymer film. As the coating becomes more polar, the affinity for the moderately polar benzene and TCE becomes progressively lower. The water might also reduce any interchain interactions within the polymer, thereby rendering the polar ester groups in the DEGA more available to interact with the vapors. For the moderately polar PDPP and PCP, any effects of water vapor on the substrate or the coating would tend to offset one another.

The implications of these findings for practical sensor array applications will depend on the application. Where humidity levels are relatively constant, baseline drifts will be small, with the possible exception of the DEGA (and probably other highly polar coatings). Effects of RH on vapor responses might be addressed via calibration coupled with RH measurements using the sensor array itself or other inexpensive sensors. Alternatively, the sensor array operating temperature could be adjusted for the purpose of humidity control. For example, soil gas at 100% RH and 15 °C contains 21 mg/L of water; heating the airflow to 26.2 °C decreases the RH to 50%. In ambient applications at 25 °C and 100% RH (e.g. drum sampling), heating the airflow to 37.1 °C again decreases the RH to 50%. Temperature increases of 11 or 12 °C (and thermostating) are easily accomplished via resistance heating or Peltier devices. Thermostating should encompass the sensors and precondition the incoming gas stream.

In summary, this limited examination of the effects of relative humidity on coated sensor responses to VOCs shows that sorbed water vapor can have a significant effect on responses obtained using relatively polar sensor coatings (e.g., DEGA). For the vapors examined here a decrease in response was observed with increasing RH. For more polar vapors, such as alcohols, the effect may be reversed. Decreases in response were also observed for the highly non-polar PIB coating at high RH levels. In contrast, vapor responses for sensors with moderately polar coatings appear to be independent of RH changes. For high-humidity field applications, this factor would be either controlled via thermostating, or accounted for during initial sensor calibration and incorporated into the pattern recognition analysis.

3.6.3 Coating Stability

During the course of initial screening experiments, five coatings were eliminated from further consideration based on coating instability (PPE, ETSA, OV-25), poor response to most vapors (PMMA), and extreme water sensitivity (PHOEA). The sensitivity of OV-25 to xylene increased by 25% over the first two weeks of exposure and then remained relatively stable. For PPE, the sensitivity decreased by about 10% over the first two weeks and appeared to stabilize, but then showed a further decline over the remaining weeks of the trial period: the final value was 46% of the initial value.

For the remaining 10 coatings, repeated exposure to benzene or xylene over the course of 2-3 months (typical of the time period associated with a set of exposure experiments) indicated that the sensitivities remained quite constant, with relative standard deviations below 10% and no discernible systematic drifts over time. PCP showed a slightly higher level of variability (14%). These data are shown in Table 8.

Intercoating reproducibility was not examined in detail for most coatings -- in most cases, tests were limited to duplicate coatings examined at different times during the study. In one case, however, a more detailed investigation was performed by coating all four sensors in the array simultaneously with OV-275 and collecting repeated measurements of xylene responses over several days. Since there were slight differences in the amount of coating on each sensor, comparisons must be based on K_e values rather than sensitivities (This assumes that sensitivity is a linear function of the amount of coatings on the sensor, which is generally the case).

The K_e values for each of the OV-275-coated sensors were quite stable over time, with a relative standard deviation (RSD) of 4% (Table 8). The K_e values between coatings ranged from 1482 to 2020, giving an average of 1675 and a RSD of 14%. The uncertainty in Δf_c values used to determine K_e must be recognized, as K_e estimates depend upon an accurate measure of the frequency shift obtained after coating the sensor (see Eq. 2). Since there is considerable drift in the response occurring just after coating, some uncertainty is associated with this determination: a rapid drift associated with solvent evaporation (\approx minutes) was sometimes followed by a slower drift (\approx days) apparently associated with structural relaxations of the polymer chains. Differences in wetting and adhesion of the coating film to the substrate may also affect responses.

For the remaining coating materials for which more than one coating film was characterized, there was fairly good agreement between successive K_e values (i.e. RSDs were generally below 15%). In some instances, K_e values did vary by as much as 50%. This range of intercoating K_e variability, however, is similar to that reported by other researchers (Grate et al., 1992).

Table 8. K_e values based on responses to xylene or benzene for successive depositions of coatings.

