



FINAL PERFORMANCE REPORT

Project Title

Microsensor Arrays for the Identification of Organic Solvents Vapors

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Sponsor

National Institute for Occupational Safety and Health
of the Centers for Disease Control

Grant K01-OHO0077

Date

October 5, 1993

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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 organic solvent vapors in the occupational environment. The study was motivated by the need for improved sensor technology in compact direct-reading industrial-hygiene monitoring instruments for organic vapors. The high-cost, complexity, poor selectivity and/or limited range of detectable analytes of currently available direct-reading instruments preclude their use in routine personal exposure monitoring applications. Instruments employing SAW sensor arrays can provide rapid identification and quantification of a wide range of organic vapors of occupational health concern. The small size, sensitivity, selectivity, versatility and potential low cost of instruments based on SAW sensor technology promise improvements in the quality and quantity of data used to guide industrial hygiene exposure assessment and control efforts.

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. 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 and decreases the elastic stiffness of the surface coating film which causes a commensurate 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, can 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 single array can identify and quantify a wide range of different vapors, when present individually or in simple mixtures. A key challenge to the development of this technology is determining which sensor coatings to include in the array to optimize sensitivity and selectivity.

The prototype instrument tested here included an array of four sensors. The instrument occupied about 0.3 ft^3 and required about 2 W of power, but was not optimized for field use. Calibrations were performed for SAW sensors overlaid with each of 16 different isotropic polymer coatings. Sensors coated with these materials were exposed to from 14 to 40 organic vapors, representing 12 different chemical classes, commonly found in the industrial

environment. Certain coatings were found to be unstable and were eliminated from further consideration. For the remaining stable coatings, responses to all vapors were rapid and reversible and varied linearly with concentration over the concentration ranges examined.

Limits of detection ranged from about one ppm to several hundred ppm, with less volatile and more polar vapors giving lower detection limits. Measurement of most vapors below their ACGIH-TLV values is possible. Recent improvements in SAW sensor design promise a reduction in detection limits of up to an order of magnitude. Sensor responses are dependent on temperature and, in certain cases, on relative humidity, indicating that compensation or control for these variables is necessary. The sensors provide stable, reproducible responses for periods of at least eight months indicating that recalibration requirements are minimal.

A new pattern recognition method was developed during this project for determining which coated sensors would maximize the selectivity and accuracy of detection of a given subset of vapor contaminants. Using this method in conjunction with a Monte Carlo simulation procedure, optimal subsets of coated sensors can be selected for inclusion in the array for any potential exposure situations. This approach to coating selection allows the assessment of sensor array performance in terms of correct vapor identification rates, quantification accuracy, and the influence of potential interferences.

Also developed during this project were several predictive models of sensor responses. Models based on vapor boiling points, coating/vapor solubility parameters, and coating/vapor solvation parameters used in conjunction with linear solvation energy relationships (LSER) were examined. The LSER model provided the most accurate correlation of modeled and experimental responses. Use of this model, together with the pattern recognition method described above permits the selection of optimal coatings and the estimation of array performance without the need for experimental calibrations.

These investigations showed that with a simple four-sensor array, it is possible to identify and quantify each of a large number of vapors individually or in binary and ternary mixtures. Using optimized arrays, errors in identification are generally restricted to cases of mixtures where one component is present at concentrations near the detection limit and the mixture is identified as the dominant component alone. In addition, while surprisingly good discrimination between vapors both between and within chemical classes is possible, identification errors are observed for some vapors of similar structure and/or solubility properties. A preliminary investigation of liquid crystals as sensor coatings shows that this class of sensor coatings can enhance discrimination by virtue of subtle size and shape differences between otherwise similar (e.g., isomeric) vapors.

Chapter 1 presents an overview of the project, including the background, significance and goals of the research performed, a basic discussion of the sensor operating principles, coating-vapor interactions, experimental methodology, data analysis and pattern recognition methods as applied to sensor arrays. Chapter 2 describes the new pattern recognition method, referred to as extended disjoint principal components regression analysis (EDPCR), that was developed to aid in the selection of coated sensors to include in the array, to predict the performance of a specified sensor array with respect to sensitivity and selectivity of vapor measurement, and to 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. The development of the method is demonstrated with previously published data. The use of EDPCR on data generated in this project is described in subsequent chapters.

Chapter 3 describes the three semiempirical models of sensor responses developed from data on the response of a four-sensor to 40 different organic vapors. The models are based on the prediction of sensor responses using vapor boiling points, vapor/coating solubility parameters, or vapor/coating solvation parameters and LSERs. As part of this effort, it was shown that the SAW sensor can be used for determining the solubility parameters and solvation parameters of any coating. This is normally performed by gas chromatography. Use of the sensors to obtain such information has several potential advantages including, simplicity of sample preparation and analysis, room temperature or high-temperature operation, compensation for humidity and substrate effects, and simultaneous testing of several coatings. Each of the three models has been used to develop regression equations from which predicted responses can be derived. Best results were obtained with the model based on solvation parameters and LSERs, with modeled sensor responses values falling within 25 percent of experimental values for the vast majority of vapors and coatings. With this model, array response patterns can be modeled accurately and the performance of the array for any number of vapor exposure scenarios can be determined apriori.

In Chapter 4, the responses of 16 coated sensors to as many as 20 different vapors are examined. Using this larger data set, a focus is placed on employing EDPCR in conjunction with a Monte Carlo simulation procedure to select optimal arrays for any potential exposure to binary or ternary vapor mixtures, based on the calibrated sensor responses to the individual vapors comprising the mixtures. The use of modeled sensor responses (determined from the LSER model described in Chapter 3) in the optimal coating selection procedure is also explored. Exposures to a series of binary mixtures confirm that mixture responses are additive functions of the component vapor responses. Optimal coating selections are demonstrated for

several binary and ternary vapor mixtures. Humidity, temperature, and aging effects are then examined for a subset of vapors and coatings.

Chapter 5 describes the results of tests using liquid crystals as sensor coatings for discriminating between isomeric and structural similar organic vapors. Results are interpreted in terms of size, shape, and functional group interactions affecting the observed responses. The utility of including LC coatings in an array to improve selectivity is demonstrated.

SIGNIFICANT FINDINGS

The laboratory research in this project demonstrated the potential for coated SAW sensor arrays in monitoring applications related to industrial hygiene exposure assessment. Several fundamental issues were examined that impact the ultimate application of this technology as well. For the vapors examined, relatively simple and rapid sensor measurements provided compound-specific concentrations of organic vapors. The following significant findings highlight the capabilities and limitations of this technology as revealed in this project, and the needs for further research.

Response Characteristics and Limits of Detection. Sensor responses to individual vapors are linear functions of concentration over wide concentration ranges, and responses to binary mixtures are additive functions of the mixture components. Both of these factors are important with respect to ease of calibration and accuracy of pattern recognition analysis. The latter factor is particularly important with respect to identifying and quantifying mixture components from the composite response pattern provided by the array. Limits of detection (LOD) vary significantly from one vapor to another, depending on the volatility and structure of the vapor, the coatings employed in the sensor array, and the operating temperature, however, LODs in the range of 2 to 250 $\mu\text{g/L}$ (or about 1 to 80 ppm), which are below the ACGIH-TLV values for most of the vapors, are achievable at 25°C for many vapors of concern. The inherent selectivity for less volatile vapors can be used to advantage in diminishing the effects of potentially interfering vapors that are more volatile. However, it would be desirable to be able to measure low concentrations of the more volatile vapors in certain situations as well. The use of SAW resonators, rather than the SAW oscillators employed here, could reduce LODs for all vapors by an order of magnitude. The SAW resonator functions in an analogous fashion to the SAW oscillator except that it has significantly lower baseline noise. Given the demonstrated capabilities of SAW sensor technology shown in this study, the development of SAW-sensor based field instruments employing these resonators is recommended. Alternatively, a simple preconcentrator could be incorporated into the instrument to lower the detection limits. In this case, a short collection cycle (e.g., 1-2 min) would precede each analytical determination. Although this would add to the complexity of the instrumentation and would allow only intermittent sampling, it would expand the range of detectable analytes to include even the most volatile of vapors.

It should be noted that the LOD range given above is based on assessments of sensitivity to individual vapors. Results of analyses on binary and ternary mixtures revealed that the LOD must also take account of the nature and number of potential co-contaminants,

as the ability to detect low concentrations of one vapor will be affected by the other vapors present. Additional research is needed to address this issue so that the performance limits of the SAW sensor array can be better defined.

Identification of Vapor Mixtures. 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 the components of vapor mixtures. Correct identification and quantification of binary and ternary vapor mixture components was possible both within and between chemical classes using a four-sensor array. Most other portable instruments that respond to organic vapors do not have this capability. In this regard, the selectivity of the SAW sensor array approaches that of larger, more complex instruments such as gas chromatographs and FTIR spectrophotometers. 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 instruments. These investigations have been limited to consideration of simple (i.e., binary and ternary) mixtures of vapors with a four-sensor array. More complex mixtures (i.e., greater than four components) would not be reliably determined because the case is underdetermined statistically. It is possible, however, to consider the use of larger arrays for more complex mixtures. This would not add significantly to the complexity of the instrumentation and would permit selective measurement of several components simultaneously.

Environmental Factors and Aging Effects. Humidity effects on sensor responses can be significant for highly polar and highly non-polar sensor coatings and must be compensated or controlled for during calibration and field operation. Further characterization of humidity effects should be pursued for a wider range of vapors than examined here. It may be possible to use the sensor array itself to monitor humidity levels and to compensate for the effects of humidity using software-based calibration corrections. This appears feasible but was not explored in detail in this study. Sensor responses to organic vapors show a negative Arrhenius temperature dependence which can be readily accounted for via calibration and thermostating of the array. As shown here, differences in the magnitude of the temperature effect between vapors can be used to enhance the selectivity of the array. This issue deserves further study. Medium-term (2-8 months) aging effects are small for most of the coatings tested, reducing the need for recalibration of the sensors. Coating-to-coating response reproducibility was quite good in most cases, however, there were exceptions involving variations of more than 15 percent around average responses in others. Use of the frequency shift upon coating deposition as a measure of the "amount" of coating deposited is not completely reliable, owing

apparently to differences in adhesion, elasticity, or stress between successive coating films. This indicates that an initial calibration of the individual sensors would be required. This is not an unusually constraining requirement, and improvements in coating deposition techniques or use of pre-conditioning techniques (e.g., thermal annealing) might be successful in eliminating the need for this procedure.

Sensor Response Models and Coating Selection Strategies. 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 in conjunction with a Monte Carlo simulation of sensor responses which incorporates likely random errors in responses to individual vapors and their mixtures) increases the ability of the array to discriminate among vapors. Complementing the capabilities of EDPCR, we have developed several models that can predict, to varying degrees of accuracy, responses to vapors from known or readily measured physicochemical parameters. Use of these models to predict sensor responses, followed by EDPCR to model the ability to identify and quantify vapors using an array of sensors, represents a complete approach to coating selection that does not require apriori calibration.

Ancillary Components. 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 could be considered in certain applications, active transport (via a small pump) is advisable at this point to maintain rapid responses, to ensure all sensors in the array are presented with the sample simultaneously, and to facilitate field zeroing of the instrument. A small gas scrubber (e.g., Tenax or activated carbon) and valving would be required for periodic baseline measurements. Thermostating of the sensor array will also be required in most cases and could be accomplished with small Peltier devices mounted in good thermal contact with the sensors. Since operation at or near ambient temperature is advisable, power requirements are low. 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. The ability to

replace sensors to respond to different contaminant mixtures should not be underemphasized, as it adds a degree of versatility to the SAW sensor array that is not possible with other portable organic vapor detection instruments. Interchangeable modules of four (or more) sensors could easily be incorporated into the instrument design. Coupled with other advantages of this technology, i.e., ruggedness, low power requirements, expected low cost of large-scale manufacture (~\$1000 for a four-sensor array), and the capability for continuous unattended operation, these results support the continued pursuit of SAW sensor instrumentation for applications such as personal exposure monitoring. Although the instruments used in this study were not optimized for such an application, it is feasible to develop battery powered instruments that could be worn by individuals and operate for at least eight hours.

LIST OF PUBLICATIONS

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3. S. J. Patrash and E. T. Zellers, "Characterization of polymeric surface acoustic wave sensor coatings and semiempirical models of sensor responses to organic vapors," Anal. Chem. 65, 2055-2066 (1993).
4. S. J. Patrash and E. T. Zellers, "An investigation of nematic liquid crystals as surface acoustic wave sensor coatings for discrimination between isomeric aromatic vapors," Analyt. Chim. Acta (in press).
5. D. S. Ballantine, S. J. Martin, R. M. White, A. J. Ricco, E. T. Zellers, G. Frye: Acoustic Wave Sensors: Theory, Design, and Physicochemical Applications, Academic Press: Boston, MA (in press).
6. E. T. Zellers, S. A. Batterman, M. W. Han, S. J. Patrash, and W. A. Groves, "The influence of temperature and humidity on the responses of a surface acoustic wave sensor array to organic vapors," (in preparation).
7. E. T. Zellers, S. A. Batterman, M. W. Han, S. J. Patrash, and W. A. Groves, "Coated surface acoustic wave sensor arrays - coating selection for the selective determination of organic vapors and vapor mixture components," (in preparation).

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CHAPTER 1

INTRODUCTION

Synopsis

This chapter provides an overview of the project, including the background, significance, and goals of the research performed, and basic discussions of the sensor operating principles, coating-vapor interactions, experimental methodology, data analysis and pattern recognition methods as applied to sensor arrays.

Project Overview

This report describes an investigation of the use of arrays of coated surface-acoustic-wave (SAW) microsensors for the identification and quantification of organic vapors from several different chemical classes. The study was motivated by the need for improved sensor technology in direct-reading industrial-hygiene monitoring equipment. Currently available portable monitoring instruments for organic vapors can neither identify unknown contaminants nor discriminate between the components of even simple mixtures. A microsensor array comprising SAW sensors with partially selective responses can provide a "spectrum" that is characteristic of a given contaminant or class of contaminants. By employing pattern recognition analysis of the multidimensional sensor-response data it is possible to identify and determine the quantity of unknown vapors and vapor mixtures. The small size, low power requirements and versatility of the SAW sensor array will facilitate incorporation into miniaturized instrumentation suitable for real-time personal monitoring of organic vapor exposures and, possibly, respirator-cartridge breakthrough applications.

The research described here entailed testing the responses of SAW sensors having different chemically sensitive coating materials deposited on their surfaces upon exposure to each of several organic vapors over a range of concentrations. Vapors from 12 different chemical classes were examined. An array consisting of four 158-MHz SAW oscillators, each with an active area of about 5 mm², was employed to test sets of coating materials sequentially. The sensors were calibrated for each target vapor over a relevant range of concentrations at 25°C and 50% relative humidity using a dynamic test-atmosphere generation system. The sensor responses were stored and then analyzed collectively using pattern recognition methods to determine both the optimal number and types of coated sensors

necessary for a given exposure situation and the ability of the sensor array to identify the components in various vapor mixtures. Experimental verification of the results predicted from the pattern recognition analysis were performed for several relevant binary vapor mixtures. Additional testing was performed on a subset of coatings and vapors to assess the effects of temperature and relative humidity on sensor responses, and to examine aging effects and inter-coating response reproducibility.

The coating films tested consisted of organic polymers, oligomers, and non-volatile liquids capable of rapidly and reversibly absorbing organic vapors. By using coatings with different hydrogen-bond donating/accepting strengths, polarities, and polarizabilities, partial selectivity based on the differential equilibrium solubility of each vapor in the coatings was achieved. Several room-temperature liquid crystals were also tested as coating materials. The anisotropic nature of the liquid crystals provided additional discrimination based on subtle size and shape features of otherwise similar compounds. Initial plans called for measuring both the equilibrium sensor response and the response time for each coating/vapor pair. The latter quantity was to be used to obtain an estimate of the vapor diffusion coefficient which might then be used to further enhance the selectivity of the array (based on differential vapor diffusion rates in the coating films). It was found, however, that response times were extremely rapid and that differential response times could not be determined.

The primary goal of the study was to establish a data base of coated SAW sensor responses to a wide range of organic vapors to determine whether and to what extent arrays of SAW sensors could provide responses patterns capable of uniquely identifying individual vapors and the components of simple (i.e., binary or ternary) vapor mixtures. In addition to achieving this goal, we have determined the effects of environmental variables (i.e., humidity and temperature) on sensor responses, examined response reproducibility and aging effects, developed models of sensor response that can be used in selecting coatings for inclusion in an array for a given exposure situation and in predicting the responses of vapors for a given array.

Background and Significance

A major problem facing occupational health professionals is the lack of adequate data to characterize worker exposures to toxic chemicals. One factor that contributes to this situation is the dependence of conventional (i.e., time-integrating) sampling methods upon capital equipment and professional time: costs associated with operating and maintaining sampling equipment, chemically analyzing collected samples, and cataloging exposure data undoubtedly result in a reduction in both the size and quality of the exposure data base. Furthermore, the delay in obtaining chemical analyses makes it difficult to correlate exposure

peaks with specific work practices, and can often impede a timely intervention to reduce exposures. One reason for the dependence on time-integrating methods is the prevalence of mixtures of contaminants in the occupational environment which generally precludes the use of personal direct-reading instruments for quantifying individual contaminant concentrations due to their lack of selectivity. The development of sensitive and selective chemical microsensors that could be used in miniaturized direct-reading instruments would greatly improve the quantity and quality of worker exposure measurements. This, in turn, would improve our ability to characterize and control occupational exposure hazards.

Another important occupational health concern is the accurate determination of gas and vapor penetration through personal protective equipment such as organic vapor respirator cartridges. Currently, the determination of contaminant breakthrough for air-purifying respirator (APR) cartridges depends on the ability of the wearer to sense the contaminant within the facepiece. This factor restricts the use of APRs to those chemicals with adequate warning properties. NIOSH/MSHA certification testing procedures for organic vapor cartridges using carbon tetrachloride vapor [1] are often not indicative of the adsorption behavior (or protection) observed with other compounds [2].

A number of theoretical models have been applied to predicting breakthrough times for organic vapor cartridges containing activated charcoal [2-5]. Unfortunately, for many chemicals the predicted values significantly underestimate the experimental service life. This situation demands that respirator users perform empirical testing of cartridge efficiencies for the specific contaminants for which protection is needed [6]. However, even these approaches are limited in their ability to account for all possible relevant variables encountered in actual workplace situations (e.g., fluctuations in humidity, the presence of contaminant mixtures, improper storage leading to unaccounted exposure time, etc.). The development of microsensor-based instruments for use as real-time end-of-service-life indicators or miniature field-testing monitors would improve the effective protection afforded by APRs and expand the range of contaminants for which they could be used.

Several compact industrial-hygiene monitoring instruments developed recently combine gas detection capabilities with on-board microprocessors to provide several desirable operating features [7]: the instruments are small enough to be worn by the worker, they operate continuously, and they can be equipped with alarms to provide immediate warning of excessive exposures. In addition, some of the instruments incorporate datalogging electronics that permit collecting exposure histories over the entire sampling interval. Direct computer interfacing also reduces the data management burden. While these features greatly facilitate monitoring worker exposures, most instruments suffer from limitations associated with the types of sensing components employed. For example, the majority of the truly portable

instruments used for monitoring organic gases and vapors (i.e., those capable of collecting breathing zone exposure measurements) detect contaminants on the basis of one of the following mechanisms: catalytic combustion, semiconductor charge transfer, or flame- or photo-ionization. The sensitivity of these detectors is generally satisfactory, but detection of specific organic compounds or classes of compounds is not possible: the presence of even simple mixtures of organic contaminants can preclude an accurate determination of the exposure hazard due to any of the mixture components. Use of chromatographic preseparation is generally required to obtain selectivity. Unfortunately, portable GC instrumentation is generally too large to consider for routine personal monitoring. Portable instruments employing electrochemical oxidation/reduction detectors or impregnated paper-tape photometers provide improved selectivity, but their use is limited chiefly to reactive inorganic gases. Importantly, none of the aforementioned detectors can actually identify an unknown contaminant. Thus, while the "intelligence" of available instruments is quite advanced, their overall utility is compromised by their limited sensing capabilities.

Over the past decade an increasing number of reports have appeared on miniaturized chemical sensing elements produced using integrated-circuit (IC) microfabrication technology [8-10]. The research proposed here concerns one of these microsensors, the coated surface-acoustic-wave (SAW) oscillator. In this device, a high-frequency mechanical wave propagates along the surface of a piezoelectric substrate which has been coated with a chemically-sensitive film. Using a simple feedback amplifier to connect the input and output transducers of the device results in oscillation at a fixed resonant frequency. Small changes in the mass or elastic properties of the coating film caused by interactions with gases or vapors result in a change of the velocity of the propagating wave, and hence of the oscillator frequency. The simple design of the SAW oscillator translates into a low-cost of manufacture and the low power requirements will facilitate their use in miniaturized field monitoring equipment.

The coated-SAW sensor response is a function of both the extent of vapor-coating interaction and the operating frequency of the oscillator, with higher operating frequencies yielding better sensitivity. A key advantage of the SAW sensor compared to other microsensors is the versatility imparted by the ability to use a wide range of coating materials. Since a number of chemical or physical interactions between the vapor and the coating film can be utilized, the range of applications is quite broad, that is, it is not restricted to ions or readily oxidized or reduced species as is the case with many other sensors. This feature is particularly attractive for occupational exposure monitoring where a wide range of possible contaminants is encountered. At the same time, this requires that the coating material exhibit a high degree of selectivity. Indeed, the primary challenge to this microsensor technology is the development of effective coating materials.

Coated-SAW sensors have been used successfully for the detection of a range of organic and inorganic gases and vapors, including, H_2S [11], NO_2 [12,13], SO_2 [14], H_2 [15], H_2O [16], dimethyl acetamide [17], and cyclopentadiene [18]. Detection limits in the part-per-billion concentration range have been reported by several authors [11,14,17]. However, these studies have generally focused on the detection of a single target compound; very limited testing of relevant potential interferences has been performed. Two exceptional reports described an approach to using an array of polymer-coated SAW sensors for selectively detecting nerve-gas simulants [19,19a]. Pattern recognition algorithms were used to decode the collection of overlapping sensor signals and identify the target analytes. The patterns obtained for the target compounds were found to differ significantly from those of several other potentially interfering solvent vapors. In commenting about the generalizability of this approach, the authors noted several correlations between the sensor response patterns for a given vapor and those expected from considerations of the solubilities of the analytes in the coating films. Unfortunately, the data sets were too limited to provide any general guidelines for coating material selection for other vapor detection applications.

The idea of using sensor arrays coupled with some type of pattern recognition analysis for gas/vapor detection is not new. Carey et al. [20,21] and others [22] have described several approaches to the interpretation of multisensor data using pattern recognition methods. Reports have appeared recently on arrays of bulk acoustic-wave piezoelectric (BAW) sensors [23-25], electrochemical sensors [26], chemiresistors [27], metal-oxide semiconductor gas sensors [28,29], and recently on coated SAW sensors as well [19a,29a]. The work on BAW sensors is of interest due to the similarity in the operating principles of the SAW and BAW sensors and the focus of that work on organic vapor detection.

Carey and Kowalski demonstrated the use of a coated-BAW sensor array for monitoring vapors of methylene chloride, hexane and water in a simulated drying operation [24]. In another study [25], a series of organic polymer sensor coatings was tested in a BAW-sensor array for detection of organophosphorus compounds and a few organic vapors. Using the equilibrium frequency shifts as the measured parameters, the authors performed principal components analyses on the data set and found that structurally related coatings were generally grouped together indicating similar mechanisms of interaction with the vapors. The pattern recognition analysis also revealed that, due to the high level of redundancy, the number of required sensors could be reduced with no significant loss of descriptive information. No specific comments were made, however, on the ability of the array to discriminate between the specific analyte gases and vapors or on the detection limits of the array. In addition, several of the coatings consisted of glassy or highly crystalline polymers which often exhibit non-linear sorption behavior as well as hysteresis and aging effects [37].

In a related paper, Carey et al. [23] examined the problems encountered in predicting the identities and concentrations of solvent vapors when the sensors in the array give very similar responses to different vapors. An array of nine coated BAW sensors was used to measure separately three different organic vapors. While the vapors examined, m-dichlorobenzene, 1,2-dichloropropane, and 1,1,2-trichloroethane are ostensibly quite different with respect to, for example, molecular size, polarizability, and vapor pressure, the response patterns (i.e., equilibrium frequency shifts) were very similar for all three vapors. Due to the high level of correlation of the data, the discriminating power of the array was significantly reduced as was the effective signal-to-noise ratio for each of the analytes. This underscores the fact that even in the overdetermined case (i.e., nine sensors and only three possible vapors) the ability to identify a given vapor is critically dependent upon the selectivity of responses of the individual sensors.

While it has been shown that coated BAW and SAW multisensor arrays used in conjunction with pattern recognition methods are capable of identifying unknown organic vapors, the range of analyte vapors and vapor mixtures examined to date is very limited. Most reports have focused on obtaining a pattern that is characteristic of a single compound, without adequately addressing the effect of co-contaminants on the response pattern. The effects of environmental factors, such as temperature and humidity, on sensor responses has also not received much attention.

The research described here extends the approaches described above to the problem of identifying and measuring the concentrations of a wide range of organic vapors, many of which are found routinely as contaminants in the workplace. Furthermore, a focus has been placed on determining the ability of a sensor array to identify components of mixtures of compounds from the same or different classes that are present simultaneously and on optimizing the selectivity of the array for any possible target vapors that one might wish to monitor. The effects of temperature, relative humidity, and aging have also been studied. Members of each of 12 classes of organic vapors were tested, including aromatic and aliphatic hydrocarbons, alcohols, amines, esters, ketones, ethers, aromatic and aliphatic olefins, and chlorinated aromatic and aliphatic compounds, and amides.

Operating Principle of the SAW Sensor

The operating principle of the SAW chemical microsensor is similar to that of the BAW crystal detector first reported by King [31], and studied extensively by Guilbault [32] and others [33]. Both devices are based on acoustic wave propagation in a piezoelectric substrate. The SAW sensor, however, has several potential advantages compared to the BAW sensor,

including smaller size, potentially greater sensitivity (due to the ability to operate at higher frequencies), more rugged construction, and the ability to be batch-fabricated cheaply and reproducibly using standard microfabrication techniques. This latter feature also facilitates the production of matched multisensor arrays.

Figure 1 shows the basic structure of the SAW oscillator. It consists of a polished piezoelectric substrate, a pair of thin, evaporated-metal interdigital transducers (IDTs), and a feedback amplifier. An electric signal applied to one (input) of the IDTs is transformed into a mechanical wave by means of the piezoelectric effect. The wave then travels across the surface of the substrate to the other (output) IDT where it is transformed back into an electrical signal, amplified to account for losses in transit, and returned to the first IDT where the cycle starts again. In this configuration, the device oscillates at a resonant frequency, f_0 .

The width of the transducer electrodes, and the spaces between adjacent electrodes are each made equal to one-fourth of the desired wavelength. Since the velocity of the acoustic wave in the substrate is constant, the spacing of the transducer electrodes determines the resonant frequency (i.e., $f=V/\lambda$). The distance between each of the IDTs, called the delay path, is set to an integral number of wavelengths so that the propagating wave arrives at the second transducer in phase. The actual value of this distance is somewhat arbitrary: longer pathlengths improve the stability of the oscillator but also require higher amplifier gain. Typically, the pathlength is on the order of a few hundred wavelengths. The width of the IDT, which defines the aperture of the acoustic wave, is constrained by the need for impedance matching with the other circuit elements (e.g., the amplifier) and is generally on the order of 50-100 wavelengths. Note that for a constant impedance and acoustic pathlength (in units of k), the active area of the device scales as $1/f_0^2$. The devices used in this work consisted of a slightly modified design, where the input and output IDTs had different numbers of electrodes and the delay path was somewhat shorter than described above. This design results in a more stable output frequency, as it prevents the occurrence of so-called "mode-hops" where the frequency shifts by large amounts spontaneously.

Eq. 1, derived from the perturbation theory of Auld [34,35], gives an approximate expression for the change in oscillator frequency upon deposition of a thin, non-conducting, isotropic coating film,

$$\Delta f_c = (k_1 + k_2) f_0^2 h \rho_c - k_1 f_0^2 h^4 \mu [(\gamma + \mu)/(\gamma + 2\mu)] / V^2 \quad (1)$$

where Δf_c is the change in frequency due to coating deposition, k_1 and k_2 are negative substrate-dependent constants of the order 10^{-8} ($m^2/kg\cdot sec$), f_0 is the resonant frequency (Hz), ρ_c is the density of the coating film (kg/m^3), h is the coating film thickness (m), V is the

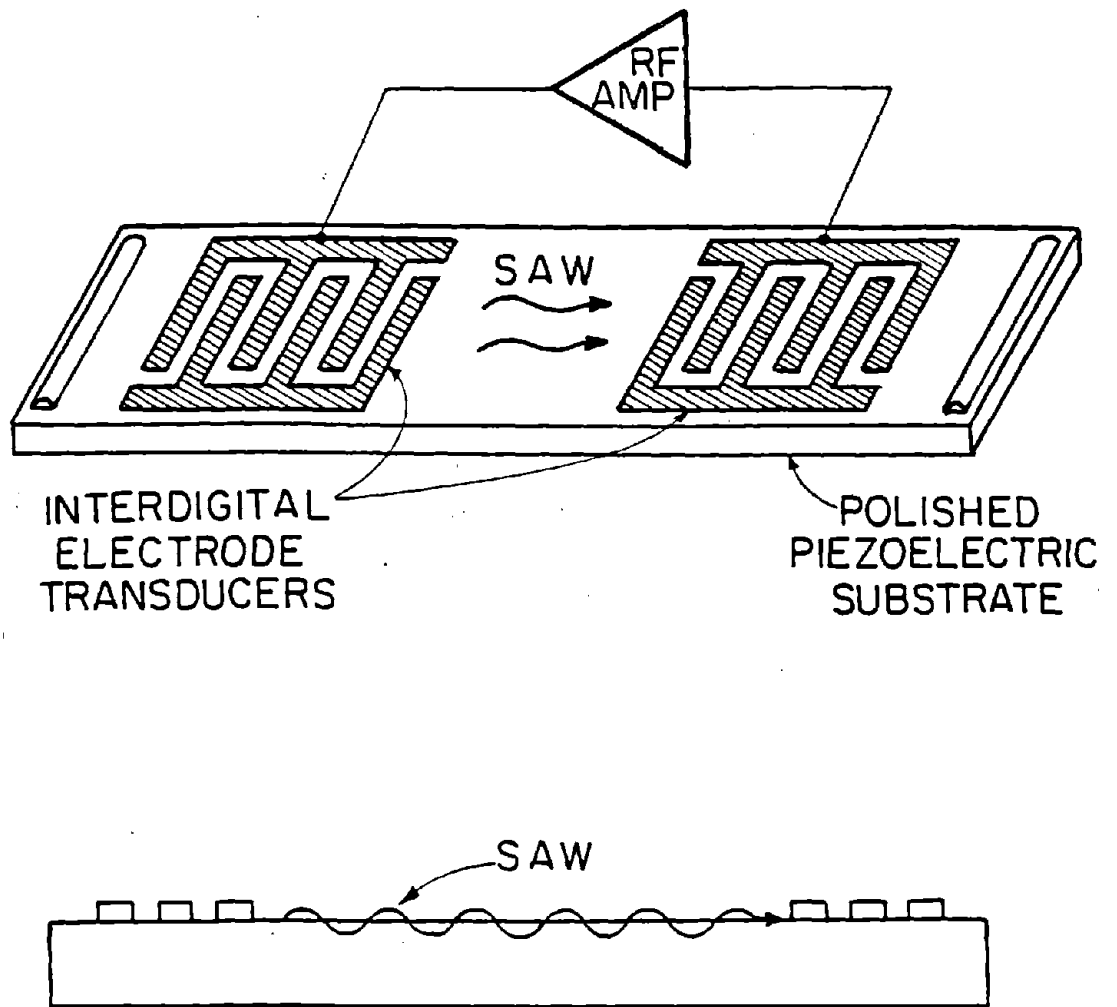


Figure 1. Basic components of the surface-acoustic-wave (SAW) oscillator and side view of wave propagation across the substrate surface.

acoustic wave velocity (m/sec), and γ and μ are respectively the Lamé constant and shear modulus of the film (N/m²). For most polymers, the first term on the right hand side of Eq. 1 is much larger than the second term, and Eq. 1 can be used to estimate the mass of coating deposited (note: $h\rho_c$ is equivalent to the mass per unit area m/a).