COATING	VAPOR	MEAN SENSITIVITY (Hz/(μ g/L))	STANDARD DEVIATION (Hz/(μ g/L))	RSD (%)
PECH	BENZENE	0.157	0.0148	9
PDPP	BENZENE	0.107	0.0126	11
OV-215	BENZENE	0.043	0.0037	9
DEGA	BENZENE	0.082	0.0046	6
PIB	BENZENE	0.127	0.0086	7
PHA	BENZENE	0.184	0.0149	8
TBEP	BENZENE	0.162	0.0124	8
ABC	BENZENE	0.200	0.0235	12
OV-275	m-XYLENE	0.350	0.0144	4
PCP	BENZENE	0.080	0.0110	14

3.7 Performance of Sensors

3.7.1 Validation of EDPCR with Mixtures

The capabilities for EDPCR and the optimal array to identify and quantify the vapors were assessed using experimental responses to 37 individual vapor concentrations and 62 binary mixtures (with varying relative concentrations of the mixture components). Overall, the correct classification rate was 91%, in close agreement with the 95% rate predicted from the synthesized response data described above.

For the mixtures, at least one of the components was correctly identified in all cases. Classification errors were most often associated with cases of mixtures where one component was present in excess and the mixture was identified as being the higher concentration component alone. Errors in identifying individual vapors were limited, with two exceptions, to cases where the vapor was identified as a mixture and where the second component was predicted to be present at low concentrations. The only cases of complete misclassification were for one concentration of benzene, which was identified as TCE, and one concentration of isooctane, which was identified as hexane. These errors are not surprising given the similarity in response patterns for these latter two vapors.

Concentration predictions for the correctly classified vapors were generally very accurate. For the 149 concentrations predicted, the geometric mean of ratios of predicted-to-actual concentrations was 1.02, indicating a very slight tendency toward overestimation. Overall ratios ranged from 0.5 to 4.2, but the vast majority of predicted concentrations were within 10% of the experimental values. This is reflected in the geometric standard

deviation of the ratios, which was a very low 1.26, and in the 95% confidence interval around the mean ratio, which was 0.98 to 1.06. As with the classification errors, the large errors in concentration predictions usually occurred at the lower vapor concentrations.

3.7.2 LOD and Dynamic Range

LODs for SAW sensors are a function of many factors, including SAW device configuration, temperature, vapor, coating, application, and data reduction and analysis techniques. Individual sensor sensitivities and LODs for the six vapors have been provided at 25 °C in Tables 2 and 4, and at varying temperatures in Table 6. Overall, LODs range from a few $\mu\text{g/L}$ to several thousand $\mu\text{g/L}$. As discussed earlier, higher LODs are associated with more volatile vapors and/or with low coating-vapor solubility interactions.

For several vapors, e.g. benzene, TCE, m-xylene, LODs are sufficiently low to consider applications such as soil-gas and groundwater monitoring where detection of vapors in the low- $\mu\text{g/L}$ range is often needed. However, several vapor/coating combinations yielded LODs of several thousand $\mu\text{g/L}$. Coating selection for the optimal array emphasized selectivity, rather than LODs, however, examination of LODs for the screening set (in Table 2) shows few coatings have much greater sensitivity than those in the optimal set.

Several techniques can be used alone or together to lower LODs. These include (1) lowering the sensor temperature; (2) preconcentrating the vapor on a sorbent; (3) replacing the coating(s); (4) using SAW resonators (rather than SAW oscillators used here) that provide up to a 10-fold improvement in signal-to-noise ratio (Bowers and Chuan, 1989) and thus a commensurate reduction in the LOD; and (5) reducing noise by improved data filtering and other design, operation and data handling techniques. The use of SAW resonators, devices that became available after this research started, is the simplest and possibly most cost-effective approach to improving LODs.

The LOD needed to quantify vapor concentrations differs from the LOD needed to identify vapors. For quantification, the LOD for the most sensitive sensor in the array will apply, assuming that a single vapor is present and that the vapor has been identified. If multiple vapors are present, quantification of each component requires measurable signals from several sensors. For identification, measurable signals from several sensors are usually required, whether single or multiple components are present. This discussion shows the complexity of determining LODs for the array. Such circumstances are not unusual, as many instruments have LODs and other performance characteristics that vary with the number and nature of components present and on factors related to a specific application.

3.8 Applications Related to Hazardous Waste

This section reviews applications of vapor sensors in hazardous waste applications. Models and experiments are used to gauge the suitability of the sensor array in these applications.