Upon exposure to a vapor, the polymer coating on the sensor will swell and soften in response to a given mass of vapor partitioning between the air and the coating. The following simplified equation can be used to describe the sensor response:

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

where Δf_v is the sensor response to the vapor, C_v is the vapor concentration in the air and K_e is an effective partition coefficient whose magnitude is affected by changes in the amount of mass in the coating and the degree of softening in the coating caused by the vapor. A more detailed discussion of this issue is provided in Chapter 3.

Interactions of Vapors with Sensor Coating Materials

The coating materials used in this study were polymers, oligomers, non-volatile liquids, and liquid crystals, many of which have been employed as stationary phases in gas chromatography. The selective partitioning phenomena employed for separations in GC can also be used to advantage here. These materials possess several advantages as chemically-sensitive surface layers in SAW sensors: they can be deposited as thin films of controllable average thickness, they are non-volatile and of homogeneous composition, and their physical and chemical properties (e.g., solubility) can be adjusted by varying their functionalities. The factors affecting the uptake and diffusion of gases and vapors in these materials will be reviewed briefly here. The (liquid) oligomers to be used are expected to behave like other non-volatile liquids and, therefore, will not be discussed specifically. Since liquid crystals represent a special case, they will be discussed separately in the next section.

The uptake (sorption) of vapors by a polymer can swell the polymer as the penetrant molecules increase the free volume between the polymer chains. Both the physical and chemical properties of the polymer are important in determining the rate and extent of vapor sorption. Of the physical properties, the glass-transition temperature, degree of crystallinity, and the extent of crosslinking are most important.

Below the glass transition temperature, T_g , the polymer is rigid, or glassy, because the individual polymer chains are relatively immobile. Above T_g , the polymer is referred to as rubbery since the polymer segments have a high degree of rotational and translational freedom

[36]. Due to this conformational freedom, the rate of sorption in rubbery polymers is governed by diffusional forces and sorption proceeds rapidly and reversibly. In glassy polymers, sorption is governed by a combination of diffusion and segmental relaxation. The latter process has a relatively long time constant, resulting in slower attainment of equilibrium. Often, these relaxations are irreversible, giving rise to anomalous hysteresis and memory effects [37]. Sorption hysteresis is also observed in highly crystalline and crosslinked polymers because of irreversible deformations of the crystalline order or the crosslinked sub-networks, particularly at high penetrant concentrations [36]. Glassy, crystalline and crosslinked polymers can also exhibit non-linear sorption behavior indicative of adsorption on specific sites in the polymer. The well-known 'dual-sorption' model [38], characterized by a linear region at low penetrant concentrations followed by a non-linear region is often used to characterize sorption in these types of polymers. In contrast, for amorphous, rubbery polymers it has been found that the sorption isotherms are linear over large concentration ranges, in accordance with a solution model of sorption (i.e., Henry's Law behavior) [36,39]. These factors render amorphous, rubbery polymers more desirable for consideration as SAW-sensor coatings.

Diffusion of gases and vapors in amorphous, rubbery polymers is described by Fick's Laws [40], with diffusion coefficients ranging from about 10^{-6} to 10^{-9} cm²/sec [41,42]. The vapor diffusion coefficient can be calculated from the slope of the absorption curve in the early stages of the sorption process [43]. Thus, the response time for equilibrium sorption in a given polymer can be related to the diffusion coefficient of the vapor by this equation. Note that the slope of the curve for a given polymer/vapor pair should not vary with concentration provided the polymer is initially free of vapor.

For thick polymer films, the concentration dependence of the diffusion coefficient can cause deviations from linearity in the initial stages of the sorption process, particularly for high vapor concentrations [44]. This is because the sorption process is long enough for the penetrant which initially diffuses into the film to swell the polymer and make it easier for subsequent penetrant molecules to be accommodated. This same effect is thought to be responsible for the increase in diffusion of vapors in polymers that already contain a certain amount of vapor (i.e., pre-swollen polymers). However, according to Park [44], for thin polymer layers and low vapor concentrations, such as used in this research, the sorption process is rapid enough that the linear region should be preserved.

For non-polymeric liquids, the diffusion coefficient of a vapor solute is inversely proportional to the viscosity of the liquid as well as inversely related to the molar volume of the vapor molecule according to the Stokes-Einstein and Wilke-Chang equations (D varies as $V^{0.3}$ or $V^{0.6}$, where V is the molar volume, depending on which of the previous two theoretical equations is used) [45]. Thus, for a given viscous liquid, the response time will be a

sensitive function of the size of the vapor molecule, and for a given vapor it will be a function of the viscosity of the liquid. The diffusion rates of vapors in polymers also depend upon the molecular size of the vapor, typically to a much greater extent than that for non-polymeric liquids [46,47]. For a given vapor, the strength of the molecular-size dependence varies with the mobility of the chains in the polymer [47]. As for liquids, this should lead to different sensor response times for a given vapor in different polymers and vice versa. An example of the magnitude of this effect is found in a recent report by Frye, et al. [48] who measured the diffusion coefficients of methanol, ethanol, and isopropanol in a polyimide film deposited on a SAW device. They found an increase of over three orders of magnitude in the experimental diffusion coefficients for this homologous series.

Monitoring the rate of diffusion, or response time, should provide a means for discrimination between different individual vapors in the sensor array. The rate curve resulting when two or more vapors with different diffusion coefficients are present simultaneously in significant concentrations would be expected to show a change of slope as each component approaches equilibrium at a different rate. By monitoring the transient response time over several short time intervals, it should be possible to detect when multiple species are present, and, by the values of the slope at different times, to gain some insight as to the nature of the different species present. However, as noted above, we have found that for the rubbery-amorphous-solid polymers and liquid polymers and oligomers used in this study, responses were too rapid to take advantage of these effects.

The amount of vapor that partitions into a polymer or non-volatile liquid at a given vapor concentration is strongly dependent upon the vapor pressure and solubility of the vapor in the stationary phase. This topic has been studied extensively in the context of gas chromatography where differential partitioning of vapor-phase analytes into the stationary phase is used to obtain separation of the analyte mixture [45]. Efforts to develop predictive theoretical models of chromatographic retention behavior based on correlations of the structures and solubility properties of the vapor and stationary phase have so far failed because the interactions involved are invariably due to a combination of several forces. However, empirical models such as that developed by Rohrschneider [49] and later refined by McReynolds [50,51], Karger [52], and Patte and Laffort [53] have provided classification schemes for an extensive list of chromatographic solutes and stationary phases. Related work by Kamlet et al. [54,55] using the phenomenon of solvatochromism has been useful in characterizing solvation interactions for a number of solvents. Several researchers have applied pattern recognition methods to the extensive chromatographic data compiled by McReynolds [51] in order to classify stationary phases according to similarities in retention behavior and, thereby, identify a subset of unique stationary phases that provide the best

separation for the widest number of compounds. We made use of such an analysis [30] to guide our initial selections of coating materials for this study.

Liquid Crystals

The term liquid crystal (LC) refers to an unusual state of matter that is intermediate between a crystalline solid and an isotropic liquid [54]. Mechanically, a compound in the LC state behaves as a liquid, but the molecules cannot rotate freely so that a certain degree of order persists. Most molecules exhibiting LC states are rod-shaped with adjacent molecules lying parallel and rotation being permitted only about the long axis. Three main types of liquid crystals are known: nematic, in which only the axis of rotation is constrained; smectic, in which the molecules are further constrained to move collectively in layers; and cholesteric, which exhibit a spiral anisotropy due to the presence of an optically active center in the component molecules. For most LCs the LC state is brought about by heating the crystalline solid above the melting point. Rather than passing directly from the crystalline to the normal isotropic liquid, these materials go through one or more stable intermediate LC states. Further heating leads to the transition to an isotropic liquid.

The anisotropy of the LC state results in optical birefringence that can be controlled by the application of an electric or magnetic field. This feature has led to their widespread use in optical displays [55]. This anisotropy also affects their solvent properties. That is, there is a preference for rigid and/or rod-like molecules to dissolve in nematic liquid crystals relative to their flexible or branched analogues due to their ability to "fit" between the parallel molecules of the liquid crystal [56]. This factor has been used to advantage in gas chromatography to achieve separations of, for example, various positional isomers of benzene (e.g., dihalo- and dialkyl- derivatives) and pyridine (e.g., 3- and 4-picoline) that were difficult to separate on conventional isotropic stationary phases [56-58]. In all cases the para-substituted ring had the longest retention time. Similar separations of various naphthalenes, PAHs, alkanes and alkenes have been achieved using LC stationary phases [59]. Other factors, such as polarity, hydrogen-bonding, etc., also influence the vapor-LC interaction; however, for similarly substituted compounds the shape factor is expected to dominate the solubility behavior.

In general, vapor partitioning in a liquid or polymer decreases with increasing temperature because the absorption process is exothermic. Since most of the liquid crystals developed for gas chromatographic applications have melting points $> 100^{\circ}\text{C}$ [59], their use in a SAW vapor sensor is of limited value: the selectivity they impart would likely be more than offset by the lack of sensitivity if used at these temperatures. Relatively few chemically stable LCs with nematic ranges at or near room temperature have been studied in the context of

vapor partitioning phenomena. One report by Oweimreen et al. [60] described the use of two room-temperature nematic LCs as chromatographic stationary phases. Retention characteristics for these materials were similar to those of other higher-temperature LCs. Unfortunately, only one of the compounds used in that study is chemically stable. The other compound is subject to hydrolysis and therefore unsuitable for our application. Hydrolytic and oxidative instability is common in many LC materials due to the presence of imino, azo, and benzoate ester linkages in their structures.

Young et al. [61] reported the synthesis of a series of highly stable trans-stilbene derivatives that exhibit liquid crystalline behavior near room temperature. Another series of compounds reported by Songsheng et al. [62] also combine room-temperature (or near-room temperature) nematic ranges with chemical stability. Since the start of this study, several other room-temperature nematic LCs were identified. In lieu of synthesizing such room temperature nematic liquid crystals, as originally planned, we employed two commercially available liquid crystal mixtures in our study of potential size/shape selectivity of this class of materials.

Pattern Recognition

Pattern recognition involves the use of multivariate statistics and other numerical analyses to uncover relationships in multidimensional data sets. The application of pattern recognition methods to chemical analyses, termed "chemometrics" [63], has been useful in interpreting complex chromatographic [64], spectroscopic [65], and other analytical data [66]. Examples of pattern recognition methods used to interpret multisensor array data have already been cited [20-22]. Similar analyses were employed here using the ARTHURTM software package [67] on one of the Microvax computers in the Department of Electrical Engineering and Computer Sciences. Subsequently, we developed an alternative pattern recognition method that could be run on a personal computer and we employed this method in all subsequent analyses (see Chapter 2).

The initial step in multisensor development is the calibration of the individual sensor responses for each of the analyte vapors. Here, a standard linear regression model was employed because the equilibrium sensor responses were found to vary linearly with the concentration of each vapor. Thus, for each sensor one obtains an equation of the form $y_i = a_i c_i$, where y_i is the sensor response for a given concentration, c_i , of the i th vapor, and a_i is the slope, or sensitivity (a zero intercept is assumed). The combination of responses to each of the n sensors in the array can be represented as a pattern vector composed of all of the sensor responses for that vapor at a given concentration. The response vectors obtained at several concentrations can be used or the slope (a_i) of the linear response curve (i.e., the sensitivity per

unit concentration) can be substituted for the actual response values. Since each vapor will give a characteristic response vector, the sensor array can be represented by an $n \times m$ matrix wherein the n columns are the sensor coatings and the m rows are the vapors.

Since the magnitudes of the sensor responses can vary greatly for different vapors it is common practice to normalize each pattern vector by dividing each response by the square root of the sum of the squared values of the individual sensors [26]. This process results in all vectors having a length of unity and permits consideration of the data independent of concentration and sensor sensitivity. Autoscaling can then be performed to standardize the data to a mean of zero and a standard deviation of one, which facilitates the subsequent multiple linear regression (MLR). From the MLR, sensors that do not contribute a significant amount of unique information can be identified and eliminated (or replaced) to optimize the array.

At this point, pattern recognition methods for displaying and classifying the data are employed. Since the matrix elements represent points in n -dimensional space, a means for displaying the data in two dimensions is required. The Karhunen-Loeve expansion method is most often used here to construct a covariance matrix from which a set of transformed variables are calculated. These new variables, called eigenvectors, consist of linear combinations of the original sensor responses that are calculated in such a way as to maximize the amount of descriptive information (i.e., variance) in the data matrix. Each successive eigenvector describes less and less of the variance. In addition, all eigenvectors are orthogonal, or independent from each other. The weighting assigned to each sensor in the eigenvector indicates its contribution to the variance. Here again, it is possible to eliminate sensors from subsequent analyses if they do not contribute measurably to the descriptive power of the array. In most cases two eigenvectors are sufficient to describe the majority of the information in the matrix. These can be displayed in a two-principal-component plot which projects the higher dimensional data onto a two-dimensional plane. A non-linear mapping routine can be used, if necessary, to aid in preserving the spatial separations in the projected display.

Several hierarchical clustering methods are available for grouping similar responses according to a chosen criterion for homogeneity. These data can then be displayed in a so-called dendrogram which indicates graphically the degree of similarity of the array responses for each vapor. From this plot or the principal-components plot, one can determine qualitatively the ability of the array to discriminate between the vapors. Chemically similar vapors would be expected to cluster somewhat near each other. If the separation obtained between the vapors is greater than the random error of measurement then unique identification of the vapor will be possible.

For mixtures of vapors the pattern vectors for each of the mixture components are linearly combined to form a new composite vector that can be treated in the same fashion as the vector for an individual vapor. Since the component pattern vectors are linearly independent, it is possible to decompose the pattern for the mixture and determine the unique identities and concentrations of each of the mixture components. An important assumption in this case is that the sensors respond additively to each vapor. That is, the presence of one vapor does not affect the sensitivity of the sensor to another vapor. Another assumption is that the number of components in the mixture is always less than the number of sensors in the array (i.e., the overdetermined case).

Materials and Methods

The 42 vapors studied are listed according to chemical class in Table 1 along with their ACGIH-TLV values [69]. Aside from including vapors having a wide range of functional groups, chemicals with recognized toxicity and assigned TLV values were chosen so that the results would have immediate relevance to occupational health professionals. In a few cases, certain compounds were included based on their structural similarity to another member of the same class in order to test the expected size/shape discriminating power of the array. All of the chemicals were available commercially as high-purity liquids and were used without further purification.

The materials tested as sensor coatings are described in Chapters 3-5. They represent a diversity of structures, functional groups and solubility properties. Many of these materials were chosen based on a pattern recognition analysis reported by Huber and Reich [30] on the GC retention data for 158 solutes on 75 stationary phases. Using several hierarchical clustering methods they found that the 75 stationary phases could be classified into 12 groups, where each group comprised phases with similar chromatographic retention values. We selected members (or structurally similar analogues) from 10 of these groups as sensor coatings in our experiments (two groups contained materials that were either hygroscopic or not commercially available). In addition to these materials, other organic polymers were included based on their anticipated selective solubility properties. All of the polymers included are above their respective glass transition temperatures at room temperature so that vapors would be rapidly and reversibly sorbed, sorption isotherms would be linear over a wide range of concentration, and diffusion would be Fickian.

Figure 2 shows a photograph of a 158-MHz dual SAW sensor mounted on a TO-8 header. The sensor was wire-bonded to the leads on the header using gold wire. For testing,

Table 1. List of vapors by class with 1992-1993 ACGIH-TLV values

Vapor	ACGIH-TLV		Vapor	ACGIH-TLV	
	(ppm)	(µg/L)		(ppm)	(µg/L)
1. Aromatic Hydrocarbons			7. Esters		
benzene	10	32	n-amyl acetate	100	532
toluene	50	188	n-butyl acetate	150	713
m-xylene	100	434	methyl methacrylate	100	410
p-xylene	100	434			
2. Aliphatic Hydrocarbons			8. Chlorinated Aromatics		
hexane	50	176	benzyl chloride	1	5.2
cyclohexane	300	1030	chlorobenzene	10	46
isooctane	--	--	2-chlorotoluene	50	259
nonane	200	1050	4-chlorotoluene	--	--
			1,3-dichlorobenzene	75	451
3. Aromatic Amines			9. Chlorinated Aliphatics		
aniline	2	7.6	chloroform	10	49
N,N-dimethylaniline	5	25	1,1,1-trichloroethane	350	1510
pyridine	5	16	methylene chloride	50	174
2,4-lutidine	--	--	trichloroethylene	50	269
2,5-lutidine	--	--			
4. Aliphatic Alcohols			10. Aromatic Olefins		
2-methoxyethanol	5	16	styrene	50	231
n-butanol	50	152	α-methylstyrene	50	242
methanol	200	262	4-methylstyrene	50	242
2-propanol	200	492			
5. Ketones			11. Aliphatic Olefins		
acetone	750	1780	1-hexene	--	--
2-butanone	200	590	cyclohexene	300	1010
cyclohexanone	25	100			
3-heptanone	50	234			
6. Ethers			12. Amide		
1,4-dioxane	25	90	dimethylformamide	10	30
ethyl ether	400	1210			
tetrahydrofuran	200	590			

sensors were incorporated into the prototype four-sensor array instrument shown in Figure 3. Each sensor could be inserted into a socket on a circuit board that had the ancillary components (reference sensor, mixer, amplifier, frequency counter) required to collect frequency measurements via personal computer. The sensors and the prototype instrument were obtained from Microsensor Systems, Inc. (Bowling Green, KY).

Thin films of the coating materials were deposited on the sensors as solutions in volatile solvents using an air brush. The amount of coating deposited was monitored via the net frequency shift of the sensor before and after coating (i.e., Δf_c). Depositions were controlled to give Δf_c values in the range of 150-225 kHz, corresponding to calculated film thicknesses of about 0.05-0.1 μm (Eq. 1). Each set of four coated sensors was then exposed to each of several vapors and/or vapor mixtures. Following exposure to a set of test vapors, the coatings were removed by washing with a suitable solvent and then other coatings were applied and tested in a similar fashion. A total of 16 coating materials were tested. Pattern recognition methods were then used to analyze the stored sensor responses and determine an optimal set of coatings for identification of certain subsets of vapors. Exposure to a series of binary vapor mixtures was performed to verify the discriminating ability predicted by the pattern recognition analysis of the individual-vapor responses.

The atmosphere-generation and data-collection system used is shown schematically in Figure 4. Dilution-air flow, temperature, and humidity were controlled with a Miller-Nelson Research HCS 301 control unit. Vapors of the liquid contaminants were introduced to the dilution air stream by passing nitrogen through a thermostatted fritted-glass bubbler containing the material. These sources were diluted as needed to cover the desired concentration ranges and properly mixed to ensure a uniform concentration before passing to the in-line gas analyzer. Vapor concentrations were monitored using an in-line infrared gas analyzer (Foxboro, MIRAN 1A) and/or by taking aliquots of the vapor stream and injecting them into a gas chromatograph (Varian, Model 2860 equipped with an FID and an HP 2290A electronic integrator). For binary vapor mixtures, a second bubbler was added to the system and the vapor concentrations were monitored by gas chromatography. Stainless-steel or Teflon tubing was used to transport the air contaminants throughout the system.

Each sensor had a separate nickel-plated lid with inlet and outlet tubing which was connected to the system via Teflon tubing. The total internal volume was < 1 mL and for the flow rates used (0.080-0.250 L/min) the mixing time was less than a few seconds. The temperature of the sensors was controlled by contacting the lids of each sensor in the array to an aluminum block through which thermostatted water was passed. A thermocouple was used to monitor the temperature above the surface of the sensor.

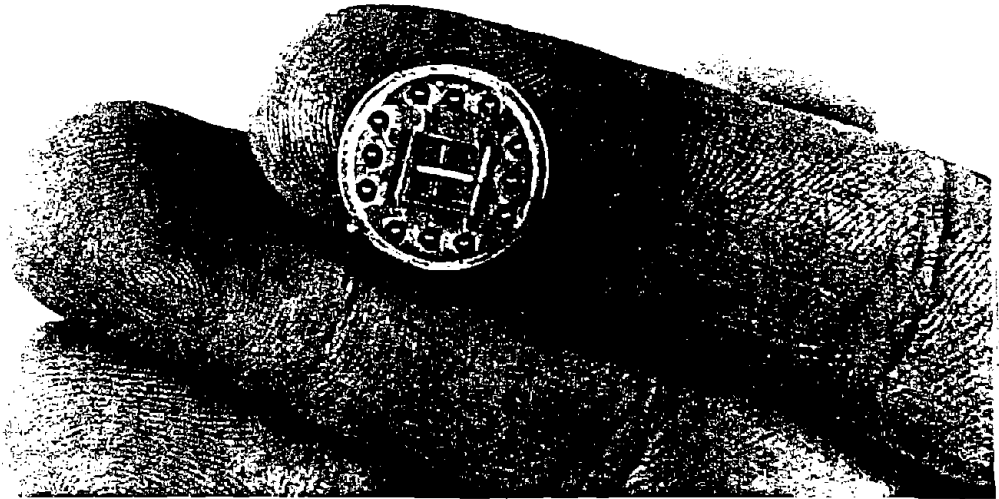


Figure 2. Dual 158-MHz sensor mounted on a T-08 header.

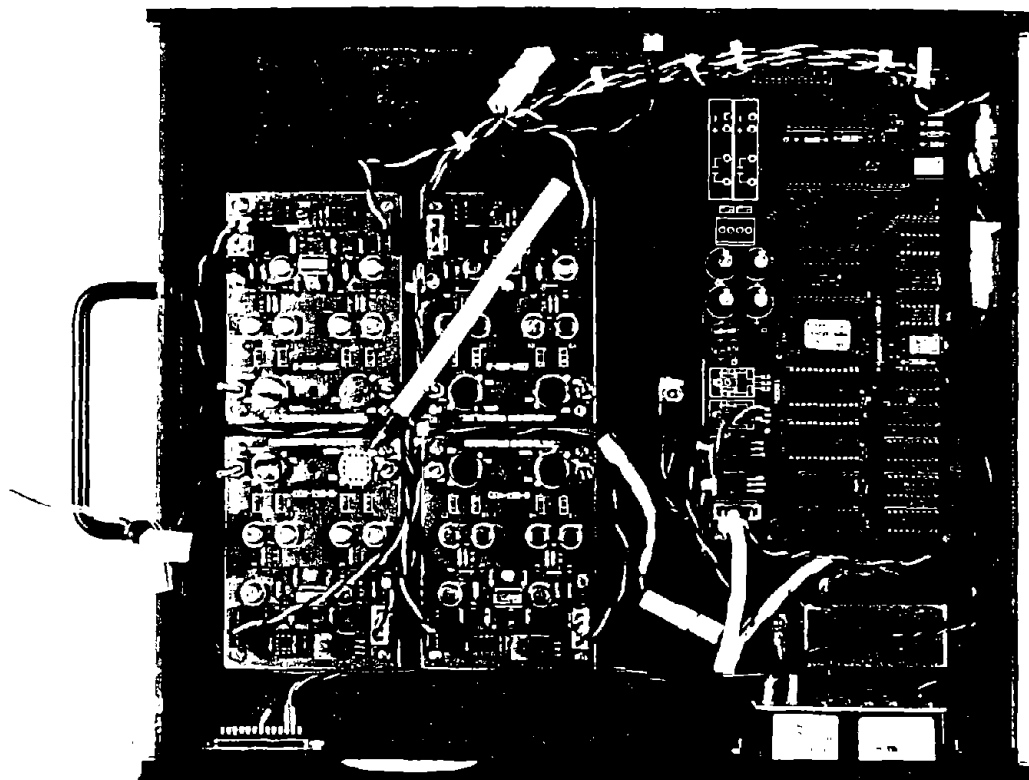


Figure 3. Prototype four-sensor array instrument used for testing coated SAW sensor responses.

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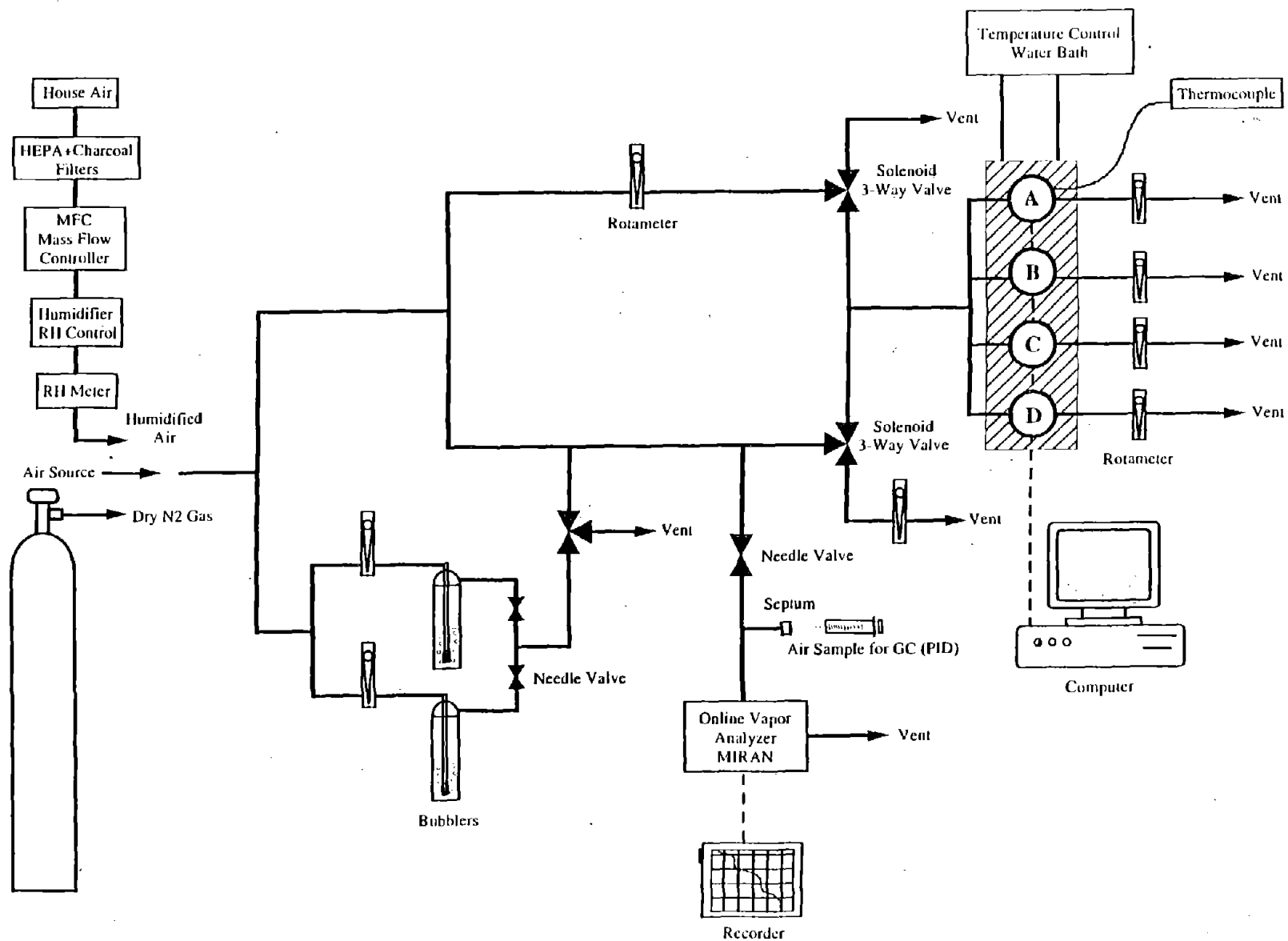


Figure 4. Schematic of the test-atmosphere generation and data acquisition system.

The flow over each sensor was controlled with a dedicated rotameter placed downstream. Continuous air flow was maintained over the sensors to avoid any convective cooling that might occur with the introduction of the contaminated airstream. Switching from clean air to contaminated air (and vice versa for purging) was achieved with a 4-port valve upstream from the array.

For each exposure, the baseline frequency was measured every 2 sec for several minutes before exposure then the vapor was introduced for 40-60 sec (enough time to ensure that equilibrium sorption had been attained), and then the sensors were purged with clean air for several minutes. This procedure was performed in duplicate for each concentration of vapor. The net frequency shift was averaged and used in the construction of response curves. The responses of the sensors to xylene or benzene vapors were tested repeatedly over the course of the study period to monitor the stability of the coatings and the accuracy of analytical instrumentation.

Response curves were subsequently generated and compiled using a spreadsheet program (Lotus 123). Pattern recognition analyses were then performed as described in detail in subsequent chapters. Additional experimental details specific to each segment of the project are also provided in subsequent chapters.

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CHAPTER 2

EXTENDED DISJOINT PRINCIPAL COMPONENTS REGRESSION ANALYSIS OF SAW VAPOR SENSOR ARRAY RESPONSES

Synopsis

The application of a disjoint principal components regression method to the analysis of sensor array response patterns is demonstrated using published data from 10 polymer-coated surface-acoustic-wave (SAW) sensors exposed to each of nine vapors. Use of the method for the identification and quantitation of the components of vapor mixtures is shown by simulating the 36 possible binary mixtures and 84 possible ternary mixtures under the assumption of additive responses. Retaining information on vapor concentrations in the classification models allows accurate vapor identification while facilitating prediction of the concentrations of individual vapors and the vapors comprising the mixtures. The effects on the rates of correct classification of placing constraints on the maximum and minimum vapor concentrations and superimposing error on the sensor responses are investigated.

Introduction

The use of sensor arrays coupled with pattern recognition analysis constitutes an effective approach to enhancing the selectivity and range of applications of chemical sensors. It has been demonstrated for several gas/vapor sensor technologies that a single sensor array can provide unique response patterns for a number of different individual species or mixtures of species [1-9]. However, few reports have addressed the problem of determining both the identity and concentration of the components of gas/vapor mixtures [7-9].