3.8.1 Water Sampling and Analysis

A major application of VOC analytical instrumentation is to determine VOC concentrations in surface and groundwater. Two commonly used techniques are headspace analysis, and purge and trap methods. Headspace analysis is applicable to field sensing, and depends on the equilibrium partitioning of VOCs between air and water media. The Henry's Law coefficient, H , which represents the ratio of air to water concentrations at equilibrium in dilute solutions at specific temperatures, provides the proportionality factor, and

$$C_{\text{water}} = C_{\text{air}}/H \quad (7)$$

where the water concentration, C_{water} , may be estimated by measuring the headspace concentration, C_{air} , using the appropriate value of H for the specific VOC and the temperature employed. As Henry's Law is linear with (low) concentration, we can base the limit of detection for contaminants in water, $\text{LOD}_{\text{water}}$, on the limit of detection in air, LOD_{air} :

$$\text{LOD}_{\text{water}} = \text{LOD}_{\text{air}}/H \quad (8)$$

These calculations neglect the volume of the headspace, which is reasonable if relatively little of the dissolved VOC partitions into the headspace. This would occur with small headspace extractions. These calculations further assume equilibrium conditions, which is also reasonable for most groundwater situations.

Henry's Law coefficients and LODs in water for the six VOCs considered here are shown in Table 9. These were determined using LOD_{air} values obtained from the final coating set, and the most sensitive coating in the optimal set. LODs range about from 0.4 to 3.7 mg/L, except for the two aliphatic hydrocarbons that are very hydrophobic, and have LODs in water that are orders of magnitude lower. These LODs are sufficiently low for field applications including drum testing, soil vapor testing, and process monitoring.

Table 9. Estimated limits of detection for VOCs in water and soil. Other physical parameters taken from Mackay and Shiu (1981).

PARAMETER	VAPOR					
	<i>Benzene</i>	<i>Chloroform</i>	<i>Hexane</i>	<i>Iso-octane</i>	<i>m-Xylene</i>	<i>Trichloroethylene</i>
Vapor Pressure at 25 oC, 1 atm. (ppm) (mg/L)	124405 397.4	257133 1255.3	197871 697.4	64445 301.0	10853 47.1	97133 521.5
Henry's Constant (atm*m3/mol)	0.0056	0.0032	1.6778	3.2569	0.0026	0.0089
Solubility in Water (mg/L)	1780	9300	13	0.56	198	1100
Sensor Limit of Detection (Vapor) (ppm) (ug/L)	100 319	100 488	300 1057	50 234	10 43	40 215
Estimated LOD for VOCs in Water (mg/L)	1.41	3.74	0.0154	0.0018	0.42	0.59
Estimated LOD for VOCs in Soil (mg/kg)	119.8	204.0	2.3	0.5	66.5	43.2

3.8.2 Soil Sampling and Analysis

Another common application of VOC instrumentation is to identify and quantify contaminants in soils. VOCs in soils can exist in several phases, namely as free liquids in interstitial voids, as solutes in soil pore water, as adsorbed species on the internal or external surfaces of soil particles, and as vapor in unsaturated voids. VOC phase partitioning increases the difficulty of accurately quantifying contaminants in soils. Common methods include methanol extraction followed by GLC analysis, supercritical fluid extraction followed by GLC analysis, CFC extraction followed by IR analysis for total hydrocarbons, and headspace sampling (using water or other solutions) with GLC analysis.

To fully explore the performance of SAW sensors for such an application, accurate isotherms relating soil concentrations to water and/or air concentrations are required. Isotherms are functions of soil type, contaminant, exposure history, environmental conditions, etc., and are difficult to measure and generally unavailable. We use an alternative approach which is adequate for estimating detection limits based on headspace extraction using water as a solvent. The Organic Leachate Model predicts leachate

concentrations in wet soils C_o in mg/L as:

$$C_o = 0.00211 C_s^{0.678} S^{0.373} \quad (9)$$

where C_s is the soil concentration (mg/L) and S is the solubility of VOCs in water (mg/L). We can solve for the soil concentrations knowing the leachate concentration as:

$$C_s = [C_o / (0.00211 S^{0.373})]^{1.47} \quad (10)$$

Based on the LOD for VOCs in water given in (8), the LOD in soil is:

$$LOD_{soil} = [LOD_{air} / (H \cdot 0.00211 S^{0.373})]^{1.47} \quad (11)$$

Table 9 lists the estimated LODs for VOCs in soils. To obtain fractional concentration measures, we assume a soil porosity of 0.4, a soil density of 2.65, and that the soil void space is saturated. This yields an overall bulk density of approximately 2.0 g/cc. Results presented in Table 9 parallel the estimates of the LODs in water, with the chlorinated and aromatic compounds having very LODs. The aliphatics again have much lower detection limits. These LODs are low enough for field screening applications such as detecting "hot spots".