We are interested in the development of portable instrumentation based on microfabricated chemical sensors for monitoring personnel exposures to toxic organic solvent vapors in the industrial environment. The use of polymer-coated surface-acoustic-wave (SAW) sensor arrays has several potential advantages for this application. First, SAW devices respond with high sensitivity to changes of surface mass and, as a result, can be used for a wide range of potential analytes [10]. Second, the amount of vapor sorbed by the sensor coating on the device is typically a linear function of the vapor concentration over the useful concentration range (i.e., < a few hundred parts-per-million by volume). Third, efficient operation is possible at ambient

temperatures. Indeed, vapor sorption decreases exponentially with increasing temperature so higher sensitivity is obtained at lower temperatures. Finally, since the response to a given vapor will depend strongly 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 [11].

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 [12-14]. Typically, principal component 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. Ideally, responses for different analytes will cluster in different regions of n -dimensional space, where n is the number of sensors used. 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). Criteria for classification are established using supervised learning methods such as the K-nearest-neighbor (KNN) technique or the linear learning machine (LLM). For mixtures, responses will usually trace a locus of points between those of the individual components [2,5]. 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) [7,14]. For sensors exhibiting non-linear responses with concentration, the data can be transformed in order to linearize the responses [3,8]. Use of MLR on matrices containing redundant or collinear sensor responses may lead to large quantitation errors, whereas PLS and PCR are less sensitive to collinearity [14].

Disjoint principal components modelling [15] and its more familiar derivative SIMCA (soft independent modeling of class analogy) [12,13,16] 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. Although these methods have been used for classification in a number of analytical chemical applications [17-19], they have not been applied to the analysis of data from sensor arrays.

As will be shown here, the concepts underlying these methods can be extended to permit identification of both individual vapors and the components of vapor mixtures from the sensor response patterns. In this extended disjoint principal components regression (EDPCR) method advantage is taken 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.

This paper describes the implementation of EDPCR for sensor-array analysis using previously reported data from an array of polymer-coated SAW sensors exposed to each of several vapors. Experimental responses to the individual vapors are combined to simulate all possible binary vapor mixtures and predictions are then made of both the identities and concentrations of vapors. Misclassification rates are examined with and without constraints placed on the vapor concentrations and then with varying amounts of Gaussian error superimposed on the sensor responses. Finally, the accuracy of classification is determined for the case where all possible ternary mixtures are included in the test set.

Data Description

The data used here were published by Rose-Pehrsson et al. [5] and consist of the responses of 10 polymer-coated SAW sensors to each of nine vapors. The vapors examined were dimethylmethylphosphonate (DMMP), dimethylacetamide (DMAC), dichloroethylene (DCE), diethyl sulfide (DES), water (H₂O), isooctane (ISO), toluene (TOL), 1-butanol (1BTL), and 2-butanone (2BTN). The original report contains the structures of the polymer coatings, which are designated here only as P1-P10.

Sensor responses are presented in Table 1 as the equilibrium frequency shifts caused by exposure to the vapors, Δf_v (in Hz), divided by the frequency shifts caused by initial deposition of the polymer coating on each sensor, Δf_c (in kHz). Presenting the data in this manner accounts for the differences in response arising from variations in the amount of polymer deposited on each sensor [5].

The relationship between the airborne vapor concentration, C_v , and the sensor response is given by

$$C_v = \Delta f_v \rho_c / (\Delta f_c K_e) \quad (1)$$

where ρ_c is the polymer density, K_e is the "effective" polymer/air partition coefficient of the vapor reflecting the potential role of changes in the polymer modulus (in addition to the added mass of sorbed vapor) on the response of the sensor [20] (see Chapter 3 for further explanation).

The data matrix consists of sensor responses to each of four or eight concentrations of each vapor. Each row can be represented as a response vector composed of the 10 sensor

Table 1. Sensor responses in Hz/kHz (from ref. 5) and linear regression correlation coefficients.

Group	Vapor	Conc ug/L	Polymer Coatings									
			P1	P2	P3	P4	P5	P6	P7	P8	P9	P10
1	DMAC	81	67.10	9.10	3.97	-0.68	2.60	3.32	158.80	-4.58	2.57	0.47
		40	57.06	7.06	2.97	-0.39	1.26	1.91	124.99	-3.81	1.34	0.29
		20	33.94	3.27	1.54	-0.24	0.55	0.93	92.21	-2.74	0.62	0.22
		11	18.83	1.69	0.81	-0.17	0.28	0.54	69.54	-1.96	0.34	0.17
		(r ²)	(0.846)	(.903)	(0.921)	(0.999)	(0.999)	(0.993)	(0.948)	(0.900)	(0.998)	(0.996)
2	DMMP	2230	257.62	90.66	38.94	-2.64	45.25	44.84	939.92	-8.46	39.53	4.31
		1100	207.48	56.64	25.05	-2.25	24.92	24.07	414.63	-8.24	21.42	2.72
		559	160.80	31.99	14.44	-1.88	14.11	11.48	346.16	-7.97	10.32	1.09
		372	142.23	24.28	10.84	-2.01	11.48	8.01	321.69	-8.00	6.73	0.74
		137	128.81	20.50	8.31	-1.45	7.02	3.90	228.80	-5.95	2.95	1.13
		84	102.79	13.44	5.53	-1.15	4.97	2.32	183.50	-4.90	1.63	1.70
		52	83.89	8.51	4.02	-0.84	3.62	1.53	157.92	-4.27	0.93	0.44
		29	58.70	4.54	2.33	-0.62	2.44	0.80	124.49	-3.18	0.44	0.40
		(r ²)	(0.873)	(.979)	(0.979)	(0.715)	(0.996)	(0.998)	(0.964)	(0.496)	(0.998)	(0.870)
3	DCE	176000	35.59	56.62	113.18	16.99	47.49	115.79	69.05	52.82	122.03	22.27
		86600	19.35	30.51	72.07	8.05	23.44	55.64	29.07	21.96	54.86	15.50
		45700	8.98	14.34	39.72	3.80	11.03	27.12	11.99	8.86	23.42	7.78
		30500	6.05	9.04	24.75	2.49	7.78	18.45	8.19	5.97	16.54	5.76
		(r ²)	(0.997)	(.997)	(0.979)	(0.999)	(0.999)	(0.999)	(0.996)	(0.996)	(0.998)	(0.959)
4	DES	137000	50.45	13.02	48.54	5.86	17.02	66.28	133.40	72.38	35.56	5.33
		68700	26.68	6.99	33.85	2.14	8.50	32.46	69.59	32.56	34.51	3.85
		35400	11.83	3.14	18.40	0.85	4.13	15.63	32.91	13.55	14.84	1.85
		23600	8.29	2.31	12.94	0.32	2.80	10.96	22.75	8.39	9.81	1.21
		(r ²)	(0.997)	(.997)	(0.961)	(0.994)	(0.999)	(0.999)	(0.999)	(0.999)	(0.728)	(0.936)
5	H ₂ O	7180	9.71	8.23	2.44	35.23	1.99	1.95	20.49	-2.20	1.35	24.44
		3550	4.86	5.41	0.48	12.85	0.32	0.28	7.57	-1.46	0.72	5.79
		1820	2.51	3.63	0.02	4.91	-0.28	-0.01	4.04	-1.20	0.52	-0.40
		1210	1.89	2.93	-0.03	2.86	-0.38	-0.13	1.58	-1.49	0.24	-2.31
		(r ²)	(0.999)	(.995)	(0.961)	(0.992)	(0.989)	(0.958)	(0.989)	(0.815)	(0.977)	(0.990)
6	ISO	129000	13.43	0.54	7.33	0.82	1.48	21.25	35.17	78.95	25.22	0.54
		64300	5.90	0.06	4.78	0.61	0.74	10.78	14.88	33.49	11.63	1.02
		33100	2.52	0.04	2.67	0.45	0.38	5.10	6.20	13.84	4.90	0.65
		22000	1.77	0.06	1.98	0.13	0.29	3.57	3.76	9.19	3.42	0.56
		(r ²)	(0.998)	(.867)	(0.982)	(0.818)	(0.999)	(0.999)	(0.998)	(0.997)	(0.999)	(0.008)
7	TOL	57300	22.07	11.73	40.07	3.22	17.94	69.59	56.83	77.31	77.83	4.07
		28400	14.53	7.41	29.82	1.28	8.67	33.95	29.95	37.10	40.68	3.29
		14500	7.68	3.91	17.24	0.56	4.11	16.52	13.32	15.66	17.89	1.95
		9680	5.11	2.68	12.11	0.17	2.91	11.58	7.84	9.36	11.15	1.25
		(r ²)	(0.971)	(.982)	(0.938)	(0.998)	(0.999)	(0.999)	(0.996)	(0.999)	(0.997)	(0.883)
8	1BTL	8730	31.90	8.06	19.37	3.46	8.92	13.68	104.22	-4.72	13.26	7.90
		4300	15.45	3.94	11.29	1.64	5.25	6.71	62.13	-4.10	7.01	4.78
		2200	7.46	2.04	6.05	0.91	2.98	4.29	52.67	-3.68	5.36	2.61
		1460	5.42	1.53	4.43	0.50	2.37	2.84	29.02	-3.04	2.87	2.33
		(r ²)	(0.999)	(.999)	(0.994)	(0.998)	(0.997)	(0.997)	(0.952)	(0.886)	(0.979)	(0.993)
9	2BTN	148000	185.01	45.37	55.67	10.36	41.18	67.73	325.67	17.58	66.37	11.15
		74800	110.72	22.77	35.05	5.69	19.57	35.52	199.64	5.81	30.60	9.33
		38700	65.33	11.27	18.91	2.80	9.68	15.83	136.41	1.32	15.22	4.48
		25800	45.78	7.51	12.62	1.49	6.88	9.73	111.75	-0.13	10.30	3.81
		(r ²)	(0.995)	(.999)	(0.984)	(0.994)	(0.999)	(0.998)	(0.999)	(0.995)	(0.998)	(0.869)

responses to a given concentration of a given vapor. For the purpose of analysis, we define a group as the set of response vectors (rows) for a given vapor over all concentrations.

In the original study a number of binary mixtures were also examined, but the mixture responses were not published and therefore could not be incorporated into our analyses. However, the authors state that the responses to vapor mixtures were additive (i.e., linear combinations of the pure vapor responses) or approximately additive in all but a few cases. Thus, the simulation of mixtures performed here under the assumption of additivity has a reasonable foundation.

Since the measured responses consisted of difference frequencies between the coated sensors and uncoated reference sensors, positive values reflect a reduction in the coated-sensor frequency. For most of the vapors the difference-frequency responses were positive as expected for the increase in mass and/or softening of the polymer coating accompanying vapor sorption. For a few vapor/polymer pairs negative frequency shifts were observed due either to significant vapor adsorption on the uncoated surface of the reference sensor or to an alternative response mechanism operating on the coated sensor (e.g., stiffening of the polymer film). Regardless, all data were used in the analyses presented below.

Method of Analysis

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 modeled using the most significant principal component(s). Rather than normalizing the response vector by its magnitude (i.e., concentration-normalization) or autoscaling, as is commonly performed prior to PCA [4,5], the only preprocessing that is performed is mean-centering (i.e., subtraction of the mean response vector from the individual response vectors for a group). Therefore, information about the concentrations of the vapors is accessible during classification.

The model used to classify vapor i is given by

$$\mathbf{r} = \mathbf{m}_i + \sum_{n=1}^N \alpha_{i,n} \mathbf{v}_{i,n} + \boldsymbol{\varepsilon} \quad (2)$$

where $\mathbf{r}$ is the response vector for the vapor at a given concentration, $\mathbf{m}_i$ is the mean response vector determined from all of the calibration concentrations measured for that vapor, $\alpha_{i,n}$ is the projection coefficient corresponding to the location of each response vector along the n th principal component represented by the unit vector $\mathbf{v}_{i,n}$, $\boldsymbol{\varepsilon}$ is the residual error vector of the model

for the vapor at the measured concentration, and N is the number of principal components.

Where it is unclear how many principal components should be included, a cross-validation method can be used to obtain the optimal number [12]. The accuracy of the model can be assessed merely by inspection of the residual error or by construction of confidence intervals.

Provided that at least some of the sensors in the array respond 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 ($\mathbf{r}_u$) can be tested for its goodness of fit to each of the models established during calibration by replacing $\mathbf{r}$ by $\mathbf{r}_u$ in Eq. 2 and solving for α_u so that $\|\varepsilon\|_2$ is minimized (see Appendix 1). The identity of the unknown is determined from the model for which the smallest $\|\varepsilon\|_2$ is obtained. Additional criteria can be imposed by constraining the residual error vector within a certain range, which would be more appropriate when there is no prior knowledge about the nature of the unknown vapor (i.e., where it may not belong to any of the vapors in the calibration set).

Once the identity of the vapor has been established, its concentration can be readily determined by interpolation or by linear regression of α_i vs. 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. Although this condition generally holds for low concentrations of most organic solvent vapors measured with polymer-coated SAW sensors [5], certain vapors may exhibit non-linear response characteristics. Transformation would then be necessary for accurate quantitation. Figure 1 illustrates the classification and quantitation processes with this approach.

For mixtures of two components whose responses are additive, 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):

$$\mathbf{r} = \mathbf{m}_i + \mathbf{m}_j + \alpha_i \mathbf{v}_i + \alpha_j \mathbf{v}_j + \varepsilon \quad (3)$$

where $\mathbf{r}$ 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 α_i and α_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.

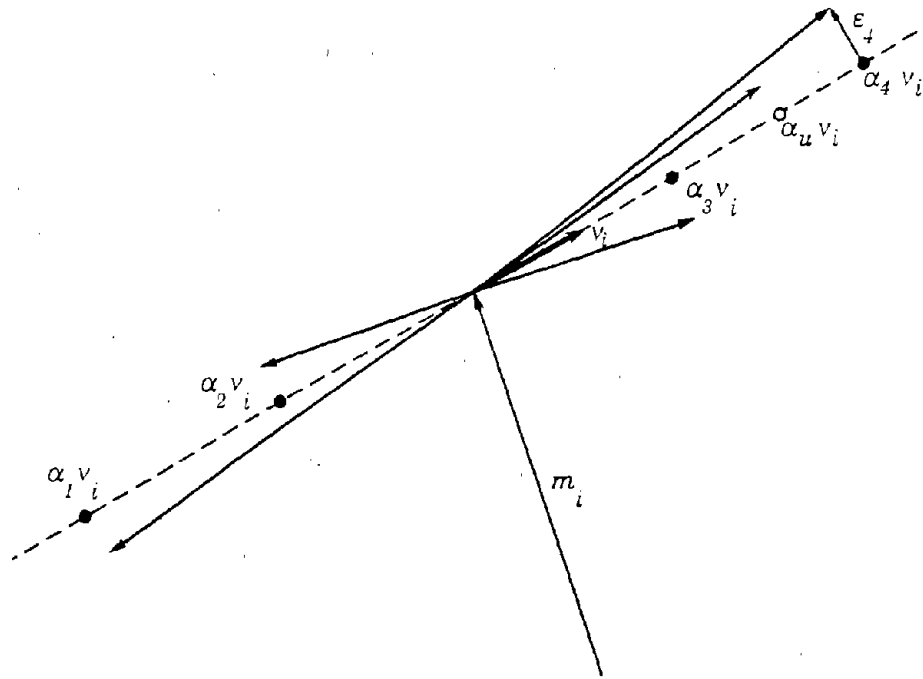


Figure 1. Graphical representation of a one-principal-component model for an individual vapor showing the four calibration responses (filled symbols), the residual error from projection onto the principal component v (represented by ϵ_4), and the projection of a hypothetical unknown belonging to this class (open symbol). The vapor concentration is proportional to the distance along the principal component.

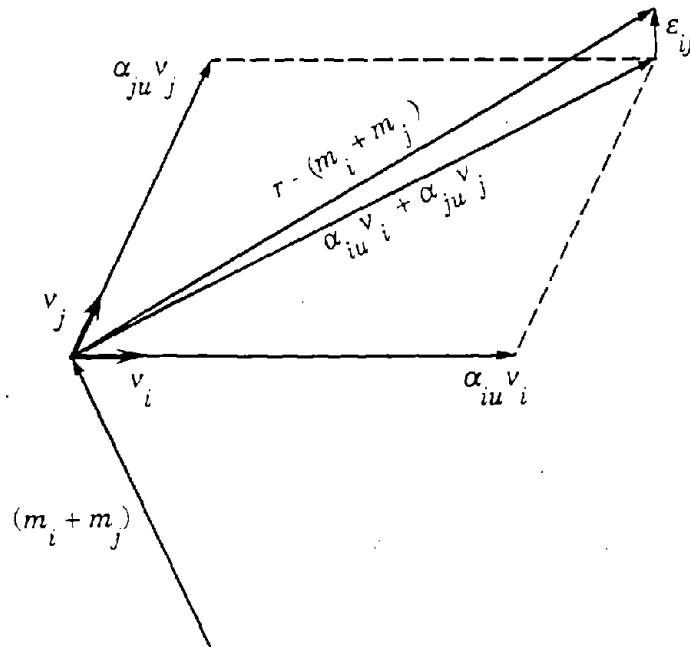


Figure 2. Graphical representation of a one-principal-component model for a binary mixture and the projections used to determine each vapor concentration (see Appendix 1).

The response vector for the binary mixture can be projected onto the principal component of each vapor and the concentrations can be obtained from the calibration data for the individual vapors. Note that the principal component for one vapor may not be orthogonal to that of the other vapor and this must be taken into account in determining the vapor concentrations (see Figure 2 and Appendix 1). Models analogous to Eq. 3 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 demand 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.

Criteria for establishing the maximum values for hazardous vapors might be based on some multiple of the allowable exposure limit (e.g., the Threshold Limit Value [21] or Permissible Exposure Limit [22]). Constraints on the minimum response would logically be based on the limit of quantitation attainable with the sensor array which, in turn, would be determined by the signal-to-noise ratio. Since the range of possible concentrations is rendered finite, the probability of misclassification is reduced. For a binary mixture, such constraints would result in a "box" such as that shown in Figure 3, which accounts for the possibility that residual errors would place the sample vector above or below the ideal mixture plane. 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.

All computations described here were performed by one of the authors (T.S.P) either on a DEC-5000 workstation using programs written in PV~WAVE® (Precision Visuals, Inc., Boulder, CO) or on a personal computer using programs written in MATLAB® (Mathworks, Inc., Natick, MA).

Results and Discussion

Classification of Individual Vapors. PCA was performed on each group in Table 1. Table 2 shows that the percentage of the total variance explained by the first principal component for each group was very high. Therefore, a one-principal-component model of the form shown in Eq. 2 with $N=1$ was adopted for subsequent analyses.

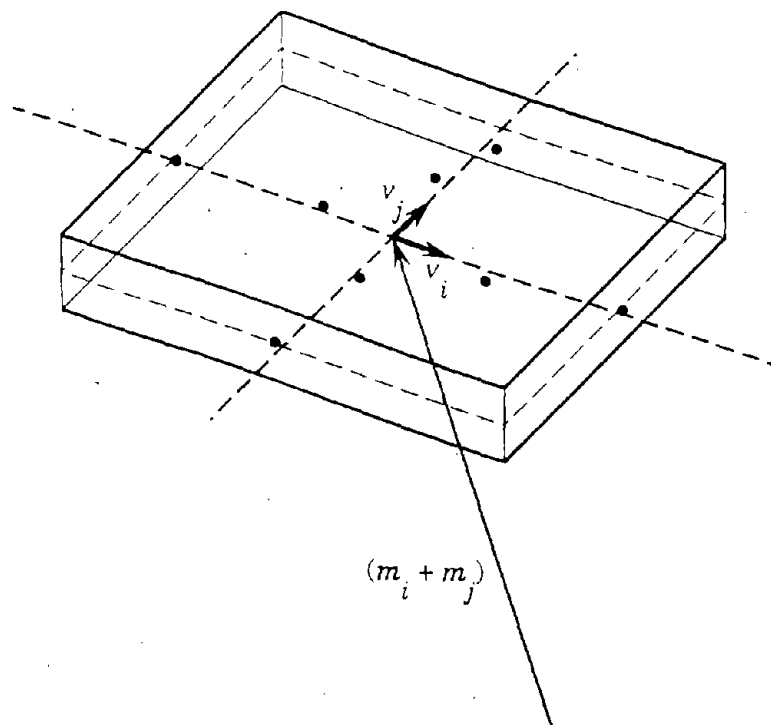


Figure 3. Binary-mixture classification space with constraints placed on the maximum and minimum concentrations of both vapors in the mixture.

The four response vectors for each vapor (or eight for DMMP) were regressed with the principal components to determine values of α_i and ϵ for each concentration of each vapor i . Table 2 presents the mean residual error of the model for each group in absolute and relative terms, where the relative errors are the averages of the ratios of the residual-error vectors to the response vectors. The relative errors are low ($< 8\%$) in all cases, however, the absolute error for DMMP is significantly larger than those for the other vapors. The larger absolute error obtained for DMMP can be attributed to the larger absolute sensor responses and to non-linearities in the responses of several of the sensors as a function of vapor concentration. Linear regression correlation coefficients (r^2) were calculated for each of the sensor responses and are presented in Table 1. Although most sensor responses are linear functions of the vapor concentrations, exceptions are seen for nearly all vapors. Deviations from linearity are most apparent with DMMP for which seven of the 10 r^2 values are below 0.99. Inspection of the individual sensor response curves (not shown) confirm the exceptional behavior of DMMP. The small r^2 value obtained for ISO with the P10 sensor has a negligible effect on the fit to the model apparently because of the very low response for this specific sensor.

Plots of the projection coefficients (α_j) versus concentration were linear ($r^2 > 0.992$) for all but three of the vapors. Those for the exceptional vapors are shown in Figures 4 a-c (note: each point represents the projection of the 10-sensor response vector onto the principal

Table 2. Variance explained by the first principal component of responses to each vapor and the residual errors of the classification models.

Vapor	Variance on First Principal Component (Percent)	Mean Residual Error (Hz/kHz)	Mean Relative Residual Error (Percent)
DMAC	99.4	2.53	2.1
DMMP	99.0	20.6	7.4
DCE	99.4	5.16	7.0
DES	98.9	5.39	7.8
H ₂ O	99.9	0.59	6.5
ISO	99.9	0.57	2.5
TOL	99.7	2.41	4.8
1BTL	99.1	2.45	5.2
2BTN	99.9	3.44	1.8

component for that vapor at the indicated concentration). Linear plots for most of the vapors would be expected because the projection coefficients are estimated from combinations of the individual (linear) sensor responses. The predominance of the non-linear sensor responses to DMMP is reflected in Figure 4a. Surprisingly, the plots for DMAC (Figure 4b) and 1BTL (Figure 4c) are also clearly non-linear. For DMAC, most of the individual sensors gave linear responses. The shape of the curve in Figure 4b reflects the influence of a minority of sensors (P1-P3 and P7) that gave large, non-linear responses. Similarly, for 1BTL the shape of Figure 4c reflects that of the sensor giving the highest response (P7) to this vapor.

That a few sensors can have such a large influence on the overall response pattern arises from the fact that the response vectors were not autoscaled prior to modelling. Thus, sensors providing higher responses have a greater influence on the group response vector. The skewness created by the dominant sensors could be reduced by applying weighting factors to the sensor responses, but this was not performed for the analyses here.

DMMP and DMAC are both high-boiling (>160°C) solvents containing polar functional groups. The shapes of Figures 4a and b reflect the influence of these factors on their interactions with several of the sensor coatings. The plateaus in the responses at the intermediate-to-high concentrations indicate interactions with, and saturation of, specific sorption sites in the polymers. The subsequent inflection point for DMMP denotes the onset of another mode of sorption at higher concentrations. The DMAC curve suggests adherence to a Langmuir or Freundlich sorption model while the DMMP curve resembles that of a BET sorption model [23]. For 1BTL, no such physical interpretation is possible and it is suspected that the non-linearity is the result of an error in calibration for the third highest concentration. Despite the non-linearities in their

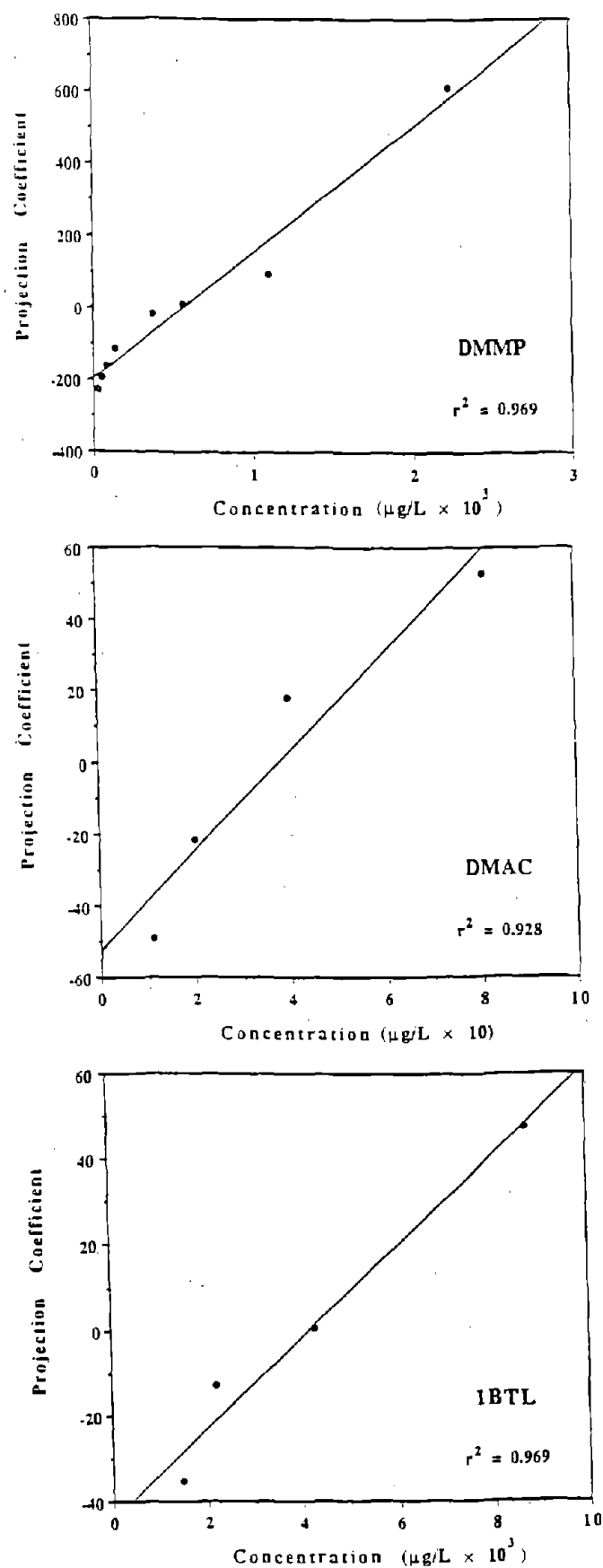


Figure 4. Plot of vapor concentration versus projection coefficient, α_i , for a) DMMP, b) DMAC, and c) 1BTL. The line and r^2 value in each plot were determined by linear regression.

responses, the residual errors for the DMAC and IBTL models are still quite small (Table 2).

Table 3 presents the normalized mean residual errors obtained by fitting the responses from one group to each of the other groups. The mean residual error for the correct group was used as the basis for normalization. Each row contains the error obtained on attempting to fit the vapor corresponding to that row to the models for the vapors listed at the top of each column. As expected, the between-group errors are larger than the within-group errors in all cases. Note, however, that for DMMP the errors obtained in attempting to classify it into the other groups are invariably smaller than those for the other vapors. This further confirms that the DMMP data are more scattered about the model values than the other vapors. It also indicates that the response vectors for DMMP fall in fairly close proximity to those for several of the other vapors.

Classification/Quantitation of Individual Vapors and Vapor-Mixture Components. To examine the use of EDPCR for classifying the pure vapors and their binary mixtures, a test set was created using the response vector for the third-highest concentration from each group. Response vectors were then calculated for all possible binary mixtures by combining the responses for the individual vapors. This yielded 45 "unknown" response vectors consisting of the nine individual vapors and the 36 binary mixtures. The limited amount of data available precluded the use of separate data for the test set. Each of these unknown vectors was then tested for goodness of fit to all possible groups using Eqs. 2 and 3.

With no constraints placed on the concentrations of the vapors, 36 of the 45 unknowns (80%) were correctly classified. The classification test was repeated with the added constraint that the predicted concentrations had to be greater than zero. In this case the correct classification rate was 38/45, or 84%. Most misclassifications (six out of seven) involved DMMP: pure DMMP was misclassified as a mixture of DMMP with DMAC; and in four of the five remaining misclassifications involving DMMP the error resulted from assignment of the unknown as a mixture of DMAC with another vapor rather than DMMP with another vapor. The misclassifications are consistent with the data in Table 3 which show that the residual between-group:within-group error ratio for classification of DMMP as DMAC is quite small (2.2 Hz/kHz).

The residual errors for these six misclassifications were relatively large (~7-16 Hz/kHz) compared to those for the 38 correctly classified samples (generally < 5 Hz/kHz). This suggests that a limit could be placed on the maximum allowable residual error as a threshold for classification. The same test set was analyzed again with the further constraint that the minimum and maximum vapor concentrations could not exceed those in the calibration set. In this case, the correct classification rate increased to 43/45, or 96%. The two misclassifications involved mixtures of DMMP with other vapors. The increase in correct classifications as increasing

Table 3. Ratios of within-group to between-group residual errors.

Vapor	DMAC	DMMP	DCE	DES	H ₂ O	ISO	TOL	1BTL	2BTN
DMAC	1	17	44	24	10	17	28	6.6	21
DMMP	2.2	1	6.4	4.3	3.2	3.8	4.8	3.2	3.0
DCE	23	67	1	11	5.4	8.2	6.9	12	37
DES	14	42	13	1	4.4	5.7	6.1	6.8	21
H ₂ O	180	564	182	141	1	70	120	96	337
ISO	194	595	163	101	35	1	69	106	345
TOL	45	138	21	17	9.3	11	1	23	76
1BTL	12	38	41	20	8.7	17	26	1	17
2BTN	5.4	30	34	18	12	17	24	5.7	1

Table 4. Correct classification rates (based on 100 trials) as a function of superimposed Gaussian error applied to sensor responses for EDPCR and KNN methods.

Superimposed Error	EDPCR		KNN	
	Correct Classification	Standard Deviation	Correct Classification	Standard Deviation
0	95.5	0	100	0
5	88.6	3.6	91.9	3.5
10	78.7	4.5	80.6	4.7
15	68.9	5.2	70.8	5.2
20	60.2	6.3	61.7	5.9
25	52.4	6.2	53.9	5.8
30	46.6	5.6	47.8	6.2

constraints are placed on the concentrations of the vapors illustrates the advantage of retaining and utilizing concentration information in the classification analysis.

For the above analyses, the test set used to examine the classification models was extracted from the calibration set. To more accurately represent practical conditions where sensors might exhibit random fluctuations about their true values, tests of classification were repeated with the addition of varying amounts of Gaussian error to the sensor responses. For each level of superimposed error, 100 simulations were performed. The rates of correct classification are presented in Table 4. Standard deviations were less than 6.3% indicating that the estimation procedure was reasonably stable. The correct classification rate is seen to decline fairly rapidly with added error. To put these results into perspective, a second classification method based on the K-nearest-neighbor technique ($K=1$) was applied to the data (after normalizing the data matrix). Table 4 also presents the classification rates using the KNN technique. Note that, by definition, the classification rate with the KNN method was 100% for the case of no superimposed error because the samples used in the test set were identical to those in calibration set. Comparing the results for the two methods shows that as the error increases, the correct classification rates are virtually the same for both methods. The slightly lower rates obtained with the EDPCR method reflect modeling error, however, this is offset by the reduction in the number of computations involved in classification relative to the KNN method.

Concentrations were then predicted for the 43 samples correctly classified with the EDPCR method under the last test condition (i.e., maximum and minimum bounds). A total of 77 predictions were made corresponding to 68 binary mixture components (i.e., 2×34 correctly classified binary mixture components) and 9 individual vapors. Projection coefficients were determined as described in Appendix 1 and concentrations were then predicted by linear regression using the relationships between the projection coefficients (α_j) and the vapor concentrations discussed above. The results showed that 66 of the 77 (86%) values were within 20% of the actual concentration values and most were within 10%. Of the 11 concentrations that were not accurately predicted, 8 of these involved 1BTL. In fact, none of the concentration predictions for 1BTL were accurate. As can be seen in Figure 4c, this is an artifact of having chosen the third highest concentration for 1BTL, which is well above the regression line. Since the prediction for pure 1BTL was in error, the predictions of 1BTL concentrations in the mixtures were also in error. The other four concentrations that were not predicted accurately involved mixtures of DMMP and DMAC with each other or with other solvents.

In practice, the approach taken above for concentration predictions would likely be modified. That is, for those vapors giving linear plots of concentration versus α_j , the concentration values obtained from linear regression would be used to create a calibration curve which would account for the slight deviations of the individual points from the overall linear

trend. This approach would reduce the errors obtained with 1BTL and would also improve the concentration predictions for most of the other vapors. For DMAC and DMMP, whose projection coefficients vary non-linearly with concentration, a log transformation could be performed prior to quantitation. Figures 5 a and b show that plots of log concentration versus α_i for these vapors (omitting the highest DMMP concentration) describe the data better than the regression lines in Figures 4 a and b. Commensurate improvements in the accuracy of predicted concentrations would be expected.

A final analysis was performed by including all possible ternary mixtures in the test set. Correct classification rates using the third sample from each of the individual response vectors from a group were 67%, 71% and 85% for the unconstrained, partially constrained (i.e., positive values only) and fully constrained (maximum and minimum bounds) conditions, respectively. For the last condition, 18 of the 19 misclassifications involved DMMP and 15 of these involved DMMP in ternary mixtures with other vapors. Correct classifications were obtained for the remaining 110 vapors and vapor mixtures.

Conclusions

The EDPCR method described here is an alternative to other methods that have been used for analyzing sensor array responses. It is particularly well-suited for arrays of polymer-coated SAW sensors where the responses to individual vapors are linear and responses to mixtures of vapors are additive. Deviations from linearity can be tolerated without adversely affecting the classification outcomes, but in extreme cases linearizing transformations may be required as a pre-processing step. Accommodation for non-additive mixture responses should also be possible with this method provided that some proportionality in responses is maintained between the mixture components over the relevant concentration ranges.

The EDPCR method takes advantage of the inherent structure of the response data in both the classification and quantitation procedures which improves the computational efficiency. Additional samples are easily incorporated into the data set since the principal components models are based on the individual vapor responses.

Due to limitations on the data available, the test set examined here was derived from the calibration set and mixture responses were simulated rather than generated experimentally. Work

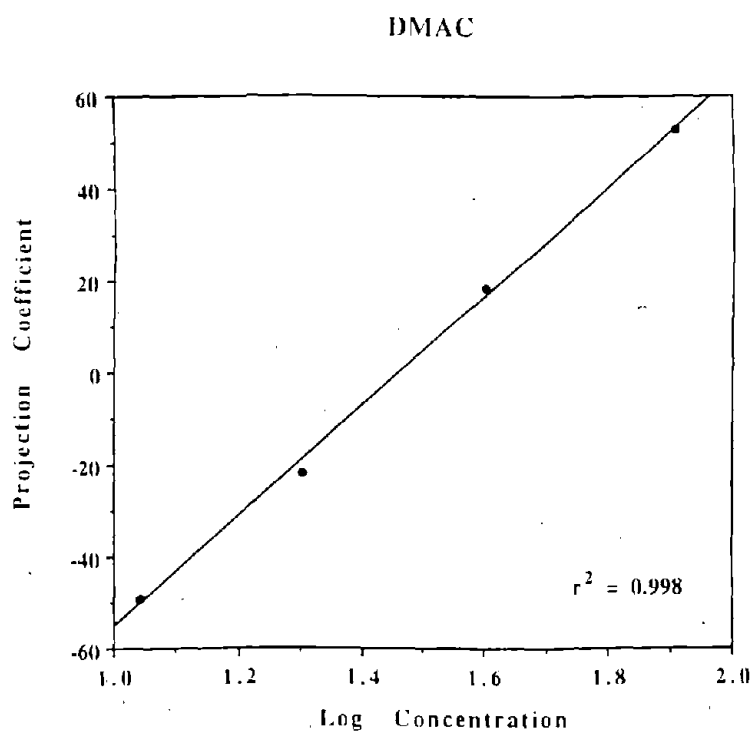
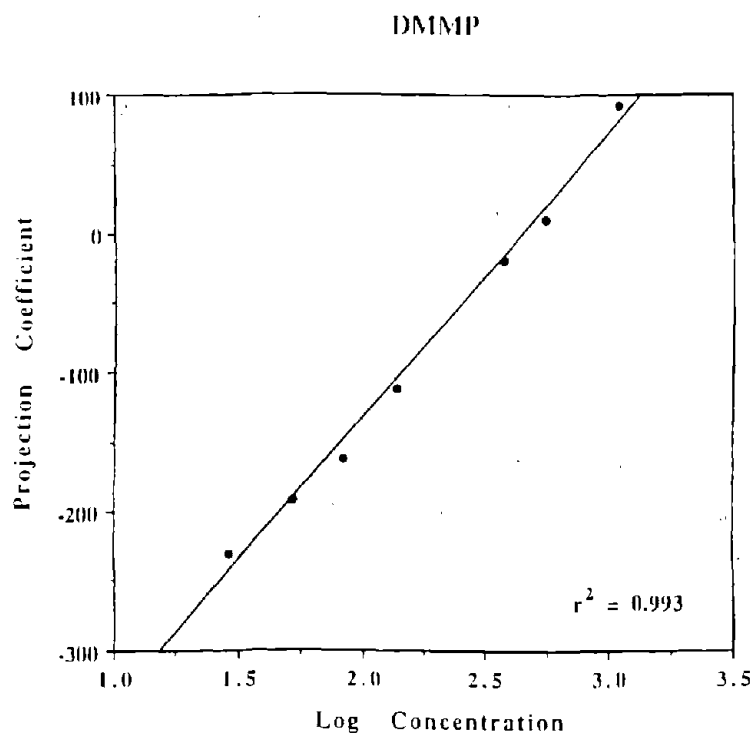


Figure 5. Plots of log concentration versus projection coefficient for a) DMMP (highest concentration omitted) and b) DMAC. The line and r^2 value in each plot were determined by linear regression.

is currently underway to generate a data set for a wide range of organic vapors using several different polymer coatings that will yield separate calibration and test samples. Mixture responses are also being collected to further test the validity of the additivity assumption. EDPCR analyses of these data will be discussed in Chapter 4.

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Appendix 1.

The procedure for determining the projection coefficients used to fit an unknown response vector r_u to models based on pure vapor i or a mixture of vapors i and j using a one-principal-component model is described. From Eq. 2, classification of r_u as a specific vapor i is indicated if

$$r_u = m_i + \alpha_{ui}v_i + \epsilon_u \quad (A1)$$

and the Euclidean distance $\|\epsilon_u\|$ is small. From the orthogonality principle [24], $\|\epsilon_u\|$ is minimized when ϵ_u is orthogonal to v_i , which means that the inner product of ϵ_u and v_i is zero, i.e., $(\epsilon_u, v_i) = 0$. Therefore, taking the inner product of Eq. A1 with v_i and solving for α_{ui} we have

$$\alpha_{ui} = (r_u - m_i, v_i) \quad (A2)$$

Similarly, if r_u consists of a mixture of vapors i and j , r_u can be expressed as

$$r_u = m_i + m_j + \alpha_{ui}v_i + \alpha_{uj}v_j + \epsilon_u \quad (A3)$$

and, again, $\|\epsilon_u\|$ has to be small. In this case, ϵ_u has to be orthogonal to v_i and v_j , i.e., $(\epsilon_u, v_i) = 0$ and $(\epsilon_u, v_j) = 0$. Taking the inner product of Eq. A3 with v_i and v_j separately,

$$(r_u - m_i - m_j, v_i) = \alpha_{ui} + \alpha_{uj}(v_j, v_i) \quad (A4a)$$

and

$$(r_u - m_i - m_j, v_j) = \alpha_{ui}(v_i, v_j) + \alpha_{uj} \quad (A4b)$$

One can derive, in matrix notation,

$$\begin{bmatrix} \alpha_{ui} \\ \alpha_{uj} \end{bmatrix} = \begin{bmatrix} 1 & (v_i, v_j) \\ (v_i, v_j) & 1 \end{bmatrix}^{-1} \begin{bmatrix} (r_u - m_i - m_j, v_i) \\ (r_u - m_i - m_j, v_j) \end{bmatrix} \quad (A5)$$

Inversion of the matrix is performed to account for the fact that v_i and v_j may not be orthogonal.

CHAPTER 3

CHARACTERIZATION OF POLYMERIC SURFACE-ACOUSTIC-WAVE SENSOR COATINGS AND SEMI-EMPIRICAL MODELS OF SENSOR RESPONSES TO ORGANIC VAPORS

Synopsis

Responses from an array of four polymer-coated surface acoustic wave sensors exposed to a series of 39 organic vapors were used to investigate sensor response models based on vapor boiling point, solubility parameters, and solvation parameters in conjunction with linear solvation energy relationships. As part of this effort, sensor response data were used to estimate the solubility parameters and solvation parameters of the sensor coatings by adaptation of methods originally developed for use with gas-liquid chromatographic retention data. Values of these parameters were found to be consistent with the structures of the coatings though in some cases different from those determined by other methods. Discrepancies were attributed to differences in the conditions used for the determinations. Sensor responses were linear over the concentration ranges examined and could be summarized using the empirically determined partition coefficient, K_e , for each vapor/coating pair. Linear correlations were found between $\log K_e$ and vapor boiling point and the slopes of the regressions lines were similar to those expected for ideal behavior. The strength of the correlations decreased with increasing coating polarity, and it was necessary to divide the vapors into two or three broad chemical classes in order to obtain satisfactory results. Improved correlations were found by use of Hildebrand solubility parameters in a model based on regular solution theory which attempts to account for non-ideal vapor-coating interactions. The use of solvation parameters in linear solvation energy relationships, however, provided the strongest correlations, with modeled K values falling within a factor of two of experimental values in all cases and within $\pm 25\%$ of experimental values in 83% of the cases. Application of these models to the prediction of sensor-array response patterns appears promising.

Introduction

Numerous reports have appeared over the past three decades on the use of bulk-acoustic-wave (BAW) and surface-acoustic-wave (SAW) devices for the measurement of organic vapors [1-4]. Typically, a polymer or high-boiling liquid is coated on the surface of the device to sorb the vapor and thereby enhance sensitivity relative to the uncoated device. Advantages of using such coatings include the rapid and spontaneously reversible sensor

responses obtained, and the ability to expose the sensor repeatedly without significant changes in the physical or chemical properties of the coating. At the same time, the low energy of the sorptive vapor-coating interactions involved results in many vapors being capable of partitioning into the coating which, in turn, limits the selectivity achievable.

Recognition of this limitation has led to research on sensor arrays comprising a set of individual BAW or SAW sensors each coated with a different partially-selective sorptive material [5-7]. The collective response from the array yields a pattern that can be used ideally to identify a given vapor or at least to classify it in terms of structure or solubility properties. With proper design, such an array can measure several different vapors individually or in simple mixtures.

Deciding which coatings to include in the array for such an application hinges on two criteria, sensitivity and selectivity. As a general rule, each coating should contribute unique information about the identity of the vapor, meaning that coatings of similar structure which will provide redundant or colinear responses should be avoided. Qualitative guidance in the selection process can be obtained through considerations of coating and vapor physicochemical properties affecting the magnitude of the solubility interactions [8] or by use of principal components or cluster analyses of sensor calibration data [9]. However, a satisfactory method for accurately predicting sensor responses has not yet emerged.

The analogy between the partitioning phenomenon that governs the responses of polymer-coated BAW vapor sensors and the separation of analytes in gas-liquid chromatography (GLC) was recognized many years ago [10-12] and has been revisited recently in studies of polymer-coated SAW vapor sensors [13,14]. The partition coefficient, K , which can be determined from GLC specific retention volumes, is a useful summary measure of equilibrium vapor-polymer solubility at a given temperature that can be defined by [15]:

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

where C_c is the concentration of a vapor in the chromatographic stationary phase and C_v is the air concentration of the vapor. The following equation has been reported as a means of deriving vapor partition coefficients from the responses of a polymer-coated SAW oscillator [13]:

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

where Δf_v is the sensor frequency shift (i.e., sensor response) caused by the vapor being sorbed

by the coating, Δf_c is the initial frequency shift caused by deposition of the coating, ρ_c is the coating density, and the subscript e is used here to indicate that K is determined experimentally using sensor responses.

Inherent in Eq. 2 is the assumption that the sensor response is dominated by mass-loading effects. Under this condition, K and K_e should be equivalent. In a recent report [14], however, it was found that K_e values determined for several vapor-polymer combinations via Eq. 2 were much larger than K values determined from GLC measurements - K_e was about four times greater than K on average. It was suggested that the increased SAW responses were due to changes in the polymer modulus accompanying swelling by the vapor and a model was proposed to account for the modulus effects.

Although computer modeling using high-frequency polymer modulus data for several polymers has shown that the change of frequency due to a given fractional change of coating mass is greater than that due to comparable fractional changes of modulus [16], there is evidence indicating that changes of polymer modulus accompanying vapor sorption may be very large relative to changes of mass [14,17]. Unfortunately, data on high-frequency polymer moduli and the effect on the moduli of vapor sorption are not available for many polymers suitable for SAW sensor coatings, so that a complete assessment of the importance of modulus changes on sensor responses is not possible. To the extent that modulus changes contribute to the measured value of K_e , it cannot be considered a true partition coefficient as defined in Eq. 1. Nonetheless, the evidence cited above [14] and further evidence presented in this report indicates that K_e is, within error, proportional to K and that K_e can serve as a useful summary of the sensitivity of the sensor to a given vapor in a manner analogous to the use of K to summarize the GLC retention behavior of a vapor analyte. So, for sensor coatings consisting of liquid or rubbery-amorphous solid polymers that provide linear increases in sensor response with vapor concentration, Eq. 2 provides an accurate description of sensor responses.

It is reasonable therefore to seek to apply models developed for describing GLC solute retention behavior to the estimation of polymer-coated SAW sensor responses to organic vapors. Perhaps the simplest model to consider is based on the correlation between vapor boiling point, T_b , and $\log K$, which is approximately linear within an homologous series of vapors and generally yields a series of parallel lines for different homologous series on a given GLC stationary phase [18-20]. For non-polar phases, vapors from several different homologous series have been described quite well by the same line. Even on more polar stationary phases, different series of vapors could be described by the same K- T_b relationship. A few examples of the correlation between T_b and sensor responses can be found in early reports on sorption-based BAW sensors [10,12], but the potential for general application in predicting responses has not been explored.

Another modeling approach that has been used in GLC is based on regular solution theory [21], where Hildebrand solubility parameters are employed to account for the non-ideality of vapor-stationary phase interactions [22]. In a limited investigation reported by Snow and Wohltjen, the responses of a poly(ethylene maleate)-coated SAW sensor to five vapors were compared to those expected from a consideration of the vapor and coating solubility parameters [23]. Although the order of sensor responses to the vapors agreed reasonably well with expectations, a quantitative model was not developed.

A third approach to modeling GLC partition phenomena entails the use of solvation parameters in conjunction with linear solvation free energy relationships (LSER) [24-28]. In this case, the partition coefficient is defined empirically in terms of the various intermolecular interaction forces (e.g., dispersion, dipole-dipole, hydrogen-bonding) that affect solubility. The concept of using LSERs in the context of characterizing and selecting SAW sensor coatings has been described [8], but experimental studies of LSERs for the purpose of quantitatively modeling sensor responses have not been reported.

In this paper we investigate models of SAW vapor sensor responses based on vapor boiling point, solubility parameters, and solvation parameters in LSERs. After discussing the theoretical background and key simplifying assumptions of the models, each model is tested using experimental response data obtained by exposing four polymer-coated SAW sensors to each of 39 organic vapors representing 11 chemical classes. The correlations between experimental and modeled results are assessed and the potential for practical application of the models in the development of SAW vapor sensors is discussed. We also describe how SAW sensor response data can be used to estimate solubility parameters and solvation parameters of sensor coatings by simple adaptation of methods originally developed for use with GLC data.

Theoretical Background and Model Descriptions

Boiling Point (BP) Model. The solubility of a vapor in a polymer is a function of the volatility of the vapor and the strength of the intermolecular vapor-polymer interactions [29]. The partition coefficient, K , is a measure of vapor solubility that can be described by the following well-known expression used to characterize the retention of vapors in GLC [19]:

$$K = \rho_1 RT / \gamma_2 M_1 p_2 \quad (3)$$

where ρ_1 and M_1 are the density and molecular weight of the stationary phase, respectively, p_2 is the saturation vapor pressure of the solute vapor, γ_2 is the vapor activity coefficient ($\gamma = 1$ for ideal solutions), and K is unitless. Thus, at a given temperature K is ideally inversely

proportional to p_2 .

The following approximate expression, based on Trouton's Rule and the Clausius-Clapeyron equation, relates p_2 to T_b [19]:

$$\log p_2 \approx 7.7 - T_b(t/2.303RT) \quad (4)$$

where t is the Trouton constant for the vapor.

Taking logarithms of both sides of Eq. 3, combining constants and substituting into Eq. 4 yields

$$\log K = C'' + T_b(t/2.303RT) \quad (5)$$

where C'' is a constant. For most non-hydrogen-bonding vapors t varies from 22-24 cal/mole-K [15]. So, for an operating temperature of 298 K, the second term on the right hand side of Eq. 5 will range from 0.016(T_b) to 0.018(T_b). The linear relationship between $\log K$ and T_b predicted by Eq. 5 is the basis for the BP model examined here.

Solubility Parameter (SP) Model. Deviations from the ideal vapor-polymer solution behavior described above are observed in most real systems even in the dilute concentration range. The activity coefficient in Eq. 3 can be used to account for non-ideal behavior. The regular solution theory developed by Hildebrand et al. [21] assumes that deviations from ideality arise from the non-zero heat of mixing, which can be related to the infinite-dilution activity coefficient and to the solubility parameters of the polymer, δ_1 , and solute vapor, δ_2 by²²

$$\log \gamma_2^\infty = \Delta H_m/(2.303RT) = V_2(\delta_1 - \delta_2)^2/(2.303RT) \quad (6)$$

where V_2 is the vapor molar volume.

The solubility parameter of a substance is defined as the square-root of the molar vaporization energy per unit volume and, as such, is a measure of cohesive energy (or enthalpy) [30]. Solubility parameter values for many common solvents and polymers have been published [30,31]. Since they generally increase with increasing polar substituents in a molecule, solubility parameters are commonly used as indices of overall polarity. In general, the more similar the solubility parameter values of two materials, the lower their heat of mixing and the greater their mutual solubility.

The simplifying assumptions inherent in the regular solution theory are most closely

approximated for interactions between non-polar or slightly polar materials. For systems where specific oriented chemical interactions such as hydrogen-bonding are predominant; the theoretical assumptions break down and discrepancies between expected and observed solubility behavior generally increase. Although a number of more complex approaches have been developed that expand the solubility parameter concept to account for such interactions [31], the original approach has the advantage of simplicity and still finds many useful applications [30,31].

Combining Eq. 6 and Eq. 3 yields

$$\log K = \log[\rho_1 RT/(M_1 p_2)] - V_2(\delta_1 - \delta_2)^2/(2.303RT) \quad (7)$$

which illustrates that for situations where δ_1 and δ_2 differ appreciably (ie, where the activity coefficient will be greater than unity) the partition coefficient will be correspondingly reduced relative to the ideal case.

Since most commercially available polymers have a range of molecular weights, it is difficult to define M_1 precisely. As shown by Snow and Wohltjen [23], it is possible to define a relative partition coefficient, K_r (atm^{-1}), that can be used to compare the partitioning of different vapors in a given polymer at a given temperature:

$$\log K_r = -(\log p_2) - V_2(\delta_1 - \delta_2)^2/(2.303RT) \quad (8)$$

Thus, K_r can be calculated from known or readily measured constants for the vapor and polymer. The expectation of a linear correlation between K_r and K_e forms the basis for the SP model used here.

LSER Model. Solvation parameters have been used in LSERs to characterize solubility interactions in a diverse range of systems, including GLC [24-28]. Through this work solvation parameters have been established for a large number of organic solvents and solvation parameter coefficients have been established for several polymers and GLC stationary phases.

For the application of interest here, we use the following LSER [26]:

$$\log K = C_0 + rR_2 + s\pi_2^H + a\alpha_2^H + b\beta_2^H + l\log L^{16} \quad (9)$$

where C_0 is a regression constant; R_2 is a term that reflects the polarizability of n and p

electrons in the vapor; π_2^H is a vapor dipolarity/polarizability term which is roughly proportional to the molecular dipole moment for compounds having a single strongly polar functional group; α_2^H is a vapor hydrogen-bond donation term; β_2^H is a vapor hydrogen-bond acceptance term; and L^{16} is the Ostwald solubility coefficient of the vapor in hexadecane at 25°C, which provides a measure of cavity formation and dispersion interactions.

The corresponding coefficients r , s , a , b , and l in Eq. 9 characterize the polymer properties that complement those of the vapor. That is, they reflect the strengths of these various interaction forces in effecting vapor solubility in a given polymer. For example, b provides a measure of the extent to which the polymer can donate hydrogen-bonds to hydrogen-bond-accepting groups in the vapor. In some cases, certain terms may be eliminated because the interactions they characterize do not contribute significantly to overall solubility. Although the LSER approach is empirical, correlations have been established between solvation parameter scales and fundamental physical and thermodynamic quantities [25].

To implement the LSER model in the present application, the solvation parameter coefficients for each sensor coating must be known. Coefficients for many common stationary phases have been determined using K values calculated from GLC retention data at high temperatures in inert atmospheres [24-28]. As we show here, the same methods can be adapted to determine these coefficients from SAW sensor response data under conditions more relevant to sensor applications. This involves performing a multiple linear regression using experimental K_e values and the known solvation parameters for a series of solvent vapors. Once the polymer coefficients have been determined, modeled K_e values can be calculated for any vapor for which the required solvation parameters are available.

Determination of Coating Solubility Parameters. Solubility parameters for volatile solvents can be determined from vaporization energies or vapor pressures [30,31]. Solubility parameters for non-volatile materials must be determined indirectly. Methods employed for this purpose include immersion of the material in a series of solvents or use of the material as the stationary phase in inverse-gas chromatography (IGC) [31-34]. Estimates of solubility parameters can also be calculated using molecular group-contribution methods [35-37].

The IGC method reported by DiPaola-Baranyi and Guillet [33] has been adapted here to derive coating solubility parameters from SAW sensor response data. In this method, K is related to the Flory interaction parameter, χ , and to the vapor and coating solubility parameters by

$$\ln(RT/p_2KV_2) - 1 - p_2(B - V_2)/RT = \chi = \chi_s + V_2(\delta_1 - \delta_2)^2/(RT) \quad (10)$$

where χ_s is an "entropic" correction term used to account for orientational effects and specific chemical interactions between the vapor and polymer, and B is the second virial coefficient of the vapor, which can be estimated provided that values of the critical volume, critical temperature and critical pressure for the vapor are known [33].

Using the quantities on the left hand side of Eq. 10 to solve for χ and then rearranging yields

$$\delta_2^2/RT - \chi/V_2 = (2\delta_1/RT)\delta_2 - \delta_1^2/RT - \chi_s/V_2 \quad (11)$$

Plotting $(\delta_2^2/RT - \chi/V_2)$ versus δ_2 should give a straight line and estimates of δ_1 can be obtained from either the slope or intercept by linear regression. Note that the last term on the right hand side of Eq. 11 generally contributes less than a few percent to the value of the intercept and can therefore be ignored [38].

Use of K_e in the Sensor Response Models. The modeling approaches described above are all based on partition coefficients determined from GLC retention volumes (ie, K in Eq 1). The application of these approaches to modeling SAW sensor responses, on the other hand, is based on K_e values determined using Eq 2. Under the assumption that K_e is proportional to K, the correlations expected in the BP and LSER models should be unaffected because the proportionality factor will be absorbed into the regression constants of the models in both cases. For the SP model, however, there may be an effect on the calculated value of the polymer solubility parameter which, in turn, may affect the correlation between K_T and K. This issue is addressed in the analyses presented below.

Experimental

The sensor coatings examined were poly(bis(cyanoallyl) siloxane) (OV-275), poly(methylphenylsiloxane) (25% methyl, OV-25), poly(phenylether) six-rings (PPE) (Anspec, Ann Arbor, MI) and poly(isobutylene) (PIB) (Aldrich, Milwaukee, WI). OV-275, OV-25 and PPE are all liquids and PIB is an amorphous rubbery solid. Solvents were obtained from Aldrich and were all > 98% pure with the exception of 2,4- and 2,5-lutidine which were 96% pure. Solutions of PPE, OV-25, PIB (0.2% by weight in toluene) and OV-275 (0.2% by weight in 1:1 toluene:acetone) were applied by airbrush to the sensors. The resulting values of Df_c were 192, 220, 199 and 196 kHz, respectively. For the sensor array used here, all of the reference sensor frequencies were higher than the coated sensor frequencies prior to coating, and the 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).

Data were collected using an 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), rf electronics modules and frequency counters. Difference frequency measurements between the coated and reference sensors were collected every 2 s and logged on a personal computer.

Test atmospheres of the vapors were generated by passing N₂ through a fritted bubbler containing the liquid solvent and into a metered dilution air stream maintained at 25°C and 50% relative humidity (RH) using an HCS-202 Flow-Temperature-Humidity Control System (Miller-Nelson Research, Monterey, CA). After passing through a calibrated infrared gas analyzer (MIRAN 1A, Foxboro, Bridgewood, MA), a portion of the contaminated stream was diverted to a manual four-port valve which was used to direct the flow of clean or contaminated air to the sensor array.

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 at 25 ± 0.1°C by circulating thermostatted water through the aluminum blocks in contact with the sensor lids. 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).

Flow rates over the sensors were maintained at 0.080 L/min and monitored continuously with four downstream rotameters. For an internal volume of about 1 cm³, the mixing time is approximately 2 s. Humidified contaminant-free air was continuously passed over the sensors to establish a baseline frequency. The average noise level of the baseline response was about 15 Hz and limits of detection (LOD) for the vapors were calculated using 45 Hz as the minimum detectable sensor response.

For a typical run, the array was exposed twice for 40 s to a given concentration of vapor, with each exposure separated by a 40-s purge with clean air. The last five frequency measurements in each exposure period were averaged and compared to the baseline frequency to determine the sensor response. This procedure was repeated for four different concentrations of each test vapor covering a 3-10 fold concentration range, depending on the vapor. The minimum vapor concentration was that giving a response typically three times the

LOD for the least sensitive sensor.

Following initial testing, it was found that at the higher N₂ flow rates needed to generate high concentrations of certain vapors, a measurable baseline shift occurred in several of the sensors, due to changes in RH (typically less than 5%). Therefore, all tests were performed with N₂ gas being 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 was somewhat lower than 50%.

Over the course of the 1.5-month data collection period, the response of m-xylene was repeatedly examined to monitor the stabilities of the coatings. For the OV-275 and PIB coatings the partition coefficients remained quite constant, with relative standard deviations of < 3% around the mean of the daily K_e values and no discernable systematic drifts over time. The m-xylene K_e values for the OV-25 coating increased by 25% over the first two weeks of exposure and then remained relatively stable. For PPE, K_e 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 study: the final value was 46% of the initial value.

The factors responsible for the observed aging effects in the liquid OV-25 and PPE coatings could not be determined definitively. Thin-film samples of all of the polymers were applied to KCL plates and stored in a container at room temperature and 50% RH. IR spectra taken periodically over a 2-month period revealed no changes in the absorption peaks, indicating that the coatings were chemically stable. Since the coatings were all exposed simultaneously to the atmospheres in the sensor test system, calibration errors could be ruled out. The loss of sensitivity for the PPE coating might be ascribed to a slow evaporation from the sensor surface, although no significant change in Δf_c was observed. The slight increase in sensitivity for the OV-25 coating may be attributable to segmental relaxations or some other re-orientation of the polymer chains in the coating. For the purposes of this study, the shift in sensitivity for the PPE and OV-25 coated sensors was compensated for by multiplying the vapor responses obtained on a given day by the ratio of the highest-observed m-xylene response to the m-xylene response observed on the same day.

Statistical analyses were performed using SAS^R Version 6.07 (SAS Institute, Cary, NC) on an IBM ES-9000 series mainframe computer.