Because of the simplicity of the Organic Leachate Model, these estimates are very approximate, providing only order-of-magnitude estimates. Variations in soil structure, composition, exposure history, and other factors could have large effects. In practice, isotherms would be developed to relate vapor and water concentrations to the total contaminant in the soil.

3.8.3 Laboratory Demonstrations of Soil and Headspace Sampling

Several laboratory demonstrations using the SAW microsensor were performed to test potential applications and to identify issues that might affect field deployment. Two specific sets of experiments were conducted: (1) continuous flow experiments to portray vapor transport, diffusion and sorption in soil columns; and (2) headspace monitoring. These experiments provided valuable experience and design constraints relevant to the development of field instrumentation.

Soil column simulations. Soil column simulations were used to demonstrate the feasibility of using SAW sensors in applications where continuous (real-time) measurement is necessary or desirable. The experiments were designed to simulate vapor-laden flows in unsaturated soils in order to compare three measurement approaches: FID, FT-IR, and the SAW sensor array. Additional details are presented in Appendix III, a conference paper presented on these experiments.

A wide range of toluene, TCE and hexane concentrations were used to develop breakthrough curves that represent advective and diffusive transport of the contaminants in

the soil columns. Because the columns were nearly water-saturated, the relative humidity of the discharge air was high. Results obtained for step changes in inlet vapor concentrations showed that SAW responses paralleled those of the other detectors for most vapor-coating combinations. This applied to both the individual vapors and vapor mixtures used. The breakthrough curves typically obtained start at low or zero concentrations, and then gradually reached a peak (approximately 10-20% of saturation concentration), following a logistic curve.

These experiments did not use the optimal coating set. In some cases, anomalous results were obtained with several coatings, largely due to signal-to-noise problems at low concentrations. This concentration range exceeded levels used in the calibration of the SAW sensors, and also approached or fell below estimated sensor LODs. One SAW sensor responded significantly to humidity changes. Additionally, some baseline drift over the duration of the experiment was apparent for the sensors, which was problematic at the lower vapor concentrations.

Several results are generalizable. Such soil column experiments with SAW sensors have the potential to estimate diffusion, retardation and recovery (e.g., mass balances relevant to vacuum extraction) parameters in contaminated and clean soils. ("Treatability" tests measure these parameters, which are complex functions of the contaminant(s), soil conditions, exposure history, etc.) The use of SAW sensors in these and *in situ* applications (in-wells, for VES monitoring, etc.) appears feasible, given the following constraints: special care is required at high relative humidities. In this case, humidities must be held constant or decreased (e.g., by dilution or by increasing the sensor operating temperatures). In addition, baseline drift of the sensors must be accounted for where long duration measurements -- without baseline references -- are involved.

Headspace experiments. In the headspace experiments, the SAW array was adapted to a conventional automated headspace analysis instrument for parallel tests. The headspace systems consists of a Tekmar 7010 GT, interfaced to a Varian 3700 GC equipped with FID and computer data acquisition system. Such headspace systems can analyze soil and water samples placed in small (22 mL) vials. The vials are pressurized (nominally to 5-10 psi), a small quantity of the headspace vapor from the vial is extracted into a sample loop (nominally 1 cc) for injection into the GC. This section describes parallel analyses obtained using the GC-FID and SAW sensors.

SAW sensor responses obtained using this setup were not very reproducible despite several modifications to the system. The major problem was the insufficient headspace volume in the small vials. Normal vial pressurization provided the SAW sensor array with a total sample volume of only 5 - 10 cc. While this is greater than the array dead volume (approximately 2-3 cc), the sample volume and pressure available was probably insufficient for distribution among the four sensors. Additionally, the vapor pulse was short, and failure to reach sorption equilibrium may have affected the results. The small pulse of sample introduced to the sensor array may have had a different temperature and humidity from the purge gas used to take baseline references.

Two alternative headspace sampling systems could be employed that would resolve the problems encountered. (1) A static system might directly expose the sensors to the headspace vapor. The sensors, covered by a permeable screen or membrane for physical protection, would be set directly into the headspace. Vapors would diffuse to the sensors. This requires a much smaller configuration in order to allow the sensors to be mounted directly on the (5 cm diameter) lid of standard sampling bottle. Baseline could be established prior to sampling by active purging. (2) A dynamic system requiring fewer modifications would use a small sampling pump that continuously passed headspace vapor over the sensor and then back to the sampling container. This system would allow real-time purging using multiport valves. The design and engineering for both systems appears practicable.