Results and Discussion

Sensor Responses and K_e Values. Figure 1 shows a series of response profiles for each sensor upon exposure to 475 $\mu\text{g/L}$ of cyclohexanone. These responses are typical of those obtained for all of the vapors. OV-275 and PIB sensor responses and recoveries generally

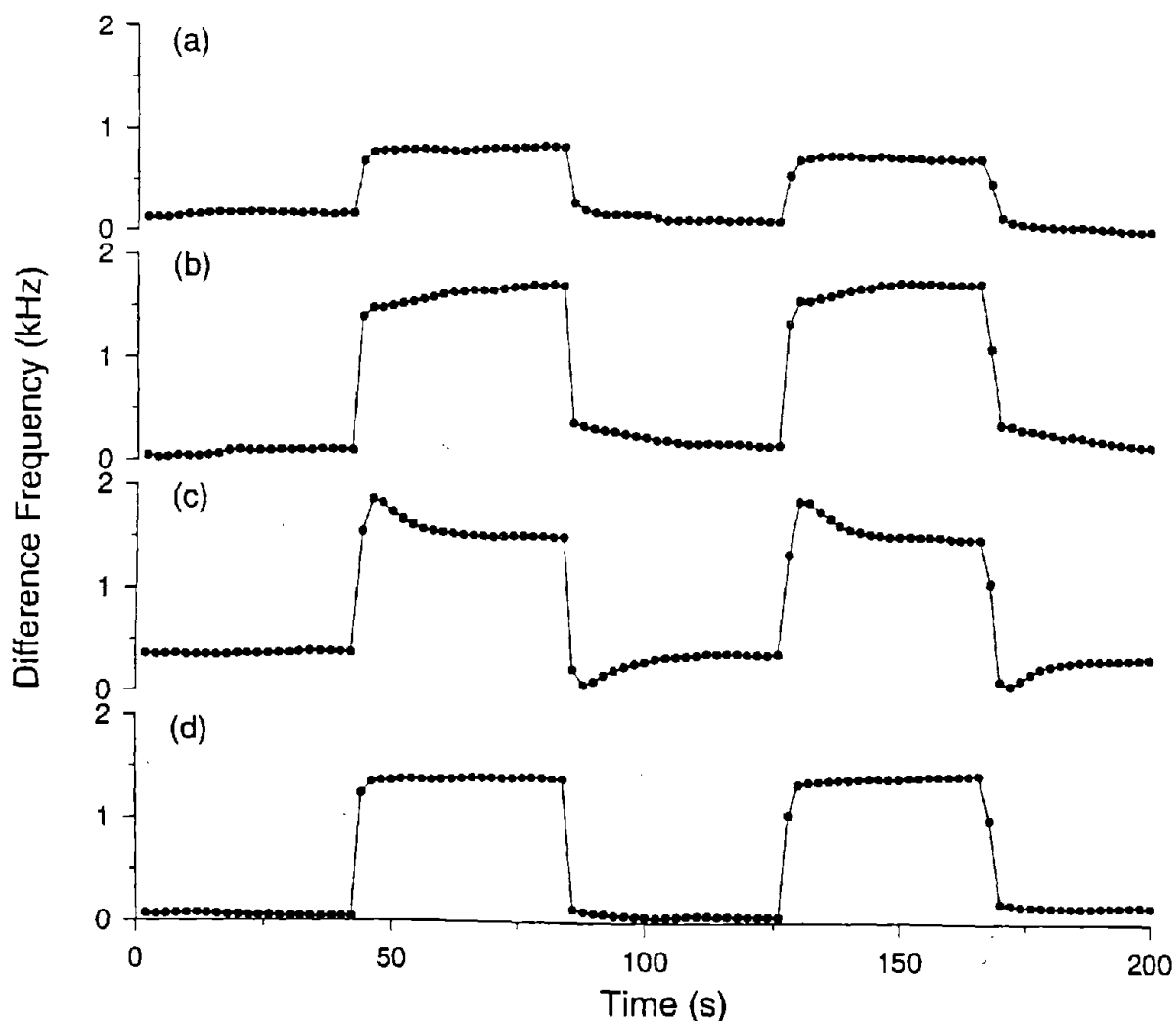


Figure 1. Frequency response vs. time for sensors exposed to 475 $\mu\text{g/L}$ of cyclohexanone: a) PIB, b) OV-25, c) PPE, d) OV-275.

reached $>90\%$ of their equilibrium values within 6-10 s of introduction and removal of the vapor, respectively. The OV-25 and PPE sensors were somewhat slower to respond but still attained $>90\%$ of equilibrium within 20 s of exposure. Curiously, in the case of PPE a slight overshoot was observed immediately after introduction or removal of the test vapors. Rearranging the positions of the sensors in the array did not affect this behavior, suggesting that it arises from transient stresses within the PPE coating film associated with vapor sorption and desorption.

Table 1 presents average K_e values calculated from the sensor response data using Eq 2. In most cases, estimates of K_e at each different vapor concentration agreed quite well as indicated by the low standard deviation of the estimates shown in Table 1. Consistent with this, plots of vapor concentration versus Δf_v were generally linear with regression correlation

Table 1. Experimental K_e values, LODs and modeled:experimental K value ratios (K_m/K_e)^a.

vapor	OV-275				
	K_e	LOD ($\mu\text{g/L}$)	K_m/K_e		
			BP	SP	LSER
benzene	561 (48)	401	0.64	0.90	0.79
toluene	1090 (50)	206	1.07	1.11	0.87
m-xylene*	2040 (210)	110	1.74	1.51	1.00
p-xylene*	2230 (170)	101	1.55	1.32	0.92
hexane*	43 (15)	5300	5.46	1.56	0.76
cyclohexane*	69 (34)	3250	5.29	4.05	1.16
isooctane*	47 (20)	4770	15.93	1.13	1.26
nonane*	396 (143)	569	14.14	2.98	0.69
aniline	193000 (2000)	1	0.11	0.22	0.91
N,N-dimethylaniline	36600 (3400)	6	0.82	1.75	1.12
pyridine	6480 (370)	35	0.22	0.34	0.60
2,4-lutidine	16800 (900)	13	0.46	nd	nd
2,5-lutidine	14500 (1000)	16	0.51	nd	nd
methanol	919 (32)	245	0.22	0.19	0.83
isopropanol	926 (48)	243	0.42	1.08	1.02
1-butanol	4240 (180)	53	0.36	1.25	1.11
2-butanone*	1120 (60)	201	0.31	0.48	0.72
3-heptanone	5800 (370)	39	0.83	0.58	0.96
cyclohexanone*	14800 (500)	15	0.46	0.52	0.93
ethyl ether*	40 (6)	5620	1.51	0.89	1.78
tetrahydrofuran*	578 (54)	390	0.37	0.54	1.00
1,4-dioxane	2320 (90)	97	0.35	0.58	1.22
methylmethacrylate*	979 (126)	230	0.81	1.10	1.24
n-butyl acetate	1880 (50)	120	1.16	0.90	1.15
amyl acetate	4230 (210)	53	1.25	1.11	1.03
benzyl chloride	22100 (1400)	10	0.77	1.10	1.11
chlorobenzene	2670 (160)	84	1.01	1.21	0.99
2-chlorotoluene	4340 (250)	52	1.78	nd	1.23
4-chlorotoluene	4440 (500)	51	1.95	1.42	1.31
1,3-dichlorobenzene*	7660 (370)	29	1.74	2.13	1.29
methylene chloride*	286 (9)	788	0.26	0.56	1.15
chloroform*	449 (32)	502	0.39	0.63	1.35
1,1,1-trichloroethane	205 (47)	1100	1.38	1.52	1.16
trichloroethylene	454 (29)	496	1.03	1.38	0.67
1-hexene*	51 (11)	4420	3.65	1.19	0.86
cyclohexene	127 (4)	1770	3.16	2.83	1.14
styrene*	4590 (580)	49	0.98	1.14	0.81
α -methylstyrene	7130 (590)	32	1.29	0.97	0.93
4-methylstyrene	9080 (860)	25	1.26	1.44	0.89

Table 1 (cont.)

vapor	OV-25				
	K _e (sd)	LOD ($\mu\text{g/L}$)	K _m /K _e		
			BP	SP	LSER
benzene*	1200 (100)	216	0.61	0.76	0.91
toluene*	2950 (70)	88	0.81	0.86	0.95
m-xylene*	7230 (640)	36	1.01	1.00	0.98
p-xylene*	7580 (460)	34	0.94	0.91	0.94
hexane*	261 (8)	991	1.80	1.36	0.96
cyclohexane*	527 (5)	491	1.41	1.53	1.07
isooctane*	480 (31)	539	3.21	1.11	1.13
nonane*	3270 (80)	79	3.55	2.41	1.09
aniline	47300 (700)	5	0.90	1.06	1.00
N,N-dimethylaniline	75400 (2400)	3	0.83	1.27	1.12
pyridine	5120 (100)	50	0.57	0.46	0.84
2,4-lutidine	21700 (1200)	12	0.74	nd	nd
2,5-lutidine	20900 (1500)	12	0.73	nd	nd
methanol	86 (6)	3000	4.67	1.39	1.04
isopropanol	270 (25)	958	2.95	3.15	1.05
1-butanol	1590 (30)	163	1.96	2.66	0.87
2-butanone*	915 (8)	283	0.78	1.02	1.00
3-heptanone	11100 (600)	23	0.90	0.88	1.03
cyclohexanone*	20200 (1000)	13	0.69	0.52	0.91
ethyl ether*	192 (7)	1350	0.64	0.73	1.04
tetrahydrofuran*	1010 (50)	256	0.43	0.56	1.09
1,4-dioxane*	2420 (130)	107	0.68	0.75	1.36
methylmethacrylate*	2060 (60)	126	0.79	0.96	1.00
n-butyl acetate	5470 (300)	47	0.82	0.88	0.83
amyl acetate	13200 (200)	20	0.83	1.09	0.81
benzyl chloride	31900 (700)	8	1.11	1.04	1.32
chlorobenzene	6840 (300)	38	0.81	0.77	0.96
2-chlorotoluene	16100 (200)	16	0.99	nd	1.01
4-chlorotoluene	15500 (1500)	17	1.15	0.94	1.12
1,3-dichlorobenzene*	26700 (2200)	10	1.03	0.88	1.07
methylene chloride*	327 (22)	791	0.46	0.72	1.03
chloroform	606 (18)	427	0.58	0.80	1.10
1,1,1-trichloroethane	651 (30)	397	0.88	1.12	1.15
trichloroethylene	1400 (60)	185	0.68	0.80	0.79
1-hexene*	281 (21)	921	1.34	1.08	0.95
cyclohexene	783 (31)	330	1.04	1.17	1.00
styrene*	11600 (700)	22	0.80	0.81	0.85
α -methylstyrene	23600 (800)	11	0.81	0.83	0.88
4-methylstyrene	24800 (600)	10	0.95	1.08	1.03

Table 1 (cont.)

vapor	PPE				
	K _e	LOD (µg/L)	K _m /K _e		
			BP	SP	LSER
benzene ⁺	909 (85)	302	0.68	0.89	1.00
toluene ⁺	2650 (60)	104	0.83	0.86	0.89
m-xylene ⁺	6090 (600)	45	1.17	1.07	1.00
p-xylene ⁺	5880 (440)	47	1.18	1.05	1.03
hexane ⁺	181 (12)	1520	2.16	1.26	0.86
cyclohexane ⁺	240 (13)	1140	2.65	2.63	1.56
isooctane ⁺	310 (23)	885	4.42	0.95	1.10
nonane ⁺	2480 (250)	111	4.68	2.17	0.93
aniline	59700 (1400)	5	0.77	0.96	1.19
N,N-dimethylaniline	81200 (4000)	3	0.86	1.32	1.11
pyridine	5530 (130)	50	0.49	0.46	0.80
2,4-lutidine	25100 (1400)	11	0.65	nd	nd
2,5-lutidine	22700 (2000)	12	0.69	nd	nd
methanol	129 (10)	2130	2.57	1.01	0.88
isopropanol	283 (26)	970	2.41	3.31	1.13
1-butanol	2040 (140)	135	1.41	2.47	0.84
2-butanone ⁺	1040 (40)	264	0.58	0.81	0.83
3-heptanone	12100 (900)	23	0.82	0.69	0.91
cyclohexanone ⁺	19600 (300)	14	0.72	0.57	1.01
ethyl ether ⁺	149 (15)	1840	0.63	0.64	0.99
tetrahydrofuran ⁺	904 (61)	304	0.40	0.55	1.06
1,4-dioxane ⁺	2040 (150)	135	0.72	0.88	1.61
methylmethacrylate ⁺	1960 (140)	140	0.73	0.93	0.96
n-butyl acetate	4810 (280)	57	0.88	0.85	0.86
amyl acetate	12600 (800)	22	0.87	0.98	0.79
benzyl chloride	33700 (1600)	8	1.12	1.09	1.33
chlorobenzene ⁺	6820 (370)	40	0.78	0.75	0.87
2-chlorotoluene	14300 (500)	19	1.15	nd	1.03
4-chlorotoluene	14800 (1000)	19	1.25	0.90	1.09
1,3-dichlorobenzene ⁺	30300 (2800)	9	0.96	0.83	0.90
methylene chloride ⁺	301 (16)	912	0.39	0.70	1.04
chloroform ⁺	522 (35)	526	0.55	0.82	1.20
1,1,1-trichloroethane	439 (37)	625	1.10	1.37	1.33
trichloroethylene	1260 (70)	218	0.65	0.80	0.68
1-hexene ⁺	191 (8)	1440	1.62	1.04	0.92
cyclohexene	470 (30)	584	1.49	1.58	1.18
styrene ⁺	10200 (600)	27	0.90	0.90	0.88
α-methylstyrene	23000 (2500)	12	0.85	0.75	0.83
4-methylstyrene	23500 (2600)	12	1.05	1.11	1.01

Table 1 (cont.)

vapor	PIB				
	K _e	LOD ($\mu\text{g/L}$)	K _m /K _e		
			BP	SP	LSER
benzene*	799 (93)	259	0.79	0.89	0.94
toluene*	2460 (20)	84	0.77	0.84	0.90
m-xylene*	7260 (190)	28	0.73	0.78	0.87
p-xylene*	6930 (80)	30	0.74	0.78	0.91
hexane*	597 (8)	346	0.70	1.10	0.91
cyclohexane*	898 (19)	230	0.71	1.01	1.19
isooctane*	1300 (110)	159	0.96	1.14	1.01
nonane*	11000 (200)	19	0.73	1.13	1.02
aniline	14700 (1800)	14	1.82	1.56	1.24
N,N-dimethylaniline	38500 (1600)	5	1.00	1.13	1.18
pyridine*	2340 (370)	88	0.97	0.49	0.65
2,4-lutidine	13400 (1100)	15	0.81	nd	nd
2,5-lutidine	11700 (600)	18	0.90	nd	nd
methanol	85 (19)	2420	4.26	0.60	0.68
isopropanol	232 (26)	890	2.94	1.51	1.06
1-butanol	1280 (190)	161	1.88	1.10	1.06
2-butanone*	431 (30)	479	1.43	1.63	0.81
3-heptanone	7300 (250)	28	0.97	1.17	0.94
cyclohexanone*	6350 (540)	32	1.51	0.85	1.13
ethyl ether*	158 (8)	1310	0.77	1.47	1.24
tetrahydrofuran*	578 (35)	357	0.68	0.83	1.19
1,4-dioxane*	1080 (120)	191	1.24	1.00	1.19
methylmethacrylate*	1090 (60)	189	1.20	1.28	1.01
n-butyl acetate	2920 (80)	71	1.15	1.51	0.97
amyl acetate	8230 (290)	25	0.93	1.52	0.92
benzyl chloride	14100 (1000)	15	1.60	1.09	1.28
chlorobenzene	4680 (300)	44	0.88	0.70	0.86
2-chlorotoluene	12700 (300)	16	0.86	nd	0.91
4-chlorotoluene	11600 (1600)	18	1.04	0.97	1.06
1,3-dichlorobenzene*	22500 (1600)	9	0.80	0.51	0.82
methylene chloride*	157 (12)	1320	0.94	1.19	1.19
chloroform	368 (24)	561	0.88	1.05	1.39
1,1,1-trichloroethane	501 (23)	412	1.01	1.39	1.31
trichloroethylene	1200 (70)	172	0.67	0.72	0.89
1-hexene*	471 (34)	439	0.73	1.17	1.00
cyclohexene	1070 (30)	193	0.65	0.88	1.09
styrene*	7570 (400)	27	0.87	0.78	0.87
α -methylstyrene	18300 (200)	11	0.70	0.93	0.86
4-methylstyrene	19500 (400)	11	0.80	0.87	1.00

* Values in parentheses are standard deviations (n=4). Asterisks indicate solvents used in determining coating δ_1 values; nd = not determined.

coefficients (r^2) > 0.99. Somewhat greater variability in K_e was observed in certain cases, particularly for vapors giving low responses on a given coating. This can be attributed to the relatively greater influence of both random oscillator noise and errors in concentration measurements for these vapor-coating combinations. Small differences in RH between the clean and contaminant flow streams may also have contributed to the variability in the OV-275 sensor responses since this highly polar coating shows the greatest sensitivity to RH fluctuations.

Calculated LODs, also listed in Table 1, range from a few $\mu\text{g/L}$ 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. These issues are discussed in more detail below in the context of the response models.

For the PPE-coated sensor, it is possible to compare several of the K_e values determined in this study to K values determined from McReynolds' compilation of GLC specific retention volumes [39]. In the latter case, K values at 25°C were obtained by extrapolation from specific retention volumes determined at 120 and 160°C [19]. For the 20 vapors common to both studies, the average $K_e:K$ ratio was 1.6. For most vapors K_e/K was in the range of 1.2-1.8. Methanol and *n*-butanol comprised the exceptions, giving K_e/K values of 3.2 and 2.2, respectively. A similar comparison of K_e values determined from an apiezon-coated SAW sensor [40] to McReynolds' K values gave an average $K_e:K$ ratio of 1.4. In this case, isopropanol and *n*-butanol gave higher ratios of 2.0 and 2.1, respectively. Thus, with the possible exception of lower alcohols, there does appear to be a rough proportionality between K and K_e for vapors partitioning into a given coating/stationary phase. The differences in $K_e:K$ ratios may be attributable, in part, to differences in the nature and morphology of the substrates, i.e., a polished quartz SAW substrate in one case and a granular, microporous GLC stationary-phase support material in the other.

It is also possible to compare several of our K_e values for PIB to the K_e and K values reported by Grate et al. [14]. For the five vapors common to both studies, the K_e values determined here were within 14% of the average K_e values reported in that study and were an average of six times greater than the K values determined by GLC at 25°C for the same vapors.

The fact that the $K_e:K$ ratios for PPE and apiezon are similar to each other and lower than those for PIB is consistent with the notion that K_e values are enhanced by modulus changes in the polymer. Since PPE is a viscous liquid and apiezon is a grease, their modulus values, even at the high-frequency at which SAW devices operate, should be relatively small and modulus changes upon vapor sorption should be relatively less important for these

materials than for solid polymers such as PIB.

Humidity Effects. Sorption or 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 a number of reports have examined the former issue [41-43], the latter has not been investigated. A limited test of RH effects was therefore performed as part of this study.

The response of each sensor to atmospheric humidity changes was determined by exposing the array alternately to dry N₂ and to air at 50% RH. Responses were rapid and reversible and the single-point estimates of K_e for water vapor were 3510, 685, 416, and 144, for OV-275, PPE, OV-25, PIB, respectively. This order would have been anticipated since water has a greater affinity for more polar coatings. Note that PIB, which is a non-polar aliphatic hydrocarbon, still sorbs water vapor from the atmosphere to some extent.

The effect of RH on the responses to organic vapors was then tested for a subset of vapors by comparing responses in a dry N₂ atmosphere to those in a 50% RH atmosphere. The vapors examined were n-butanol, 3-heptanone, m-xylene, and nonane, which span the ranges of structures and polarities found in the entire set of vapors. Each vapor was tested on the same day under dry and humid conditions. In only two cases was any significant difference in sensor response noted: for OV-275 the response to n-butanol was 27% higher under humid conditions and for PIB the response to n-butanol was 59% higher under dry conditions. The response to 3-heptanone was about 12% higher with the OV-275 coating under humid conditions, but this is considered a marginal change. For all of the remaining vapor/coating combinations, responses under dry and humid conditions differed by 9% or less.

The decreased response to butanol under humid conditions for the PIB-coated sensor is most likely due to competition between water and n-butanol for polar sorption sites at the surface of the underlying substrate. A similar explanation was given by Grate et al. [14] to account for variations in the responses of coated SAW devices whose substrates had been cleaned by different methods. Alternatively, the enhancement could be the result of the known tendency for alcohols to self-associate in hydrophobic solvents [44,45] which would effectively increase the n-butanol solubility in the PIB. The presence of traces of water vapor in the polymer would reduce this phenomenon and decrease the equilibrium solubility.

For the polar OV-275 the amount of water vapor present in the coating at 50% RH is greater than that in PIB and the affinity of n-butanol for OV-275 is greater than for PIB (Table 1). In this case, interfacial adsorption at the substrate probably contributes relatively little to the overall response. The observed enhancement in the n-butanol response at higher RH in

OV-275 is consistent with solvation of the n-butanol by sorbed water. The water might also reduce any interchain interactions within the polymer thereby rendering the polar cyano groups more available to interact with the n-butanol. For the moderately polar PPE and OV-25 coatings, the effects of water vapor on the substrate and the coating would tend to offset one another resulting in no significant change in response to n-butanol. Based on these representative results, similar variations in responses to other hydrogen-bonding vapors might be expected as a function of RH with sensors employing non-polar and highly polar coatings.

Coating Solubility Parameters. Solubility parameters were obtained from standard references for all but three of the 39 test vapors (2-chlorotoluene and 2,4- and 2,5-lutidine) [30,31,46]. Values of the critical parameters, vapor pressures, etc. needed to calculate B in Eq 10 were available for only 22 of the vapors [46-52]. As a result, the coating solubility parameters were determined from linear regressions of $(\delta_2^2/RT - \chi/V_2)$ onto δ_2 using δ_2 values for these 22 vapors (designated with asterisks in Table 1). The linear regression r^2 values for these plots were > 0.98 .

Values of δ_1 determined from the slopes and intercepts were within $0.1 \text{ (cal/cm}^3)^{1/2}$ and gave averages of 10.4, 9.4, 9.0 and 7.6 $(\text{cal/cm}^3)^{1/2}$ for OV-275, PPE, OV-25 and PIB, respectively (Table 2). Published Hildebrand solubility parameter values determined by other experimental methods could not be found for OV-275, PPE or OV-25. For PIB, reported values ranged from 7.8-8.1 $(\text{cal/cm}^3)^{1/2}$ [30,34].

In Table 2, the solubility parameters determined here are compared to those calculated using the group-contribution methods of Fedors [35] and Small [36]. The constants assigned to a given structural fragment and the method of calculation differ somewhat between these two methods, hence the different values. Our δ_1 value for PIB is very close to both the experimental and calculated values, and the OV-275 and OV-25 values determined here fall within the range of calculated values. Although our value for PPE is somewhat low, the

Table 2. Comparison of solubility parameters $(\text{cal/cm}^3)^{1/2}$ determined in this study and those calculated from group contribution methods.

coating	experimental	Fedors	Small
OV-275	10.4	12.2	9.1
PPE	9.4	11.6	10.0
OV-25	9.0	10.3	8.8
PIB	7.6	7.7	7.7

difference between our value and the calculated values is similar to the difference between the two calculated values. The fact that the group-contribution methods do not account for intra- or intermolecular interactions within or between polymer chains could account for some of the observed differences. In any case, the order of solubility parameter values found from our determinations and those determined with Fedors' method (ie, OV-275 > PPE > OV-25 > PIB) would be expected based on considerations of the relative polarities of the polymers (one exception to this order is seen using Small's method). Thus, the overall agreement between our results and those determined by other methods can be considered reasonably good.

To investigate the potential influence on the solubility parameter estimates of using K_e values rather than K values, all K_e values were divided by a factor of four and the solubility parameter values for all of the coatings were redetermined. This factor was chosen since it represents a rough average of the K_e : K ratios found here and reported previously [14]. The average δ_1 values derived from the slopes and intercepts were 0.4-0.5 (cal/cm³)^{1/2} lower than those determined using K_e . In addition, the values obtained from the slopes differed from those determined from the intercept by 0.3-0.5 (cal/cm³)^{1/2}. The use of K_e rather than $K_e/4$ thus appears to provide more accurate values of δ_1 , although the sensitivity of the estimates to proportional changes of K_e is not very great. We also found that the correlations between K_e and K_f (see below) were stronger than those between $K_e/4$ and K_f , lending further support to the use of K_e itself as the predictor variable in the SP model.

Coating Solvation Parameter Coefficients. The solvation parameter coefficients determined for each of the coatings from our SAW sensor response data are presented in Table 3. The solvation parameters for the vapors used in these determinations are listed in Appendix 1 [26,53]. Values for 2,4- and 2,5 lutidine could not be obtained. As shown in Table 3, the standard errors of the estimates for the coefficients are relatively small, as are the overall standard deviations of log K_e for each coating.

Plots of log K_e versus the residual errors for each of the coatings showed no curvature or systematic variation that would indicate a departure from the LSER model described by Eq 9. Examination of the Cook's distance measure to identify influential observations revealed only one combination, methanol/PIB, that can be considered significant. Removal of methanol from the regression in determining the coefficients changed the K_m values for the remaining vapors by an average of only 3.5%, hence no adjustment was performed and all vapors were included in the analysis.

The dispersion parameter, l , is appreciable for all of the coatings reflecting the general importance of cavity formation and dispersion interactions in effecting solubility. As expected, however, the largest l value is obtained for the non-polar PIB, intermediate values are obtained

for the moderately polar PPE and OV-25, and the lowest value is obtained for the highly polar OV-275.

The coating polarizability coefficient, r , is statistically non-significant for all four coatings as determined by a backward stepwise multiple linear regression. It has been noted previously that r and s (dipolarity-polarizability coefficient) can be highly correlated [25]. Indeed, the correlation of r and s in this data set was 0.655. Thus, the s coefficient apparently accounts for the polarizability interactions that would otherwise have been reflected in the r term. The value of s decreases in the order OV-275 > PPE > OV-25 > PIB (s for PIB is not significant). This trend agrees with expectations based on the structures of the coatings.

The cyano groups of OV-275 also give rise to the large hydrogen-bond acceptance coefficient, a , for this coating. The moderate a values obtained for PPE and OV-25 are consistent with their respective phenyl ether and phenyl groups. An inconsistency is found in the fact that PIB has a significant a coefficient. In addition, although the hydrogen atoms on the carbons adjacent to the cyano groups in OV-275 might give rise to some hydrogen-bond donation strength, the fact that there are significant b coefficients for the remaining coatings would not have been predicted from a consideration of the polymer structures. These unusual values may be due to RH or surface adsorption (for PIB) effects, or merely to artifacts of the regression arising from the fact that only six of the vapors tested in this study had non-zero α_2^H parameters.

Table 3. Solvation parameter coefficients of the coatings determined in this study and by others.^a

coating	c	r	s	a	b	l	sd	R ²
(b)OV-275	-0.134 (0.086)	-	1.88 (0.10)	3.03 (0.19)	0.616 (0.110)	0.615 (0.028)	0.105	0.987
PPE	0.132 (0.070)	-	1.18 (0.08)	1.08 (0.15)	0.410 (0.090)	0.773 (0.023)	0.085	0.990
OV-25	0.363 (0.046)	-	0.962 (0.052)	0.605 (0.100)	0.351 (0.059)	0.763 (0.015)	0.056	0.995
PIB	0.416 (0.064)	-	-	0.875 (0.140)	0.275 (0.065)	0.869 (0.017)	0.079	0.989
(c)OV-275	-0.171 (0.097)	-	1.90 (0.12)	3.25 (0.23)	0.565 (0.136)	0.622 (0.031)	0.105	0.989
PPE	0.152 (0.075)	-	1.24 (0.09)	0.964 (0.179)	0.418 (0.104)	0.756 (0.024)	0.081	0.993
OV-25	0.389 (0.046)	-	0.987 (0.054)	0.545 (0.110)	0.333 (0.064)	0.750 (0.015)	0.049	0.997
PIB	0.418 (0.066)	-	-	1.03 (0.16)	0.226 (0.079)	0.868 (0.018)	0.073	0.992
(d)OV-275	-0.635	0.388	1.902	1.644	-	0.241	0.080	0.994
PPE-5	-0.395	0.230	0.829	0.337	-	0.527	0.044	0.997
OV-25	-0.273	0.277	0.644	0.182	-	0.472	0.042	0.997

^a sd = overall standard deviation; R² = multiple correlation coefficient. Values in parentheses are standard errors. Hyphen = not statistically significant. ^(b) Values determined from full data set (n = 37). ^(c) Values determined from reduced data set (n = 26). ^(d) Values determined from GLC data at 121 °C (from ref. 54).

Table 3 also presents solvation parameter coefficients determined from GLC retention data on the same or similar coatings (note: PPE-5 is the five-ring analogue of the six-ring PPE oligomer examined here) [52]. A direct comparison with the coefficients determined here is not possible because the GLC retention data were collected at 121°C (lower temperature data were not available) and solvation parameter coefficients decrease with increases in temperature [55]. The fact that our values are invariably higher than those determined by GLC is consistent with such a temperature effect. Differences in relative humidity, vapor-substrate interactions, and the nature and concentrations of the vapors employed would also be expected to affect the relative values of the coefficients obtained.

Notwithstanding these systematic differences, the following trends are observed in both the GLC and SAW-sensor data: the values of s and a decrease in the order OV-275 > PPE > OV-25; OV-275 has significantly larger values for these two coefficients than the other coatings; and the l coefficient is significantly lower for the OV-275 than for the remaining coatings. The most important implication of the differences in coefficients is that those determined from GLC measurements may not be useful for modeling the characteristics of the same materials when used as sensor coatings at low temperature under typical atmospheric conditions. Determination of these coefficients from SAW sensor response data allows account to be taken of any factors affecting vapor solubility associated with the conditions of actual use.

BP Model. Table 4 presents the slopes, intercepts, and r^2 values determined from the linear regression of $\log K_e$ onto T_b (°C) for each coating. The slopes ranged from 0.0157 to 0.0180 consistent with expectations assuming ideal behavior as discussed above. The r^2 values indicate that T_b is highly correlated with $\log K_e$, but the standard deviations of the estimates are rather large. The correlation is the strongest for the non-polar PIB coating (Fig. 2a) and weakest for most polar OV-275 coating (Fig. 2b), with intermediate correlations being found for the moderately polar PPE and OV-25 coatings.

The regression equations were then used to calculate modeled K values, K_m , for the vapors in all four coatings. The K_m/K_e ratios are listed in Table 1. For the PIB coating all but two K_m values are within a factor of two of K_e and most are within the range of 0.67-1.5 (ie, $\pm 50\%$). The exceptions are methanol and isopropanol which are overestimated. For OV-25, 33 of the 39 K_m values are within a factor of two of K_e , while for PPE 30 of the K_m values fall within this range. In both cases, the exceptions comprise the aliphatic hydrocarbons, lower alcohols, tetrahydrofuran and methylene chloride. For OV-275, only 21 of 39 K_m values are within a factor of two of K_e . Again, neither the alcohols nor aliphatic hydrocarbons are well modeled and certain vapors from several of the other classes also show large differences

between K_m and K_e .

That the best results are obtained for PIB was expected because of the predominance of dispersive interactions with this coating. The alcohols which are the most polar vapors show the largest deviations from the regression line in the model, which is also expected because Trouton's Rule does not apply to hydrogen-bonding vapors due to their tendency for self-association. Using a separate linear regression to model these vapors (ie, the alcohols and aniline) gave an r^2 value of 0.991 and K_m : K_e ratios ranging from 0.75 to 1.22. The regression for the remaining (non self-associating) vapors gave an r^2 of 0.977 and K_m : K_e ratios within the range of 0.80-1.68. The regression coefficients for the stratified data are shown in Table 4 below those for the full data set. The improvements in the standard errors of the estimated K_m values in the stratified data are evident.

For PPE and OV-25, the K_m values for the self-associating vapors and the alkanes and alkenes, representing the extremes in polarity, are all overestimated. The alkanes and alkenes are also overestimated for OV-275, while the self-associating vapors are underestimated. In an attempt to address these systematic errors, regressions of $\log K_e$ onto T_b for these three coatings were repeated after stratifying the vapors into categories consisting of self-associating vapors, non-polar vapors (ie, alkanes and alkenes) and the remaining moderately polar vapors (Table 4). Once again, the stratified approach improves the correlations obtained with the BP model. For PPE and OV-25 the K_m / K_e values range from 0.63-1.75 and 0.61-1.54, respectively. The poorest fit is still observed for OV-275 but the range of K_m / K_e was reduced to 0.25-2.12.