4.0 TECHNOLOGY STATUS

4.1 Technology Development Evaluation

The laboratory research in this project demonstrated the potential for coated SAW sensor arrays in VOC monitoring applications related to site characterization and remediation process control. For the six vapors examined, relatively simple and rapid sensor measurements provided compound-specific concentrations of VOCs. In particular, our research indicated that:

- * The pattern recognition and quantification method developed during this work, called EDPCR, provides a useful means for selecting coated sensors for use in an array and for predicting, quantitatively, the performance of any set of coated sensors.
- * EDPCR is well-suited for polymer-coated SAW sensor arrays where responses to individual vapors are linear and additive. The method is computational efficient. It uses both sensor response patterns and predicted concentrations in the identification process.
- * Optimal selection of coatings (using EDPCR analysis) increases the ability of the array to discriminate among vapors. Correct identification and quantification of binary vapor mixture components was possible both within and between chemical classes.
- * Sensor responses are a linear function of vapor concentration over a wide concentration range and vapor mixture responses are additive functions of the component vapor responses, indicating no significant vapor-vapor interactions.
- * Humidity effects on sensor responses to VOCs can be significant for highly polar sensor coatings and must be compensated or controlled for during calibration and field operation. Thermostatting the array provides a viable means for limiting these effects for subsurface VOC monitoring applications.
- * Sensor responses to VOCs show a negative Arrhenius temperature dependence which can be accounted for via calibration and thermostatting of the array. Differences in the magnitude of the temperature effect between vapors can be used to enhance selectivity the selectivity of the array.
- * Medium-term (2-3 months) aging effects are small, reducing the need for recalibration of the sensors.
- * Coating-to-coating response reproducibility was less than optimal, with typical variations of +/-15% around average responses being observed. This indicates that calibration of individual sensors is required, although improvements in coating deposition techniques may reduce this problem.

- Limits of detection, while sufficiently low for monitoring most VOCs in many potential applications, could be improved. Recent advances in SAW sensor design can apparently provide an order of magnitude reduction in LOD, which would expand the range of applications.

4.2 Technology Integration Evaluation

Use of coated-SAW sensor arrays coupled with EDPCR analysis has the capacity to provide screening and process control monitoring for VOCs encountered in many activities related to site assessment and restoration. In addition to its potential for incorporation into small, rugged field instrumentation, a key advantage of this technology is the ability to identify and quantify VOCs, whether present individually, or in simple mixtures. The versatility associated with the ability to easily replace individual sensors in the array, and thereby adapt it to specific monitoring problems, represents another unique feature of this technology, relative to other portable VOC screening instruments.

The 158-MHz SAW oscillators used in this study had relatively high LODs for certain of the VOCs examined. Newer SAW resonators operating at 200-250 MHz should provide significantly lower LODs, while retaining the other features described above. The development of SAW-sensor based field instruments employing these resonators is recommended.

In addition to the sensor array, several ancillary components will be required to construct field-deployable SAW-sensor based instruments. Although diffusional transport of vapors to the sensor array can be considered in certain applications, active transport (via a small pump) will most likely be required for subsurface VOC monitoring. Thermostatting of the sensor and inlet flowstream will also be required in most cases. A small gas scrubber (e.g., Tenax or activated carbon) and valving is required for periodic baseline measurements. Additionally, a data processing module for pattern recognition analysis and output display is required. This module might also control other aspects of sample collection and data processing and archiving. In general, these components are readily available. As in any instrument, however, good engineering and design is required to integrate these components and obtain a small, self-contained, and reliable instrument.

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Appendix I. VOC Concentrations Found in Vacuum Extraction Systems

A review of literature concerning vacuum extraction systems is used to illustrate typical VOC concentrations. While not exhaustive, the review shows initial VOC concentrations ranging to saturation, and VOC levels during VES operation from 50 to 25,000 ppm. VES is typically shutdown when concentrations fall below a few ppm. In cases, concentrations reported below were estimated based on the reported flow rates and VOC quantities recovered, assuming a typical VOC molecular weight (e.g. toluene's).

1. *Reference:* Malot, J.J, R. Piniewski, "Innovative Technology for Simultaneous In Situ Remediation of Soil and Groundwater," Groundwater Control, 1991, Terra Vac, Puerto Rico.