To illustrate a potential application of this model, it might be of interest to determine which vapors would be detectable below an air concentration of, say, 500 $\mu\text{g/L}$. Using Eq 2 to solve for K_e and assuming a 200-kHz coating, the regression equations in Table 4 provide a series of limiting boiling point values for each coating. Using the stratified regressions for PPE, the limiting boiling points are 93, 103, and 65°C for the self-associating, non-polar and moderately polar vapors, respectively. Vapors with boiling points above the limiting values are predicted to be detectable below 500 $\mu\text{g/L}$. Of the 29 compounds which have boiling points above the limiting values, 28 have experimental LODs below 500 $\mu\text{g/L}$. The sole exception was 1,1,1-trichloroethane which gave a modeled LOD of 357 $\mu\text{g/L}$ where the actual LOD was 625 $\mu\text{g/L}$. Applying the same analysis to the remaining coatings yielded only one discrepancy for OV-275 (tetrahydrofuran), one for PIB (1-hexene) and three for OV-25 (isooctane, cyclohexane and cyclohexene).

Another potential application of the BP model (and the other models) is in the estimation of relative sensor response patterns from an array of sensors. This application is of critical importance in determining the selectivity of a sensor array for a given vapor analyte (or

Table 4. Full and stratified boiling point model regression data for log K_e versus T_b .^a

coating	vapor set ^b	slope	intercept	sd	r ²
OV-275	full	0.0169 (0.0018)	1.20 (0.22)	0.479	0.709
	sa	0.0205 (0.0026)	1.41 (0.31)	0.236	0.969
	np	0.0099 (0.0031)	1.02 (0.29)	0.220	0.720
	mod	0.0145 (0.0011)	1.59 (0.15)	0.260	0.861
PPE	full	0.0180 (0.0009)	1.35 (0.12)	0.256	0.906
	sa	0.0226 (0.0004)	0.629 (0.051)	0.038	0.999
	np	0.0128 (0.0021)	1.42 (0.20)	0.148	0.905
	mod	0.0160 (0.0005)	1.70 (0.06)	0.105	0.979
OV-25	full	0.0171 (0.0009)	1.49 (0.11)	0.236	0.911
	sa	0.0227 (0.0006)	0.513 (0.073)	0.055	0.999
	np	0.0118 (0.0022)	1.70 (0.21)	0.156	0.880
	mod	0.0153 (0.0003)	1.82 (0.04)	0.074	0.988
PIB	full	0.0157 (0.0007)	1.54 (0.08)	0.179	0.937
	sa	0.0185 (0.0013)	0.815 (0.151)	0.114	0.991
	nsa	0.0152 (0.0004)	1.65 (0.05)	0.100	0.978

^a sd = overall standard deviation; r² = correlation coefficient. Values in parenthesis are standard errors.
^b full = complete data set, n=39; sa = self-associating vapors, n=4; np = non polar vapors, n=6; mod = moderate polarity vapors, n = 29; nsa = non self-associating vapors. n=35.

set of analytes) and for deciding which of several possible coatings should be included in the array. Figures 4a-d show the normalized experimental response patterns for n-butanol, 1,4-dioxane, m-xylene and hexane, respectively, along with the patterns derived from the stratified BP model. The normalization procedure entailed dividing each sensor response by the sum of the responses for all sensors. As shown, the modeled patterns are very similar to the experimental patterns for n-butanol and n-hexane. For xylene and dioxane, the modeled patterns are almost identical whereas the experimental patterns are quite distinct. It is clear from the modeled data, however, that the sensor array would be capable of discriminating between n-butanol, hexane and either dioxane or xylene. Discrimination between dioxane and xylene, which appears likely from the experimental patterns, would not have been predicted from the modeled values.

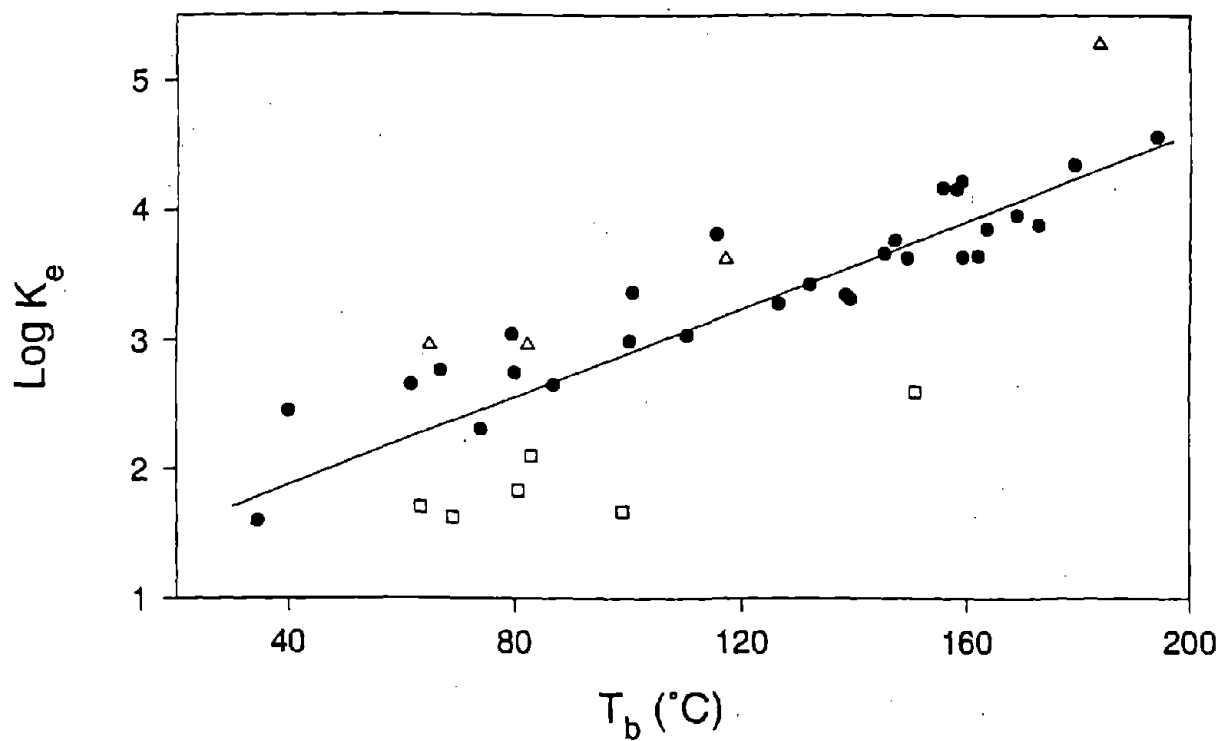
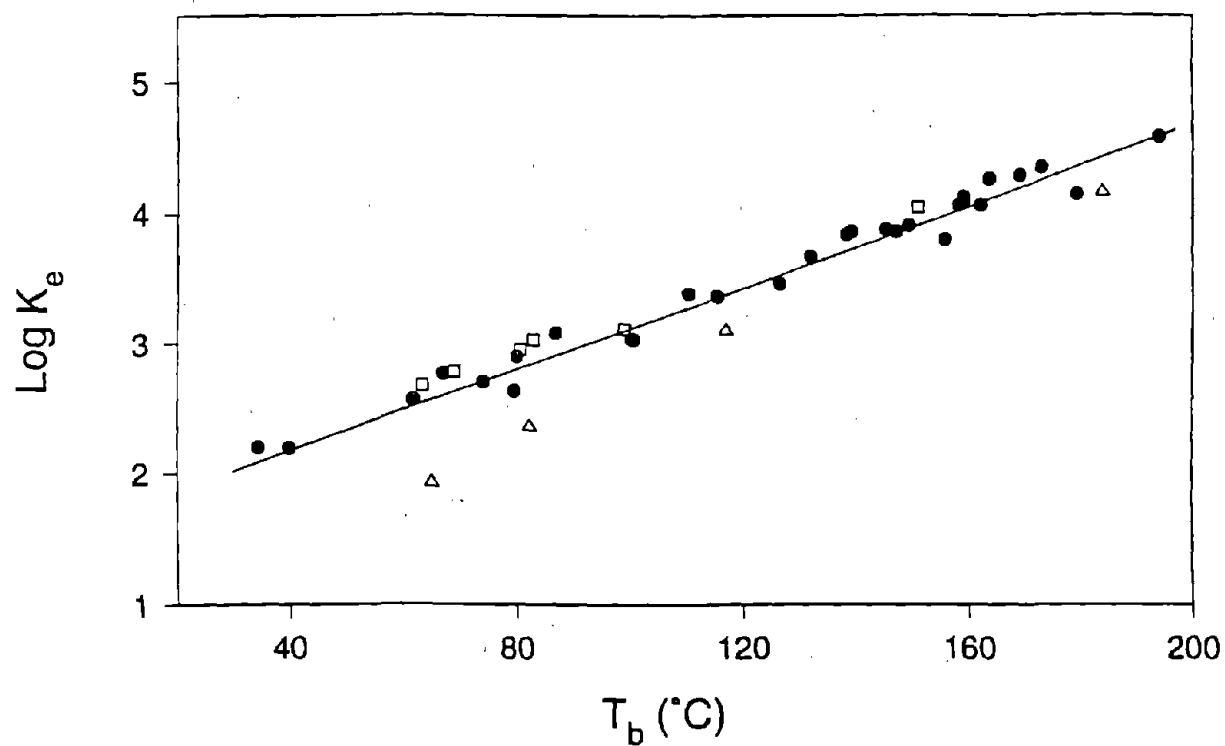


Figure 2. Plot of $\log K_e$ versus T_b for the coatings (a) PIB and (b) OV-275: unfilled triangles designate alcohols and aniline and unfilled squares designate alkanes and alkenes. The lines were determined by least-squares regression.

It can be seen in Table 4 that the slopes of the regression lines for a given subgroup of vapors do not differ greatly between the coatings. Given the range of coating structures represented by these four coatings, it is reasonable to expect that many other coatings would give results within the range found here. That is, the rate of change in sensor response as a function of boiling point found for these specific coatings may, in fact, be quite general. It should be possible therefore to obtain rough estimates of relative vapor responses for any coated SAW sensor: given the response of one vapor, the average slope from Table 4 could be used to estimate the responses of other vapors on the same coating.

SP Model. Table 5 lists the slopes, intercepts and r^2 values obtained from the regression of $\log K_e$ onto $\log K_f$ for the four coatings (note: these variables were log-transformed to accomodate the fact that their values vary over several orders of magnitude). As with the BP model the best correlation is obtained for the non-polar PIB coating, the poorest correlation is obtained for the most polar OV-275, and intermediate correlations are obtained for the moderately polar PPE and OV-25.

The regression coefficients and K_f values were used to calculate K_m for each vapor/coating pair. Table 1 presents the resulting K_m/K_e ratios. For PIB, pyridine is the only vapor for which K_m differs from K_e by more than a factor of two. For PPE, the responses to several aliphatic hydrocarbons and alcohols are significantly overestimated and pyridine is underestimated by a factor of 2.17. K_m values for the remaining 30 vapors are fairly closely estimated (recall that solubility parameters were available for only 36 of the 39 test vapors). In the case of OV-25 only four vapors have K_m/K_e values greater than two or less than 0.5, and in the case of OV-275 only eight vapors fell outside of this range: again, the exceptions consisted primarily of the non-polar and highly polar vapors.

Although there are several approximations inherent in the SP model and the regular solution theory on which it is based, the correlations obtained with this model are considerably better than those obtained with the (non-stratified) BP model for all four coatings. The generality of this model is illustrated by the fact that the individual-coating regression coefficients are not statistically different from those obtained from a single grouped regression. In the absence of detailed response data for some alternative coating material, the grouped regression coefficients could be used to estimate vapor responses provided that the solubility parameter of the coating material was known.

Figs. 4a-d show the normalized sensor-array response patterns predicted by the SP model for the four selected vapors. In this case, the predicted patterns for dioxane and xylene are improved over those determined from the stratified BP model and slight improvement is also seen for hexane pattern. For n-butanol, the stratified BP model actually performs better

Table 5. Solubility parameter model regression data for log K_e versus log K_r .^a

coating	slope	intercept	sd	r ²
OV-275	0.853 (0.050)	2.02 (0.08)	0.289	0.894
PPE	0.881 (0.035)	2.11 (0.06)	0.189	0.948
OV-25	0.854 (0.034)	2.19 (0.06)	0.176	0.948
PIB	0.825 (0.027)	2.25 (0.04)	0.133	0.965
all	0.858 (0.020)	2.14 (0.03)	0.215	0.928

^a sd = overall standard deviation; r² = correlation coefficient; all = combined regression for all four coatings. Values in parentheses are standard errors.

than the SP model because this vapor is overestimated on all four coatings by the SP model. Still, inspection of the SP-modeled patterns leads to the correct conclusion that the four vapors should be discriminated with this sensor array.

LSER Model. Using the coefficients listed in Table 3, values of log K_m were determined for each vapor and these were plotted versus log K_e for each coating. The r² values from these plots ranged from 0.987-0.995 demonstrating the improvement in the correlations with this model over those achieved with both the BP and SP models. This result was fully expected because of the use of up to four vapor/coating parameters in this model compared to only one or two parameters in the preceding models (recall that the r coefficient was not significant for any of the coatings). The K_m - K_e ratios are listed in Table 1 for each coating/vapor pair. For all four coatings, the sensor responses to all of the vapors are modeled within a factor of two and 83% fall within the range of 0.8-1.25 (ie, $\pm 25\%$). Figs. 3a and b present the plots of log K_e versus log K_m for PIB and OV-275, and illustrate the excellent correlations obtained with this model - the improvement in results for OV-275 compared to those obtained with the BP model (Fig. 2b) is particularly noteworthy. In Fig. 4a-d the response patterns obtained with the LSER are seen to compare quite favorably with the experimental patterns.

As a means of verifying this model, one vapor from each chemical class was selected to create a test set. The test set consisted of m-xylene, n-hexane, pyridine, 1-butanol, cyclohexanone, 1,4-dioxane, amyl acetate, chlorobenzene, chloroform, 1-hexene, and styrene. Coating solvation parameter coefficients were then recalculated by regression analysis of the training set consisting of the remaining 26 vapors. The resulting coefficients are listed in Table

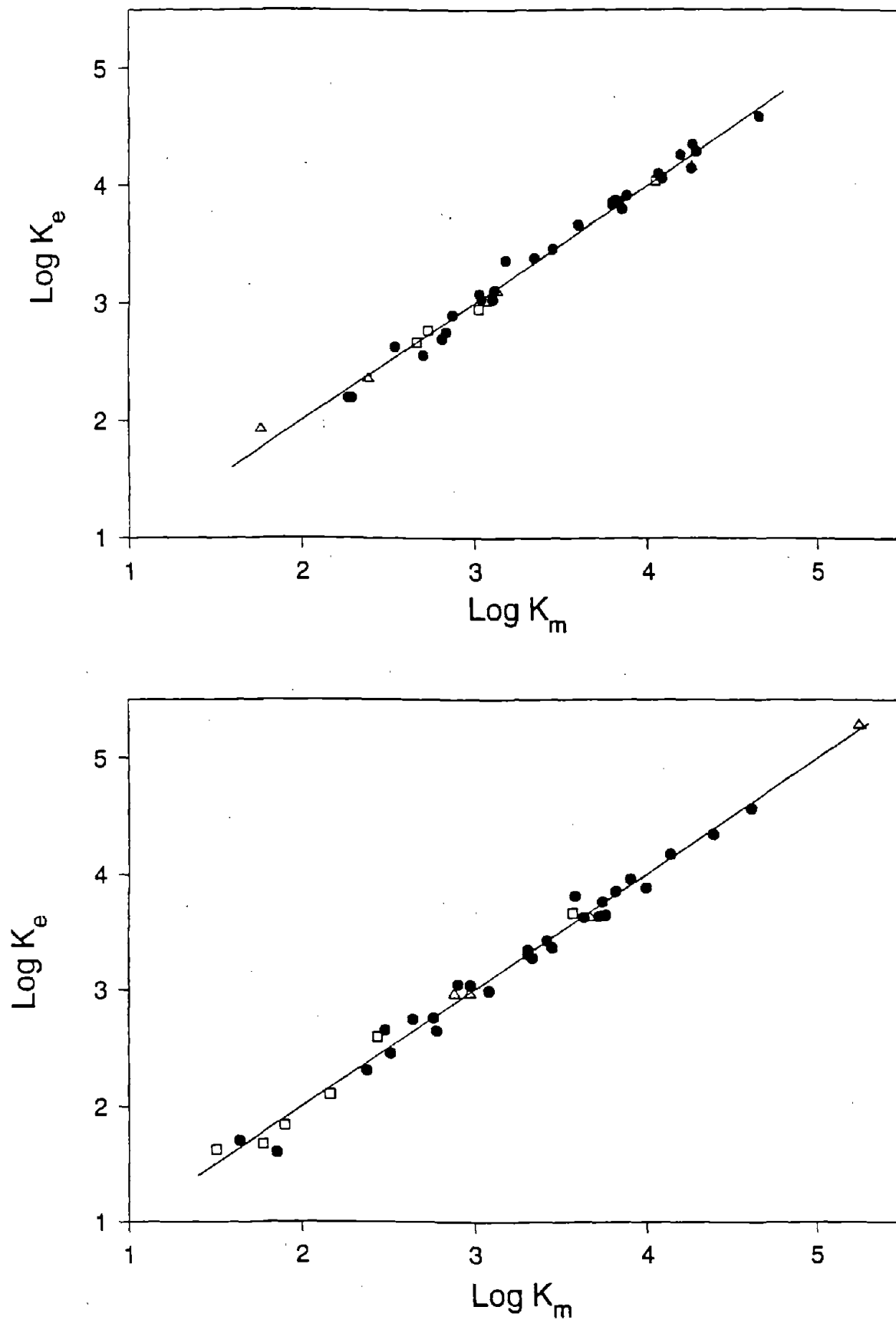


Figure 3. Plot of $\log K_e$ versus $\log K_m$ from LSER model for the coatings (a) PIB and (b) OV-275: (see Fig. 2 caption for explanation of symbols). The lines were determined by least-squares regression.

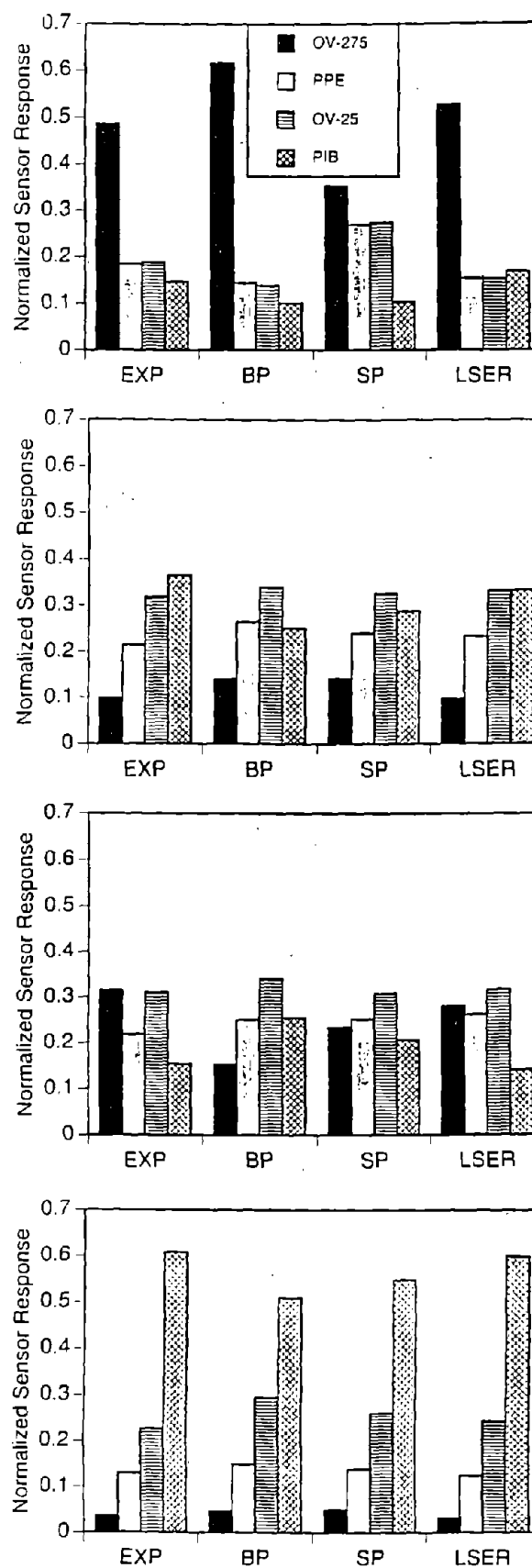


Figure 4. Normalized sensor-array response patterns from experimental data (EXP), BP model (BP), SP model (SP), and LSER model for (a) n-butanol; (b) m-xylene; (c) 1,4-dioxane; and (d) n-hexane.

3 below those obtained using the full set of vapors. As with the full data set, the r coefficients were not significant for any of the coatings and the s coefficient once again dropped out for PIB. None of the differences between the coefficients determined from the full and reduced data sets were statistically significant, though the values did change somewhat. The largest differences are seen in the a and b coefficients for PIB.

Using the coating regression coefficients determined from the 26-vapor training set to model the 11 vapors in the test set gave results comparable to those using the full data set: all K_m values were still within a factor of two of K_e and 34 of 44 (77%) were within $\pm 25\%$. The normalized response patterns for hexane, dioxane, xylene and n-butanol were similar to those shown in Fig. 4a-d for the full LSER model. In addition, a principal components plot generated from the modeled responses of the 11 test vapors gave vapor response projections that tracked closely those generated from the experimental data, providing further evidence that the modeled data could be used to screen coatings for inclusion in an array and/or to assess the potential for a given array to discriminate between each of several vapors.

Conclusions

These results demonstrate that models developed for describing the partitioning of organic vapors into polymeric materials in GLC can be successfully adapted to modeling the responses of polymer-coated SAW vapor sensors. Evidence gathered here supports earlier reports [14,17] suggesting that the experimental (or effective) partition coefficient, K_e , derived from sensor responses by Eq 2, is affected significantly by changes of the polymer modulus accompanying vapor sorption. Strictly speaking, therefore, K_e is not a partition coefficient as conventionally defined. However, the strength of the correlations observed between K_e and the various predictor variables explored in this study indicate that it can be used in manner analogous to that of a true partition coefficient. This implies that modulus changes vary in direct proportion to the amount of vapor sorbed by the polymer coating, at least for the coatings, vapors, and vapor concentration ranges investigated here.

For the three sensor response models examined in this study, the accuracy increased with the complexity of the model. With the simplest model, based on correlations of the sensor responses and vapor boiling points, response estimates within a factor of two of experimental values were obtained for the majority of coating/vapor combinations after stratifying the vapors into two or three subgroups. This model appears to be quite general and, in the absence of more detailed information on sensor coating properties, it should be useful in screening the performance of sensors and sensor arrays for many practical applications.

In the second model examined, sensor responses were estimated as a function of both

the vapor pressure of the vapor and the difference in Hildebrand solubility parameters between the vapor and coating. The strength of the correlations between observed and modeled responses improved for most vapors over the unstratified boiling point model. Furthermore, the similarity in the regression equations for all four coatings indicates that this model should be applicable to other coatings and that estimates of responses could be obtained without experimental characterization of the coating. Implementation of this model relies on the availability of solubility parameters, which have been determined, or can be calculated, for many vapors and polymers. As we have shown here, coating solubility parameters can also be estimated using SAW sensor responses.

As expected, the third model based on the use of solvation parameters in LSERs yielded the most accurate estimates of the sensor responses. These results provide experimental confirmation of the utility of the LSER approach to characterizing the solubility interactions between vapors and SAW sensor coatings as discussed previously by Grate and Abraham [8]. In the vast majority of cases, vapor-coating responses were modeled within $\pm 25\%$, even for vapors that were excluded from consideration in developing the model regression equations.

Implementation of the LSER model is currently limited by the need for solvation parameter coefficients for the sensor coating. It was shown here that the values of these coefficients determined via SAW sensor responses can be quite different from those determined by the more traditional method of GLC. Discrepancies may be attributable solely to differences in temperature; however, relative humidity, and vapor-substrate interactions may also be important. If solvation parameter coefficients are to be used for modeling of sensor responses, values derived from sensor responses are preferred to GLC-derived values since implicit account is taken of such confounding factors.

The determination of solubility parameters and solvation parameters by use of SAW sensor response data has a number of advantages: with the availability of commercial sensor-array instrumentation several coatings can be tested simultaneously; tests can be performed over a wide range of vapor concentrations at low temperatures; and tests can be performed in inert atmospheres or in air at any level of relative humidity. In addition, the influence of mixtures of vapors on the solubility properties of polymers can also be examined relatively easily with this approach.

A limited examination was performed of the effects of relative humidity on the responses of the coated sensors to organic vapors. It was shown that sorbed water vapor had no appreciable effect on responses for most coating/vapor combinations, but that it can significantly affect the responses to hydrogen-bonding vapors with both polar and non-polar coatings. For ambient monitoring of this class of vapors this factor would have to be

accounted for during initial sensor calibration and, in the case of a sensor array, incorporated into the pattern recognition analysis used for vapor identification or classification.

Limits of detection for 156 vapor-coating combinations have been provided here. For a significant fraction of the vapors examined, the LODs are sufficiently low to consider applications such as occupational and environmental monitoring where detection of vapors in the low- $\mu\text{g/L}$ range is often needed. However, for several vapor/coating combinations, LODs of several thousand $\mu\text{g/L}$ were observed. In one sense this can be an advantage since these vapors will not interfere with others. On the other hand, if one wishes to monitor these vapors at moderate or low concentrations, vapor preconcentration or replacement of the sensor coating(s) would be required. Alternatively, the use of SAW resonators rather than SAW oscillators could be considered: the former have been reported to give up to a 10-fold improvement in signal-to-noise ratio over the latter [57]. This, in turn, would lead to a commensurate reduction in the LOD.

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Appendix 1. Table A1 lists the solvation parameter values for the solvent vapors used in this study [53,54].

Table A1. Solvation parameter values for the solvent vapors.^a

vapor	R_2	π_2^H	α_2^H	β_2^H	$\log L^{16}$
benzene	0.610	0.52	0	0.14	2.786
toluene	0.601	0.52	0	0.14	3.325
m-xylene	0.623	0.52	0	0.17	3.839
p-xylene	0.613	0.52	0	0.17	3.839
hexane	0	0	0	0	2.668
cyclohexane	0.305	0.10	0	0	3.007
isooctane	0	0	0	0	3.106
nonane	0	0	0	0	4.182
aniline	0.955	0.96	0.26	0.53	3.993
N,N-dimethylaniline	0.957	0.82	0	0.48	4.728
pyridine	0.631	0.82	0	0.52	3.017
methanol	0.278	0.44	0.43	0.47	0.970
isopropanol	0.212	0.36	0.33	0.56	1.764
1-butanol	0.224	0.42	0.37	0.48	2.601
2-butanone	0.166	0.70	0	0.51	2.287
3-heptanone	0.106	0.66	0	0.51	3.776
cyclohexanone	0.403	0.86	0	0.52	3.792
ethyl ether	0.041	0.25	0	0.45	2.015
tetrahydrofuran	0.289	0.52	0	0.48	2.636
1,4-dioxane	0.329	0.75	0	0.64	2.892
methylmethacrylate	0.245	0.62	0	0.45	2.880
n-butyl acetate	0.071	0.60	0	0.45	3.353
amyl acetate	0.067	0.60	0	0.45	3.844
benzyl chloride	0.821	0.89	0	0.31	4.320
chlorobenzene	0.718	0.67	0	0.09	3.640
2-chlorotoluene	0.762	0.66	0	0.09	4.168
4-chlorotoluene	0.705	0.67	0	0.09	4.197
1,3-dichlorobenzene	0.847	0.74	0	0.03	4.419
methylene chloride	0.387	0.57	0.10	0.05	2.019
chloroform	0.425	0.49	0.15	0.02	2.480
1,1,1-trichloroethane	0.369	0.41	0	0.09	2.733
trichloroethylene	0.524	0.40	0	0.03	2.997
1-hexene	0.078	0.08	0	0.07	2.572
cyclohexene	0.395	0.20	0	0.10	3.021
styrene	0.849	0.65	0	0.18	3.856
α -methylstyrene	0.851	0.64	0	0.18	4.292
4-methylstyrene	0.871	0.65	0	0.18	4.399

^a R_2 = polarizability, π_2^H = dipolarity/polarizability, α_2^H = hydrogen bond donation, β_2^H = hydrogen bond acceptance, $\log L^{16}$ = dispersion interaction.

CHAPTER 4

COATING SELECTION STRATEGIES AND SENSOR ARRAY PERFORMANCE

Synopsis

This chapter describes results of experiments involving exposure of 16 different polymer-coated SAW sensors to each of up to 20 organic vapors over a wide range of concentrations. Using a prototype instrument containing an array of four coated SAW sensors, sets of sensor coatings were tested sequentially by exposure to the organic vapors in controlled test atmospheres at 25°C and 50% relative humidity (RH). Additional tests were performed on a subset of coated sensors and vapors to examine response reproducibility and the effects of aging, temperature, RH, and co-exposure to binary vapor mixtures. Using these data, an approach to selecting the optimal coating set for inclusion in a four-sensor array for a given exposure problem was developed. This approach involves the use of EDPCR (see Chapter 2) and a Monte Carlo simulation procedure which allows quantitative estimates of performance in terms of the fraction of correct identifications and the error in quantification for any vapor or vapor mixture, given calibration data for the vapors under consideration. The use of responses predicted from the LSER model (described in Chapter 3) to select optimal coatings was also investigated. The optimal coating selection procedure was applied to various binary mixtures and also to a series of ternary mixtures. Experimental verification of predicted performance was obtained for several of the binary mixtures.

Results indicate that sensor responses are rapid and reversible for all of the vapors examined and that responses are a linear function of concentration over the ranges examined. Limits of detection (LOD) range from about 1 ppm to several hundred ppm, depending on the coating and vapor considered. In general, lower detection limits are achieved for higher boiling vapors containing polar functional groups. LODs are below TLV values for most of the vapors examined. Responses exhibit a negative Arrhenius temperature dependence, which differs for different vapors, but which is similar for a given vapor on several different coatings. This feature may be useful in enhancing the selectivity of the array. Relative humidity did not affect the responses to the subset of vapors tested on most coatings, though a significant decline in response was observed with increasing humidity for the most polar coating considered. Several coatings were found to be unstable and were omitted from further consideration. For the remaining stable coatings, aging effects were examined and it was found that responses were reproducible over at least a 2-8 month period.

Experimental verification of the ability of the SAW-sensor array to identify and quantify individual vapors and the components of binary vapor mixtures was obtained. Both within-class and between-class discrimination is possible. Errors in identification (classification) were generally restricted to cases involving mixtures where one component was present at a low concentration and either the mixture was misidentified as being only the individual dominant

component or the minority component was misidentified as a structurally similar vapor. A limited examination of ternary mixtures indicates that accurate identification and quantification is also possible for a number of industrially relevant ternary mixtures.

The use of EDPCR coupled with a Monte Carlo simulation procedure for selecting optimal coatings for inclusion in the array represents an extremely useful way of screening coating materials, permitting determination of the optimal coating set, the percentage of misclassifications, and the identities of the misclassified vapors. Using modeled responses, as determined using the LSER model described in Chapter 3, in place of experimental calibrations in the EDPCR-based coating selection procedure appears promising. The findings in this chapter demonstrate that the coated SAW sensor array possesses performance characteristics that are superior to those of most currently available portable direct-reading instrument detectors for organic vapors.

Introduction

Microfabricated surface-acoustic-wave (SAW) chemical sensor arrays have the potential to provide rapid identification and quantification of a wide range of toxic gases and vapors at concentrations in the range of regulatory exposure limits. Incorporation of these sensor arrays into small, inexpensive instruments for continuous selective measurement of personal exposures to organic vapors would lead to considerable improvements in the quality and quantity of analytical data used to guide industrial hygiene exposure assessment and control efforts.

The research described in this chapter focuses on several aspects related to the deployment of SAW sensor array based instrumentation in occupational exposure monitoring applications. 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 tailoring the performance characteristics of the sensor array to a given exposure situation by proper selection of the coatings used on each sensor in the array. Although a number of preliminary reports have appeared on the performance of SAW sensor arrays [1-5], several details relevant to occupational exposure monitoring applications have not been examined.

In Chapter 3, we described several models for predicting the responses of individual coated-SAW sensors to organic vapors. Models based on vapor boiling point, vapor/coating solubility parameters, and vapor/coating solvation parameters in conjunction with linear solvation energy relationships (LSER) were examined, with the latter providing the most accurate modeled results. Using the LSER model, it was possible to construct modeled responses for an array of sensors which, in turn, permitted the estimation of detection limits for a given vapor and a qualitative assessment of the uniqueness of the response pattern of one

vapor compared to other potential interferences. The work also revealed that relative humidity may affect responses to certain vapors on highly polar and non-polar coatings.

An important question that remains is how one goes about selecting coatings for inclusion in an array that will provide optimal selectivity for an individual vapor or for the components of simple vapor mixtures. It is also important to know which vapors are expected to cause interferences with the target vapors. These issues are addressed in this chapter. Initial screening tests entailed measuring the responses of 16 different coated SAW sensors (in sets of four) to each of 14 organic vapors using controlled test atmospheres of the individual vapors at 25°C and 50% relative humidity (RH). Responses to an additional six vapors were collected subsequently using a subset of these coated sensors. Responses were used to establish limits of detection (LOD) for the vapors and to examine aging effects for a given coating film and response reproducibility between successive coatings. Two vapors from each of three chemical classes were then selected as being representative of solvents commonly used industrially, namely hexane and isooctane (aliphatics), benzene and xylene (aromatics), and chloroform and trichloroethylene (chlorinated aliphatics). This set of vapors was used to test the procedure developed for selecting the "optimal" set of four coatings, and to examine the effects of temperature and RH on sensor responses. A limited set of tests were also performed with mixtures of the hydrogen-bonding vapors n-butanol and 2-methoxyethanol. The optimal coating selection procedure was then extended to the case of ternary mixtures, and the use of responses predicted from the LSER model to select coatings was explored.

Polymer Coated SAW Sensor Responses.

Although discussions of the responses of polymer coated SAW sensors have been provided in previous chapters (see Chapters 1 and 3), the salient points are repeated here for continuity.

The deposition of a sorptive polymer coating onto the surface of a SAW oscillator results in a decrease in the output frequency, f_0 (Hz). Assuming that the response is dominated by mass-loading effects, and further assuming that the coating film is thin, isotropic, perfectly elastic and non-conducting, the coating mass is related to the frequency shift, Δf_c (Hz), by [6]

$$\Delta f_c = (k_1 + k_2) f_0 m/a \quad (1)$$

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

Partitioning phenomena govern responses of polymer-coated SAW sensors to organic vapors. The partition coefficient, K , typically derived from gas-liquid chromatographic (GLC) analysis, represents the equilibrium vapor-polymer solubility at a given temperature [7]:

$$K = C_c / C_v \quad (2)$$

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 [5,8,9]

$$\Delta f_v = \Delta f_c K_e C_v / \rho_c \quad (3)$$

where Δf_v is the frequency shift (i.e., sensor response) due to the vapor (Hz), ρ_c is the coating density, and the subscript e indicates that K is determined experimentally using sensor responses.

Inherent in Eqs. 2 and 3 is the assumption that the sensor response is dominated by mass-loading effects. Under this condition, Δf_c is an accurate measure of coating mass, and K and K_e should be equivalent. However, evidence reported recently indicates that modulus effects may also be important determinants of sensor responses [5,9,10]. For organic polymers, which may have shear modulus values as high as 10^9 N/m² at the operating frequency of the SAW oscillator (i.e., 158 MHz) [11], there will be a contribution to Δf_c in Eq. 1 of about -10% due to the stiffness of the polymer film. That is, modulus effects will tend to offset the negative frequency shift attributable to mass loading by a fractional amount (see Chapters 1 and 3). Perhaps more importantly, K_e values determined using Eq. 2 may exceed K values determined using GLC measurements due to changes in the polymer modulus (i.e., softening) accompanying swelling of the polymer film during vapor sorption [5,9]. During vapor sorption, mass changes and modulus changes *both* cause a negative shift in frequency. To the extent that modulus changes contribute to these measured values, K_e is not a true partition coefficient, as defined in Eq. 2. 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. 3 provides an accurate description of polymer-coated SAW sensor responses to organic vapors over a wide range of concentrations.

Coating Selection - General Considerations

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, can 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 polymer coatings for inclusion in the array can lead to significant differences in the response patterns for different vapors [3,5]. Such an array can measure several different vapors individually or in simple mixtures.

The selection of coatings in sensor arrays is based principally on sensitivity and selectivity considerations. Each coating should contribute unique information about the vapor to avoid redundancy (i.e., colinear responses). Some qualitative guidance for coating selection can be obtained from considerations of coating and vapor physicochemical properties that affect the magnitude of the solubility interactions [3], or by using principal components or cluster analyses of sensor calibration data [12]. However, a method for selecting the optimal array for a given exposure situation has not been developed. Furthermore, the problem of identifying and quantifying the components of vapor mixtures using coated SAW sensor arrays has not been extensively studied [1].

The problem of vapor identification and quantification increases in difficulty as concentration spans increase; as the possibility of more compounds increases; as exposures move from individual compounds to binary, ternary, 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 cannot 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 most occupational environments, for example, the number and nature of vapors present can usually be determined from an inventory of chemical feedstocks and reaction byproducts. Often, a relatively small set of organic vapors are present.

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 should be employed; (6) the largest number of compounds should be discriminated; and (7) 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.

To correctly identify compounds, sensor array responses to each target compound must be unique, i.e., the vector consisting of the frequency shifts from the various coated sensors for a specific compound must be linearly independent of the vectors obtained for all other compounds. Colinearity 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, but must be addressed in any effort to validate the application of sensor arrays to the measurement of vapor mixtures. The methods described in this chapter address these important issues.

Superimposed on the problem of vapor identification and quantification in field applications are the potential confounding effects of environmental variables such as humidity and temperature. These factors have not been well-characterized with respect to the performance of SAW vapor sensors. The effects of these factors must be understood prior to field applications of this technology.

With respect to humidity, organic vapors are generally present in the environment at concentrations much lower than that of water vapor. The very high concentration of water vapor may elicit a response in the sensor array and/or interfere with the sorption of organic vapors. Changes in temperature will cause a shift in the baseline of the sensor output and will also affect the partitioning of vapors into the polymer coating. Temperatures may be quite constant in some cases, and variable in others.

It may be possible to condition the sensor array and the vapor to achieve constant temperatures and humidities (e.g., by the use of thermostating and scrubbers). In cases where

responses to factors are well behaved and predictable, it may be possible merely 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.

Experimental

The sensor coatings examined are listed in Table 1. Several of the coatings consist of polymeric materials commonly used as GC stationary phases that were chosen based on an analysis of GC retention data reported by Huber and Reich [13]. Additional coatings were selected based on general considerations of structure and anticipated affinities for the test vapors. Collectively, this set of coating materials spans 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 ACGIH-TLV values [14] are listed in Table 2. Solvents were all > 98% pure (Aldrich, Milwaukee, WI) and were used without further purification.

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. 1. Values of Δf_c were all in the range of 190 - 230 kHz. Estimated film thicknesses were in the range of 0.05-0.1 μm . In most cases, the reference sensor frequencies were higher than the coated sensor frequencies prior to coating, thus difference frequencies increased steadily during coating deposition. However, in a few cases the reference sensor frequencies were initially lower and the difference frequency passed through a minimum during coating. This situation was easily identified and the net frequency shift was used to determine the amount of coating deposited.

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 (see Chapter 1). 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

Table 1. List of coatings, abbreviations, physical forms, and frequency shifts due to coating deposition for initial data set (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
16	APL	Apiezon-L (branched hydrocarbon grease)	S	200

Table 2. List of vapors and corresponding 1992-93 ACGIH-TLV values.

Vapor	ACGIH-TLV		Vapor	ACGIH-TLV	
	(ppm)	($\mu\text{g/L}$)		(ppm)	($\mu\text{g/L}$)
benzene	10	32	n-amyl acetate	100	532
m-xylene	100	434	n-butyl acetate	150	713
hexane	50	176	chlorobenzene	10	46
isooctane	--	--	chloroform	10	49
pyridine	5	16	methylene chloride	50	174
2-methoxyethanol	5	16	trichloroethylene	50	269
n-butanol	50	152	styrene	50	231
methanol	200	262	1-hexene	--	--
2-butanone	200	590	dimethylformamide	10	30
cyclohexanone	25	100			
1,4-dioxane	25	90			

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.

To screen coating materials and examine various operating characteristics, the SAW instrument was incorporated into an exposure and data acquisition system (see Fig. 4 in Chapter 1). An additional four-sensor array was used for later experiments and was placed in series with the first array. This permitted testing of eight coatings simultaneously. 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(s) 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.

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) root-mean-square 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.

In all exposure tests, 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 N₂). 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 five different concentrations of each test vapor to develop

calibration curves typically covering at least a 10-fold concentration range (exceptions were APL, OV-275 and OV-25, where the range was somewhat narrower). For calibrations performed subsequent to initial screening experiments, concentrations covering up to a 30-fold range were used. The minimum vapor concentration used was that yielding responses greater than the LOD for the least sensitive sensor. These tests were performed at 25 °C and 50% relative humidity.

Earlier testing (see Chapter 3) revealed that at the higher N₂ 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%). To account for this, tests were performed either with N₂ gas added to the clean-air stream at a relative flow rate equivalent to that used for vapor introduction into the contaminated-air stream or with humidified air (rather than dry N₂) being used as the carrier gas for introduction of vapors to the dilution stream. In the former cases, the actual exposure RH was slightly lower than 50% (~45-48%), however, the RH was held constant.

For binary mixtures an additional bubbler was incorporated into the system and exposures were 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. Air concentrations of the mixture components 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 (Hewlett Packard Model 3390A). The GC was calibrated before each experiment using solutions of the analytes in CS₂. Comparability between GC and IR analyzers was verified. In certain later experiments, the GC was used to verify individual-vapor concentrations as well.

Calibrations were performed for the coatings (typically in sets of four) and from 14-18 vapors. Following exposure to these vapors, the coating was dissolved from the SAW sensor surface and a new coating applied as described previously. Of the 16 coating materials initially examined, five were eliminated from further analysis for one of several reasons: problems with baseline and/or response instability (PPE, OV-215, TBEP), negative responses (ETSA) or extreme water sensitivity to water vapor (PHOEA). A sixth coating, PMMA, was omitted due to its very low response to all vapors. For the coating PHA, only a partial set of calibrations was performed. Analyses of the calibration curves from the remaining nine coatings used techniques presented in the next section. Subsequent testing of the effects of temperature,

humidity, and vapor mixtures on the array responses was performed on a subset of coatings selected to provide "optimal" selectivity between members of a subset of six vapors: benzene, m-xylene, hexane, isooctane, chloroform and trichloroethylene (TCE). A limited examination was also performed of binary mixtures of butanol and 2-methoxyethanol. Additional analyses were performed with other subsets of coatings and vapors as described below.

Temperature effects were examined by exposure to a subset of three vapors at 15, 25, 30 and 40°C using dry N₂ as the diluent stream. Additional tests were performed at relative humidities ranging from 0 to 77% RH, while maintaining the sensor array at 25 °C. Sensor responses to the vapors as a function of relative humidity were determined using multipoint calibration curves. Sensor responses to water vapor alone were also determined.

Data collected 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.

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.

Results and Discussion

Sensor Calibration and Linearity. Figure 1 shows a series of response profiles for four different coated sensors exposed alternately to TCE vapor (7700 $\mu\text{g/L}$) 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.

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). K_e values were calculated by Eq. 3 using the Δf_c values for each coating and limits of detection (LOD) were determined by extrapolating the response curves to a frequency shift of 45 Hz, representing 3 to 4 times the root-mean-square noise observed.

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 2 for exposure to TCE over a concentration range of 300 to 13,000 $\mu\text{g/L}$. Table 3 provides statistics for all coatings and vapors, showing typical calibration concentration ranges, sensor response ranges, average K_e values from several determinations, the standard error and r^2 for a typical K_e determination, and the calculated LOD for each vapor-coating combination based on the average of several determinations. 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.

Limits of Detection (LOD) and Dynamic Ranges. LODs for SAW sensors are a function of many factors, including SAW device configuration, temperature, vapor, coating, and data reduction and analysis techniques. Table 4 lists the calculated LODs at 25 °C for each vapor along with the vapor boiling point and the ACGIH-TLV values. These LODs are based on the single coated sensor giving the highest response for a given vapor. The variation in the LOD with temperature is provided in Table 21 for a subset of solvents and discussed

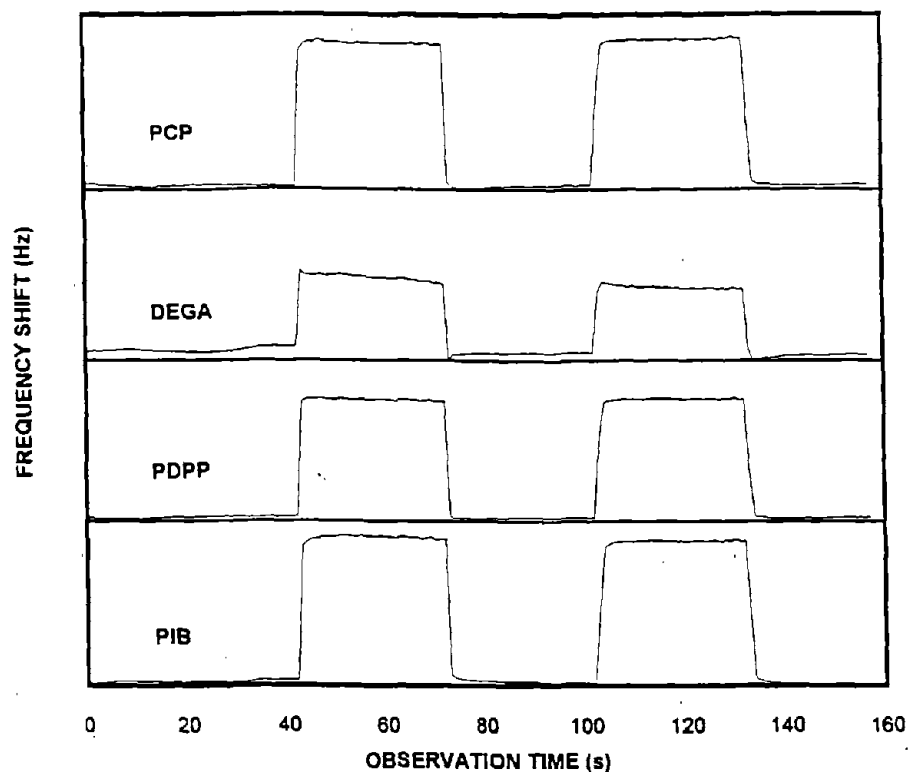


Figure 1. Response profiles of four coated sensors exposed alternately to TCE vapor (7700 µg/L) and clean air (3.0 kHz between lines).

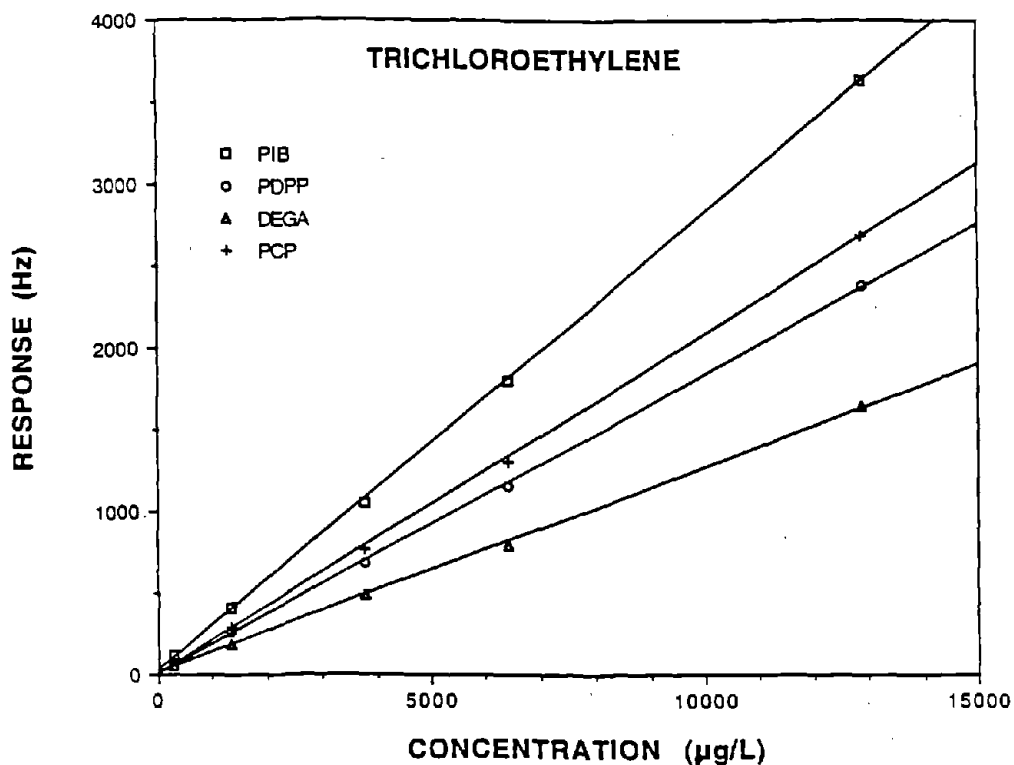


Figure 2. Calibration plots of response versus concentration for four coated sensors upon exposure to TCE from 300 to 13,000 µg/L.

Table3. Individual vapor-coating response data, K_e values and calculated LODs.

PARAMETER	PIB	PDP	DEGA	PCP	ABC	PECH	OV25	OV275	APL	TBEP	OV215	PIIA
CHLOROFORM												
conc. range ($\mu\text{g/L}$)	5680-54200	5680-54200	5680-54200	5680-54200	5680-54200	5680-54200	1720-14100	1720-14100	1760-7050	2600-26600	5700-30000	2600-26600
response range (Hz)	419-4000	389-3710	550-5250	360-3440	779-7430	492-4700	190-1640	159-1210	111-431	517-5290	133-699	460-4710
r^2	0.994	0.993	0.993	0.990	0.993	0.993	0.999	0.993	0.995	0.997	0.994	0.999
K_e	339	411	561	390	685	590	606	449	277	1070	102	1110
std.dev. K_e	10	8	19	15	22	19	18	32	12	2	1	0
LOD ($\mu\text{g/L}$)	608	652	464	714	328	517	427	502	725	226	1930	255
HEXANE												
conc. range ($\mu\text{g/L}$)	34300-246000	34300-246000	34300-246000	34300-246000	34300-246000	34300-246000	6810-23700	6810-23700	3880-10300	1400-18200	3400-41500	1400-18200
response range (Hz)	1600-11500	457-3280	41-296	410-2940	361-2590	320-2300	353-1200	85-145	283-746	69-901	15-187	66-854
r^2	0.997	0.996	0.558	0.985	0.997	0.985	0.996	0.690	0.997	0.994	0.950	0.997
K_e	215	80	7	74	53	64	261	43	317	265	20	294
std.dev. K_e	4	1	2	2	0	2	8	15	6	3	6	2
LOD ($\mu\text{g/L}$)	965	3370	37300	3760	4270	4820	991	5300	633	909	9990	959
BENZENE												
conc. range ($\mu\text{g/L}$)	2520-36100	2520-36100	2520-36100	2520-36100	2520-36100	2520-36100	1790-6790	1790-6790	912-5440	1500-8100	2100-22700	1500-8100
response range (Hz)	422-6040	391-5610	213-3050	276-3950	499-7150	432-6190	418-1730	219-767	110-636	302-1630	82-888	263-1420
r^2	0.999	0.998	0.999	0.995	0.999	0.999	0.973	0.985	0.997	0.995	0.994	0.991
K_e	770	932	489	673	990	1170	1200	561	523	1080	171	1100
std.dev. K_e	7	12	2	14	10	10	100	48	16	2	2	3
LOD ($\mu\text{g/L}$)	269	290	533	411	227	262	216	401	384	224	1150	256
TRICHLOROETHYLENE												
conc. range ($\mu\text{g/L}$)	1720-17600	1720-17600	1720-17600	1720-17600	1720-17600	1720-17600	3410-12400	3410-12400	693-3630	1500-18300	1400-22300	1500-18300
response range (Hz)	466-4770	323-3310	214-2190	184-1880	379-3880	264-2700	942-3410	314-1170	134-699	450-5490	54-859	392-4780
r^2	0.997	0.998	0.998	0.990	0.997	0.997	0.995	0.986	0.999	0.999	0.986	0.999
K_e	1250	1130	721	658	1100	1040	1400	454	872	1604	169	1637
std.dev. K_e	20	20	12	23	20	20	60	29	7	0	2	1
LOD ($\mu\text{g/L}$)	166	239	362	420	204	293	185	496	230	150	1170	172
ISOCTANE												
conc. range ($\mu\text{g/L}$)	4500-58900	4500-58900	4500-58900	4500-58900	4500-58900	4500-58900	1990-14400	1990-14400	767-4650	2600-10100	2700-20200	2600-10100
response range (Hz)	1120-14600	258-3380	45-591	206-2690	137-1790	137-1790	169-1380	9-193	124-781	260-1010	58-434	240-931
r^2	0.995	0.997	0.978	0.996	0.999	0.999	0.998	0.976	0.999	0.998	0.968	0.999
K_e	1140	345	58	281	152	207	480	47	765	537	94	578
std.dev. K_e	20	5	2	5	2	2	31	20	17	2	2	0
LOD ($\mu\text{g/L}$)	181	784	4490	984	1480	1480	539	4770	262	449	2100	488
M-XYLENE												
conc. range ($\mu\text{g/L}$)	171-2410	171-2410	171-2410	171-2410	171-2410	171-2410	420-3320	420-3320	204-5743	400-1700	1600-8400	400-1700
response range (Hz)	287-4040	194-2730	86-1210	168-2370	232-3270	200-2820	607-4210	141-1430	275-7270	606-2580	453-2380	526-2230
r^2	0.999	0.999	0.997	0.998	0.999	0.999	0.994	0.998	0.999	0.999	0.980	0.999
K_e	7720	6800	2920	6040	6780	7950	7230	2040	5650	8110	1240	8240
std.dev. K_e	80	50	50	70	50	70	640	210	220	0	2	0
LOD ($\mu\text{g/L}$)	27	40	89	46	33	38	36	110	36	30	159	34

Table 3. (continued)

PARAMETER	PIB	PDPP	DEGA	PCP	ABC	PECH	OV25	OV275	APL
CYCLOHEXANONE									
conc. range (µg/L)	63-1021	63-1020	63-1021	63-1021	63-1021	63-1021	243-922	243-922	103-3390
response range (Hz)	94-1520	182-2950	149-2420	236-3830	307-4980	333-5400	888-3670	694-2760	160-3560
r^2	0.998	0.999	0.999	0.999	0.999	0.999	0.999	0.999	0.999
K_e	6850	17400	13700	23100	24400	36000	20200	14800	5060
std.dev. K_e	90	210	200	200	300	400	1000	500	870
LOD (µg/L)	30	16	19	12	9	8	13	15	40
1-BUTANOL									
conc. range (µg/L)	780-8900	780-8900	780-8900	780-8900	780-8900	780-8900	896-3090	896-3090	598-2870
response range (Hz)	176-2010	224-2560	551-6280	454-5190	925-10600	453-5160	265-930	181-1090	106-459
r^2	0.992	0.999	0.997	0.995	0.999	0.999	0.999	0.998	0.999
K_e	1040	1720	4090	3580	5930	3950	1590	4240	752
std.dev. K_e	100	30	90	110	90	60	30	180	32
LOD (µg/L)	199	157	64	77	38	78	163	53	267
STYRENE									
conc. range (µg/L)	59-1080	59-1080	59-1080	59-1080	59-1080	59-1080	279-1460	279-1460	50-815
response range (Hz)	114-2080	119-2180	76-1390	84-1540	192-3520	143-2620	660-3130	205-1410	84-1220
r^2	0.996	0.998	0.996	0.995	0.998	0.997	0.999	0.997	0.999
K_e	8870	12100	7470	8770	16300	16500	11600	4590	6560
std.dev. K_e	210	200	160	220	300	300	700	580	480
LOD (µg/L)	23	22	35	32	14	19	22	49	31
1,4-DIOXANE									
conc. range (µg/L)	353-5930	353-5930	353-5930	353-5930	353-5930	353-5930	978-4610	978-4610	1080-5420
response range (Hz)	81-1360	108-1820	159-2680	143-2410	217-3640	215-3610	486-2150	473-2070	158-738
r^2	0.997	0.999	0.999	0.998	0.999	0.998	0.996	0.999	0.998
K_e	1050	1840	2620	2490	3070	4140	2420	2320	607
std.dev. K_e	10	20	20	30	20	40	130	90	25
LOD (µg/L)	196	147	100	111	73	74	107	97	331
AMYL ACETATE									
conc. range (µg/L)	226-3160	226-3160	226-3160	226-3160	226-3160	226-3160	274-991	274-991	112-3070
response range (Hz)	457-6390	459-6420	234-3270	376-5260	454-6350	560-7830	711-2520	244-810	140-3680
r^2	0.999	0.999	0.999	0.999	0.999	0.999	0.999	0.998	0.998
K_e	9310	12200	6010	10200	10000	16900	13200	4230	5280
std.dev. K_e	60	100	30	100	100	100	200	210	270
LOD (µg/L)	22	22	43	27	22	18	20	53	38
PYRIDINE									
conc. range (µg/L)	90-1630	90-1630	90-1630	90-1630	90-1630	90-1630	501-2330	501-2330	211-1820
response range (Hz)	90-1630	103-1860	199-3610	345-6250	334-6050	161-2920	494-2250	692-2890	68-549
r^2	0.992	0.997	0.998	0.996	0.997	0.999	0.999	0.999	0.999
K_e	4610	6860	12800	23600	18600	12200	5120	6480	1420
std.dev. K_e	240	210	300	800	600	300	100	370	50
LOD (µg/L)	45	39	20	12	12	25	50	35	141

Table 3. (continued)

PARAMETER	PIB	PDPP	DEGA	PCP	ABC	PECH	OV25	OV275	APL
1-HEXENE									
conc. range (µg/L)	14000-209000	14000-209000	14000-209000	14000-209000	14000-209000	14000-209000	5560-21400	5560-21400	1530-7290
response range (Hz)	1320-19600	503-7510	146-2180	246-3670	417-6230	365-5450	277-1250	72-182	96-476
r^2	0.996	0.989	0.938	0.994	0.996	0.999	0.995	0.957	0.996
K_e	432	216	61	108	149	177	281	51	295
std.dev. K_e	8	7	5	2	2	1	21	11	11
LOD (µg/L)	479	1250	4310	2560	1510	1730	921	4420	680
CHLOROBENZENE									
conc. range (µg/L)	336-4900	336-4900	336-4900	336-4900	336-4900	336-4900	595-2580	595-2580	148-1470
response range (Hz)	387-5650	433-6310	253-3690	253-3700	511-7460	403-5870	792-3480	323-1430	126-1220
r^2	0.998	0.998	0.999	0.993	0.998	0.999	0.995	0.988	0.999
K_e	5300	7730	4370	4640	7610	8150	6840	2670	3700
std.dev. K_e	70	120	40	130	100	100	300	160	60
LOD (µg/L)	39	35	60	60	30	38	38	84	54
METHANOL									
conc. range (µg/L)	2780-16600	2780-16600	2780-16600	2780-16600	2780-16600	2780-16600	6270-18900	6270-18900	11100-23600
response range (Hz)	41-246	59-349	315-1880	381-2280	430-2570	172-1030	110-314	1180-3340	61-138
r^2	0.956	0.993	0.981	0.999	0.998	0.990	0.976	0.999	0.992
K_e	68	126	658	844	774	420	86	919	25
std.dev. K_e	4	3	18	5	8	9	6	32	2
LOD (µg/L)	3040	2140	397	328	291	729	3000	245	8030
2-BUTANONE									
conc. range (µg/L)	2180-35700	2180-35700	2180-35700	2180-35700	2180-35700	2180-35700	2830-9500	2830-9500	1400-9270
response range (Hz)	152-2490	180-2940	156-2560	290-4750	401-6570	379-6210	493-1680	699-2040	68-474
r^2	0.956	0.951	0.953	0.958	0.990	0.984	0.999	0.998	0.999
K_e	321	494	416	817	920	1180	915	1120	223
std.dev. K_e	21	35	29	54	30	50	8	60	5
LOD (µg/L)	645	546	627	339	244	259	283	201	900
BUTYL ACETATE									
conc. range (µg/L)	138-6630	138-6630	138-6630	138-6630	138-6630	138-6630	929-2740	929-2740	299-3380
response range (Hz)	86-4140	98-4710	39-1880	93-4460	103-4930	132-6320	997-2690	350-988	129-1480
r^2	0.998	0.999	0.995	0.995	0.998	0.999	0.995	0.999	0.999
K_e	2870	4260	1640	4140	3710	6480	5470	1880	1910
std.dev. K_e	40	40	40	90	50	70	300	50	20
LOD (µg/L)	72	63	159	67	61	47	47	120	105
METHYLENE CHLORIDE									
conc. range (µg/L)	11500-192000	11500-192000	11500-192000	11500-192000	11500-192000	11500-192000	6510-39000	6510-39000	2700-9960
response range (Hz)	317-5290	321-5360	392-6550	301-5020	502-8380	365-6090	436-2290	365-2140	58-222
r^2	0.998	0.999	0.993	0.999	0.999	0.999	0.997	0.998	0.977
K_e	127	167	198	161	218	216	327	286	103
std.dev. K_e	2	2	5	1	0	2	22	9	7
LOD (µg/L)	1640	1610	1320	1720	1031	1420	791	788	1960

Table 3. (continued)

PARAMETER	PIB	PDPP	DEGA	PCP	ABC	PECH
DIMETHYLFORMAMIDE						
conc. range ($\mu\text{g/L}$)	39-511	39-511	39-511	39-511	39-511	39-511
response range (Hz)	146-3240	211-3440	544-10100	801-14100	817-14800	471-9110
r^2	0.999	0.998	0.998	0.999	0.999	0.999
K_c	17200	25400	68600	115000	95600	70400
std.dev. K_c	0	2	1	1	0	0
LOD ($\mu\text{g/L}$)	12	11	4	2	2	4
2-METHOXYETHANOL						
conc. range ($\mu\text{g/L}$)	304-4100	304-4100	304-4100	304-4100		
response range (Hz)	172-1670	90-1090	295-4660	137-1840		
r^2	0.990	0.999	0.998	0.999		
K_c	2190	1720	6110	3080		
std.dev. K_c	220	60	250	70		
LOD ($\mu\text{g/L}$)	92	166	43	102		

Table 5. Vapor LODs, boiling points and ACGIH-TLV values.