Site description: Combined vacuum vapor extraction and groundwater recovery in New York. Contaminant involved largely methylene chloride also cyclohexane, dichloroethylene, trichloroethane, methanol, etc. Phase I recovered 2675 lbs in 24 days (VES system only) with extraction rates of 100 to 320 CFM from 2 wells. In phase II, 3276 lbs were recovered in 170 days using the same system.

Concentrations: Initial concentrations were 3000 ppm. Typical concentrations ranged from 10 to 800. Average concentrations over the operational period were 6 mg/L (1500 ppm) in phase 1 and 1.1 mg/L (275 ppm) in phase 2.

2. *Reference:* US EPA, "Terra Vac In Situ Vacuum Extraction System, Groveland, Massachusetts," EPA/540/S5-89.003, May, 1989.

Site description: SITE Technology demonstration at Valley Manufactured Products NPL site in Groveland, MA. Contaminant involved largely trichloroethylene.

Concentration: Soil gas concentrations reached 3600 ppm. Concentrations during extraction ranged from 1 to 700 ppm.

3. *Reference:* Pezzullo, J.A. et al., "Full Scale Remediation at a Superfund Site Using In Situ Vacuum Extraction and On-Site Regeneration Case Study-Phase I," Superfund '90, Proceedings of the 11th National Conference, Nov. 26-28, 1990, Hazardous Materials Control Research Institute, Silver Springs, MD, pp 624-7.

Site description: A full scale remediation at the Tyson's NPL site near Philadelphia PA involving 180 vapor extraction wells, two 700 hp vacuum units. The major contaminants included trichloropropane, and BTEXs. 95,000 lbs of VOCs were removed over 27 months with a nominal flow of 5000 CFM.

Concentration: The average concentration over the operation period is 0.26 mg/L or 65 ppm.

4. **Reference:** Fuerst, D., B.L. Underwood, "Vacuum Extraction of Volatile and Semi-Volatile Compounds at a Superfund Site Remediation," Terra Vac, Atlanta, GA.

Site description: Pilot test of VES for VOCs and semivolatiles at a South Carolina site containing a variety of contaminants. The major contaminants recovered were carbon tetrachloride and TCE. Flow rates ranged from 50 to 135 CFM at three wells. 1186 lbs of VOCs were recovered after 190 hours of pumping.

Concentration: Average total VOC over pumping period is 5.6 mg/L or 1300 ppm.

5. **Reference:** Malmanis, E., et al., "Superfund Site Soil Remediation Using Large-Scale Vacuum Extraction, Monitoring and Sampling, Terra Vac Corp, Tampa, FL.

Site description: A full scale remediation at a NPL site in Michigan using 23 extraction wells with typical well flows of 150 CFM. 28,675 lbs of VOCs were recovered over 55 days.

Concentration: Typical initial wellhead concentrations ranged to 250 ppm. Average concentrations over the operation period were 1.7 mg/L or 425 ppm.

6. **Reference:** Malot, J.J., "Soil Remediation and Free Product Removal Using In-Situ Vacuum Extraction with Catalytic Oxidation," Terra Vac, San Juan PR.

Description: Subsurface contamination at a gasoline and diesel fuel terminal. 15 extraction wells operating at 40 to 120 CFM removed 52,000 lbs of VOCs in 250 days.

Concentration: Initial soil gas concentrations approached 25,000 ppm. Average concentrations over operating period were 1.5 mg/L or 375 ppm.

7. **Reference:** Malot, J.J., "Soil Remediation and Free Product Removal Using In-Situ Vacuum Extraction with Catalytic Oxidation," Terra Vac, San Juan, PR.

Description: Leak at a petroleum refinery. 1000 lbs of VOCs were removed in 28 days using a 500 CFM extraction well in initial tests; 150,000 lbs were removed after system expansion.

Concentrations: Initial concentrations were 345 mg/L (95,000 ppm). Typical concentrations range between 350 mg/L and 5 to 8 mg/L. Low concentrations indicate a vaporization of mass transfer limited with vapors partitioning from the liquid hydrocarbons at a rate nearly equal to the extraction rate.

8. **Additional reference:** Hutler, N.J., B.E. Murphy, J.S. Gierke, "State of Technology Review: Soil Vapor Extraction Systems," Risk Reduction Engineering Laboratory, Cincinnati, OH, US Environmental Protection Agency, EPA/600-S2-89/024 (1990).

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