Vapor	BP (°C)	LOD		TLV	
		(µg/L)	(ppm)	(µg/L)	(ppm)
Cyclohexanone	155	8	2	100	25
Dimethylformamide	153	2	1	30	10
Amyl Acetate	149	18	4	532	100
Styrene	145	14	4	231	50
m-Xylene	138	27	6	434	100
Chlorobenzene	132	30	6	46	10
Butyl Acetate	125	47	10	713	150
2-Methoxyethanol	124	43	14	16	5
1-Butanol	118	38	13	152	50
Pyridine	115	12	4	16	5
1,4-Dioxane	101	74	20	90	25
Isooctane	98	181	39	--	--
Trichloroethylene	87	150	30	269	50
2-Butanone	80	201	70	590	200
Benzene	80	216	70	32	10
Hexane	69	633	180	176	50
Methanol	65	245	190	262	200
1-Hexene	64	479	139	--	--
Chloroform	61	226	67	49	10
Methylene Chloride	40	788	200	174	50

below in the context of temperature effects. LODs range from about 2 $\mu\text{g/L}$ (e.g., for dimethylformamide) to several hundred $\mu\text{g/L}$ (e.g., for methylene chloride). 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. In most cases, detection below the TLV value is obtainable, however, there are exceptions. While this may be useful in cases where lower boiling vapors do not need to be measured, and merely act as potential interferences, there are cases where measurement of these vapors would be desirable.

Improvements in LOD can be achieved by each of several methods: 1) operation at lower temperature; 2) use of a vapor preconcentrator; 3) application of more coating to the sensors; and 4) use of newer SAW sensor designs employing a resonator configuration (rather than the oscillators used here) which can provide up to a 10-fold improvement in signal-to-noise ratio [15] 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.

Note that 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. The number of signals required will depend on the complexity of the mixture and the similarity in responses between target vapors and potentially interfering vapors. Such conditions 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. This issue is not dealt with in detail in this report.

The dynamic range of the sensors was not fully characterized. As shown in Table 1, however, the sensor responses are generally linear over a wide concentration range. The data indicate that all sensor responses are linear over the concentration ranges of interest in industrial hygiene monitoring.

Response Reproducibility and Aging Effects. As mentioned in the Experimental Section, during the course of initial screening experiments, five coatings were eliminated from further consideration based on coating instability (PPE, TBEP, OV-215), negative responses to vapors and difficulty in determining the amount of coating deposited (ETSA), low responses to most vapors (PMMA), and extreme water sensitivity (PHOEA). As described in Chapter 3, the sensitivity of OV-25 to xylene increased by 25% over the first two weeks of exposure and then

remained relatively stable. This coating was therefore retained in further analyses. For TBEP and OV-215, initial series of exposures indicated that these coatings were quite stable and that responses were reproducible. However, subsequent testing with different coating films of these materials showed a steady and significant decline in sensitivity over time. The same sort of sensitivity decline was observed with PPE, as described in Chapter 3. For ETSA, the Δf_c value obtained directly after coating indicated about 200 kHz of coating had been deposited, but after standing for a few hours the Δf_c value drifted toward zero. Thus, it was not possible to obtain an accurate measure of the amount of coating deposited. In addition, although the magnitudes of the responses to several vapors increased with increasing concentration, the responses were all negative (recall that we are measuring difference frequencies in all cases so that responses should be positive). Given this unusual behavior, this coating was eliminated from further analyses. The coating PHA was tested with a number of vapors and was found to give stable and reproducible responses, but for logistic reasons (i.e., the limited number of sensors that could be tested at any one time) and because it did not provide particularly unique responses relative to other moderately polar coatings, it was not included in subsequent analyses.

The remaining nine coatings were generally well-behaved. Repeated exposures to benzene or m-xylene over the course of 2-8 months (typical of the time period associated with a set of exposure experiments) indicated that the sensitivities remained quite constant, with most relative standard deviations below 10% and no discernible systematic drifts over time. The sensitivity to m-xylene with APL increased by about 7-15% over the course of 2 months owing apparently to structural relaxations within the coating film: this coating was exceptional in this respect. Table 5 provides summary data on response reproducibility for representative coating films of each material. These data were collected as part of the quality control procedures for the project.

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 are based on sensitivities normalized to a common value of $\Delta f_c = 200$ kHz (note: this assumes that sensitivity is a linear function of the amount of coatings on the sensor, which is generally the case).

Table 5. Reproducibility of coated sensor responses over time (individual coatings).

Coating	Vapor	n	Time Span (months)	Average Sensitivity ^a (Hz/(μg/L))	RSD (%)
PIB	benzene	6	8	0.170	3.8
PDPP	benzene	6	8	0.157	5.9
DEGA	benzene	6	8	0.086	12.0
PCP	benzene	6	8	0.108	9.3
ABC	benzene	5	2	0.192	5.8
PECH	benzene	5	2	0.177	5.7
OV-275	m-xylene	15	2	0.401	4.2
OV-25	m-xylene	9	1	1.49	7.4
APL	m-xylene	5	2	1.17	2.4

^a all sensitivities are normalized to a value of $\Delta f_c = 200$ kHz.

Table 6. Intercoating variations in response as reflected in average sensitivities to m-xylene or benzene for successive depositions of coatings.

Coating	n	Vapor	Average Sensitivity ^a (Hz/(mg/L))	RSD (%)
PIB	2	benzene	0.172	2
PDPP	2	benzene	0.128	30
DEGA	2	benzene	0.092	9
PCP	2	benzene	0.104	5
ABC	2	benzene	0.201	6
PECH	2	benzene	0.171	5
OV-275	4	m-xylene	0.340	13
OV-25	1	-----	-----	--
APL	3	m-xylene	1.12	11

^a all sensitivities are normalized to a value of $\Delta f_c = 200$ kHz.

The m-xylene sensitivity values for each of the OV-275-coated sensors were quite stable over time, with relative standard deviations (RSD) ranging of only 3-4%. The values between coatings ranged from 0.293 to 0.401, giving an average of 0.340 and a between-coating RSD of 13% (see Table 6). The uncertainty in Δf_c values used to determine normalized sensitivities (and K_e values) must be recognized, as these estimates depend upon an accurate measure of the frequency shift obtained after coating the sensor (see Eq. 2). Since there is some drift in the sensor output just after coating, the point in time at which the net frequency shift due to coating deposition is collected can affect this determination: a rapid drift associated with solvent evaporation ($\sim$ minutes) was sometimes followed by a slower drift ($\sim$ hours, 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 sensitivities for successive coating films (i.e. RSDs were generally below 15%) as shown in Table 6. The range of intercoating variation in sensitivity shown in Table 6 is similar to, or lower than, that reported by other researchers [9].

Optimized Sensor Array - Coating Selection Methods. For each concentration of each vapor, the responses from a four-sensor array can be represented as a vector in four-dimensional space. The vectors from each set of responses corresponding to a given vapor at different concentrations will generally cluster in similar locations in space. Binary mixtures of vapors will tend to trace a locus of points between the clusters of the component vapors. In order to visualize the cluster patterns, it is useful to perform a principal components analysis (PCA) and then to project the four-dimensional vector set into two dimensions. Figure 3 shows such a PCA plot for a hypothetical data set involving two vapors and their binary mixtures. Note that with this type of projection, the separation of clusters existing in four-dimensional space is retained in the two-dimensional plot. As shown, vapors a and b are well separated, so one would expect to be able to differentiate between the individual vapors quite readily on the basis of their response patterns. The mixture response vectors are also separated from those of the individual vapors, and one would expect to be able to discriminate mixtures of these vapors from each individual vapor. As the concentration of one vapor becomes predominant, however, the projected mixture vector will approach the location of that individual vapor and the ability to identify and detect the low concentration of the second vapor will diminish. Clearly, the broader the separation of the two vapors, the more resolution there will be between mixtures and individual vapors.

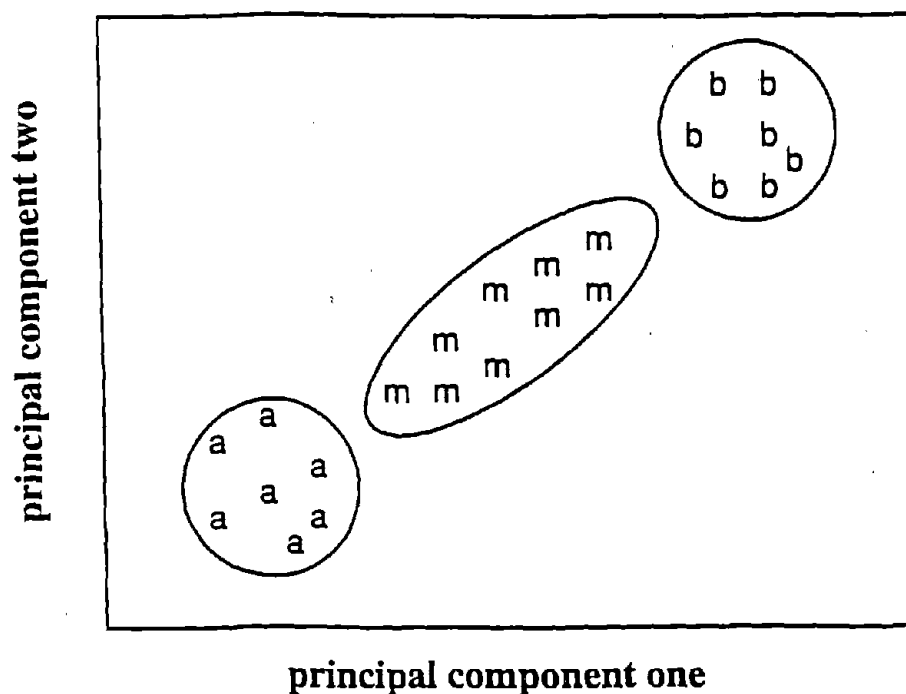


Figure 3. Hypothetical principal components projection of a binary mixture of vapors a and b.

In order to explore the issues surrounding selection of an optimal set of coating materials for use in a four-sensor array, we chose to focus initially on the following subset of vapors: hexane, isooctane, benzene, xylene, chloroform, and TCE. These represent three major classes of organic vapors commonly encountered in the industrial environment. Two members from each class were chosen to permit examination of both within-class and between-class discrimination.

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

Figs. 4a 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 Fig. 4a, 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. 4b, which used a different clustering criterion, are somewhat different and thus would provide yet more choices.

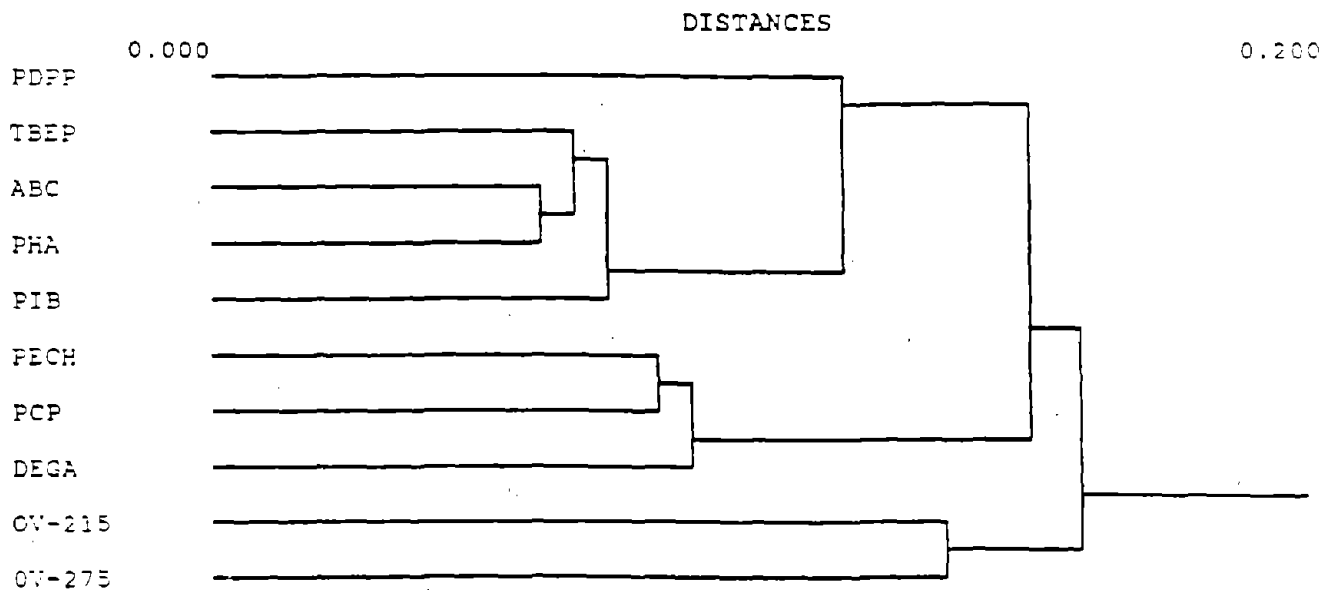
The K-means procedure is an alternative to cluster analysis that also provides groupings of similar coatings. Used iteratively, it can provide groups that satisfy a criterion such as minimum within-group variance. This procedure was performed for the data set using four groups and a large iteration limit ($n=100$). The results yielded groups of coatings similar to those obtained from the dendrograms using Euclidian distance and the complete linkage method (Fig. 4b). Again, the final selection of coatings was 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 plots, but many of these issues would remain unanswered.

Thus, 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.

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 (see Chapter 2 for an explanation of the EDPCR method). As an initial approach, we considered the general case where any of the six vapors might be present in the environment, but where only one or two might be present at any one time. To rank all 210 possible combinations of four coatings (PHA was included as the tenth coating for these analyses) in the screening set according to the percentage of correctly classified vapors 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.

**A. EUCLIDEAN DISTANCE MEASURE;
SINGLE LINKAGE (NEAREST NEIGHBOR) METHOD**



**B. EUCLIDEAN DISTANCE MEASURE;
COMPLETE LINKAGE (FARTHEST NEIGHBOR) METHOD**

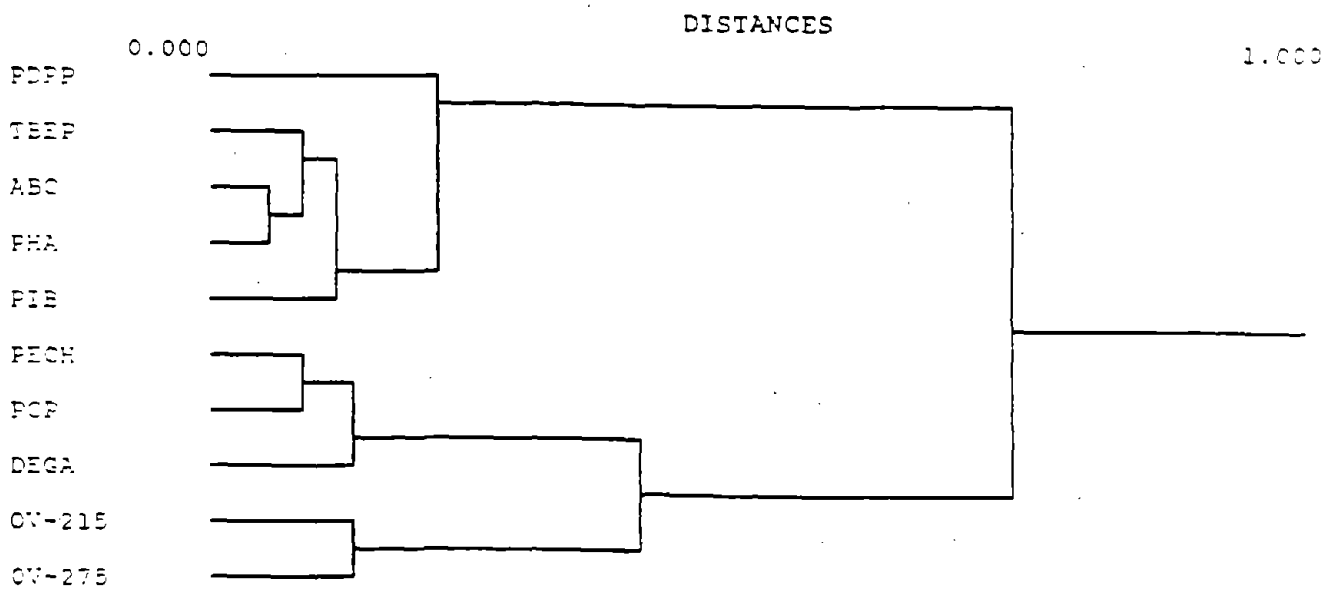


Figure 4. Two dendrograms from cluster analysis showing coating classifications.

Responses to binary mixtures were generated as linear combinations of sensor responses to the component vapors (note: the assumption of response additivity was verified experimentally, as discussed in more detail below). 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:

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

where R_j is the sensor response for coating j (Hz), $C_{i,m}$ and ΔC_i are the mean concentration and range of concentrations for vapor i ($\mu\text{g/L}$), respectively, $S_{i,j}$ 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 level of random oscillator 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 test 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 $k_3 = 15$ Hz. Using this model, concentrations were selected with equal likelihood from the entire calibration range for each vapor. The 2.5% Gaussian error (i.e., $k_2 = 0.025$) was superimposed on individual sensor responses to simulate possible temperature changes that would affect the sensor sensitivity (this number was considered a conservative estimate of calibration slope error from repeated xylene calibrations for a PIB-coated SAW sensor). The additional ± 15 Hz represents a typical level of random noise that would be unaffected by the exposure concentration. Thus, Eq. 4 produces slightly noisy but linear and additive responses at values that span experimental conditions.

The analysis of one set of four coated sensors for each possible vapor combination (i.e., six individual vapors and 15 binary mixtures) entailed 100 simulations generated using Eq. 4, or a total of 2100 analyses. This number of simulations was found to give stable results. 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 vapors yielded 0.5. For those correctly identified, the relative error in the predicted concentration was calculated. Each of the 210 possible coating sets containing 4 of the 10 coatings in the screening set was tested and ranked according to the percentage of correctly classified vapors and vapor mixture components.

Table 7 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 - the issue of the assumed error rate is discussed more fully below. Coating sets near the middle and bottom of the rankings (omitted from Table 7) had significantly lower correct classification rates. The lowest ranked coatings (rankings 200 to 210) had classification success rates from 75 to 67%. The table helps to illustrate the improvement over hierarchical clustering and K-means procedures in terms of the amount of information obtained on the performance of the various coating sets.

The coating set consisting of PDPP, PIB, DEGA, and PCP ranked first, with respect to vapor classification, so it was chosen as the "optimal" set for further analysis (note: this set would not have been chosen from the hierarchical clustering results presented above). The results of simulated responses indicate that an average of 5% misclassification is expected with this coating set.

Because the coating selection procedure maximizes the ability to discriminate among vapors, the response patterns of the optimized array for the six vapors should be quite different. Fig. 5 shows the relative responses (as sensor sensitivities) for each vapor. In most cases, the response patterns or "signatures" of each vapor are different. 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. The pairs of the aromatic and aliphatic compounds, however, have more similar patterns. In addition, hexane has very low sensitivity and thus the possibility of greater error due to higher noise levels. These two factors may make separation more problematic for isooctane and hexane.

Figure 6 presents a PCA projection plot for the six vapors. The separation between individual vapor clusters reflects the differences in their response patterns shown in Figure 5. Chloroform and TCE are well separated, whereas hexane and isooctane are grouped quite closely. The separation between benzene and xylene is intermediate between those of the other pairs.

Additivity of Sensor Responses for Binary Mixtures. 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. reported results of binary mixture exposures and claimed additivity of responses in most cases, they also indicated some exceptions [1]. Unfortunately, data were not provided in their report and could not critically assessed. As mixtures are present in many environmental applications, additivity is a critical assumption.

Table 7 Ranking of top 40 coating combinations, correct classification rates and standard deviations around each estimated rate.

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

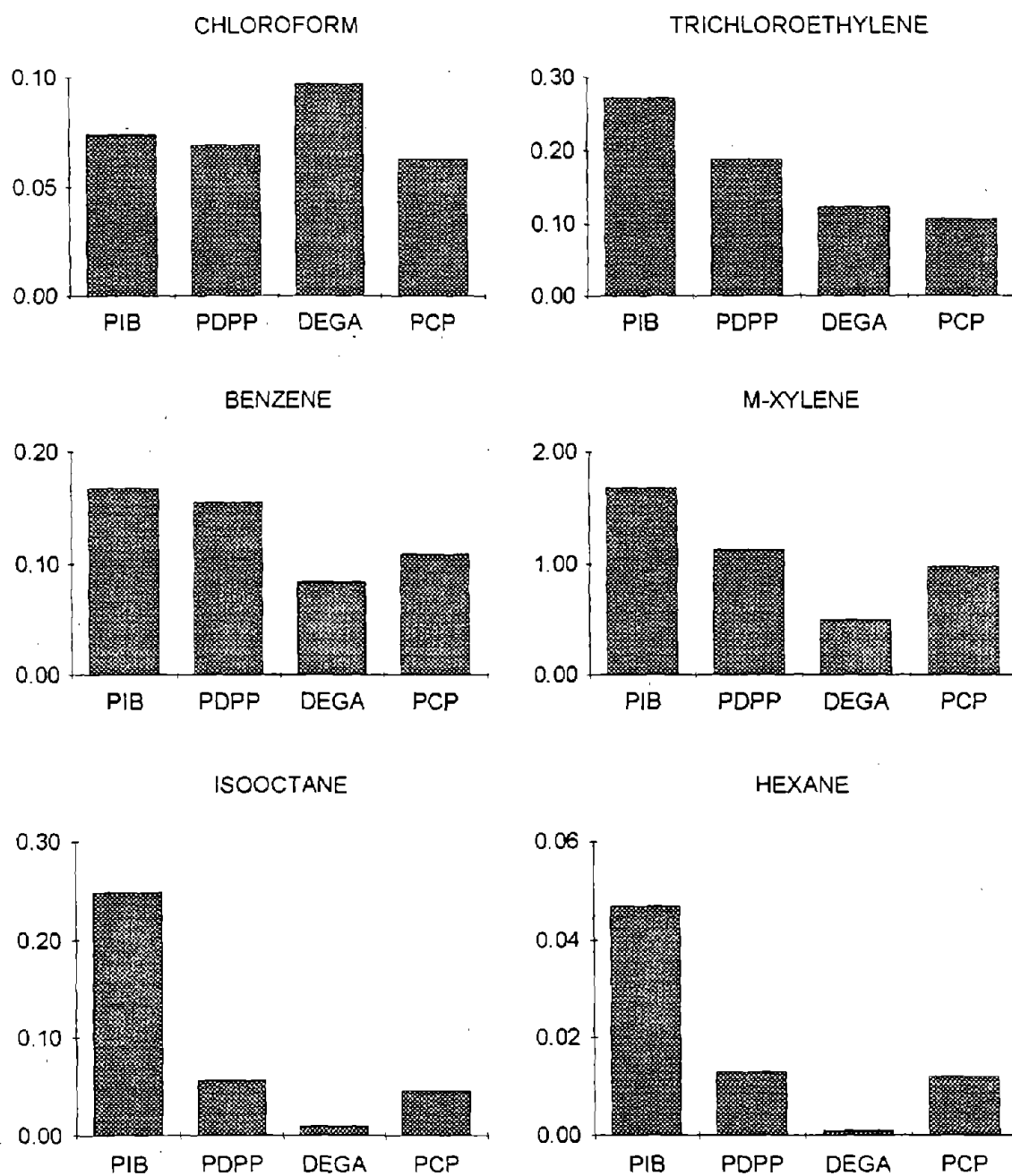
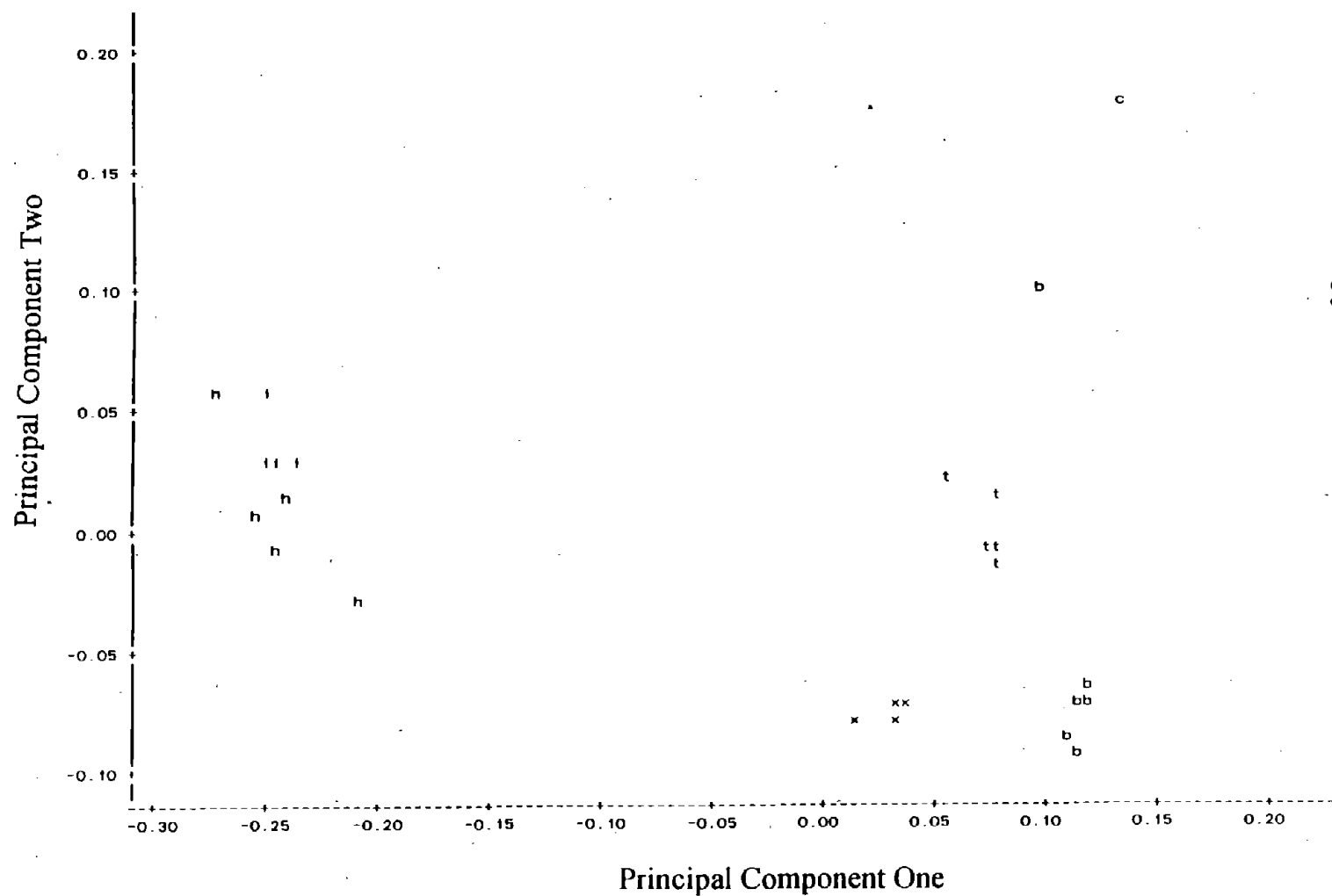


Figure 5. Response patterns for six organic vapors with optimized sensor array, y-axis in each plot is the sensitivity in Hz/(μg/L).

Figure 6. Principal components projection of response vectors for each vapor using optimized array. Legend: h (hexane), i (isooctane), x (m-xylene), b (benzene), c (chloroform), and t (TCE).



Experiments were performed to evaluate the assumption of additivity using six binary mixtures of four vapors, namely, benzene + isooctane, benzene + xylene, benzene + chloroform, chloroform + TCE, TCE + isooctane, and isooctane + hexane. Thus, both within- and between-class combinations were tested. For each mixture, the sensor array consisting of PIB, PDPP, DEGA, and PCP 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 33 individual-vapor exposures and 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. Table 8 summarizes the deviations from linearity for this data set.
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 9 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. 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

Table 8. Percentages of experimental mixture responses within specified ranges of responses expected under the assumption of additivity of responses from individual components.

mixture	range	PIB	PDPP	DEGA	PCP
benzene	±5%	43	71	71	71
isooctane	±10%	71	100	86	100
	±25%	100	100	100	100
benzene	±5%	60	70	30	70
m-xylene	±10%	100	100	80	100
	±25%	100	100	90	100
chloroform	±5%	38	50	0	50
benzene	±10%	100	100	88	100
	±25%	100	100	100	100
chloroform	±5%	36	55	45	27
TCE	±10%	82	91	82	55
	±25%	100	100	100	100
hexane	±5%	89	89	11	67
isooctane	±10%	100	100	44	100
	±25%	100	100	78	100
TCE	±5%	76	24	24	29
isooctane	±10%	100	94	59	88
	±25%	100	100	100	100
sum of all mixtures	±5%	58	52	33	48
	±10%	94	97	71	89
	±25%	100	100	95	100

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, ternary, or more complex mixtures. Finally, it permits calibrations when mixtures can not be generated, or would not be relevant. Table 9 also 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.

Table 9. Sensitivities to individual vapors and binary mixtures using optimized coating set.

VAPOR	TEST	PIB		PDPP		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	

The average sensitivities and relative standard deviation (RSD) among sensitivities obtained using Methods 2 and 3 above are listed in Table 9. 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.

Experimental Responses to Binary Mixtures - Validation of EDPCR. The capabilities for EDPCR and the optimal array to identify and quantify the vapors were assessed using experimental responses to 33 individual vapor concentrations and 62 binary mixture concentrations with varying relative concentrations of the mixture components. Overall, the correct classification rate was 88%, which is somewhat less than that predicted (95%). This may be attributed to the fact that only a small number of exposures were performed experimentally, and to the fact that all vapor mixtures were not tested - inclusion of the hexane and isooctane mixture would tend to increase the proportion of misclassifications. In light of these factors, the agreement with predictions is considered fairly good. It is also possible that the error assumed in the EDPCR analysis used to select the optimal coating set was too low.

PCA plots for the individual vapors and the binary mixture responses obtained experimentally are shown in Figure 7 for all data and in Figures 8 and 9 for two selected mixtures. Table 10 provides a detailed accounting of the identification and quantification results. For the mixtures, at least one of the components was correctly identified in all but one case. 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 individual-vapor misclassification were for one concentration of benzene which was identified as TCE, one (low) concentration of TCE which was identified as a mixture of chloroform and hexane, and one concentration of hexane which was identified as isooctane. These errors are not surprising given the similarity in response patterns for these latter two vapors.

Concentration predictions (via EDPCR) for the correctly classified vapors were generally very accurate. For the 140 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

Figure 7. PCA plot of the sensor response vectors to six vapors and their binary mixtures. Legend: h (hexane), i (isooctane), x (m-xylene), b (benzene), c (chloroform), t (TCE), 1 (isooctane+benzene), 2 (xylene+benzene), 3 (benzene+chloroform), 4 (TCE+chloroform), 5 (hexane+isooctane), 6 (isooctane+TCE).

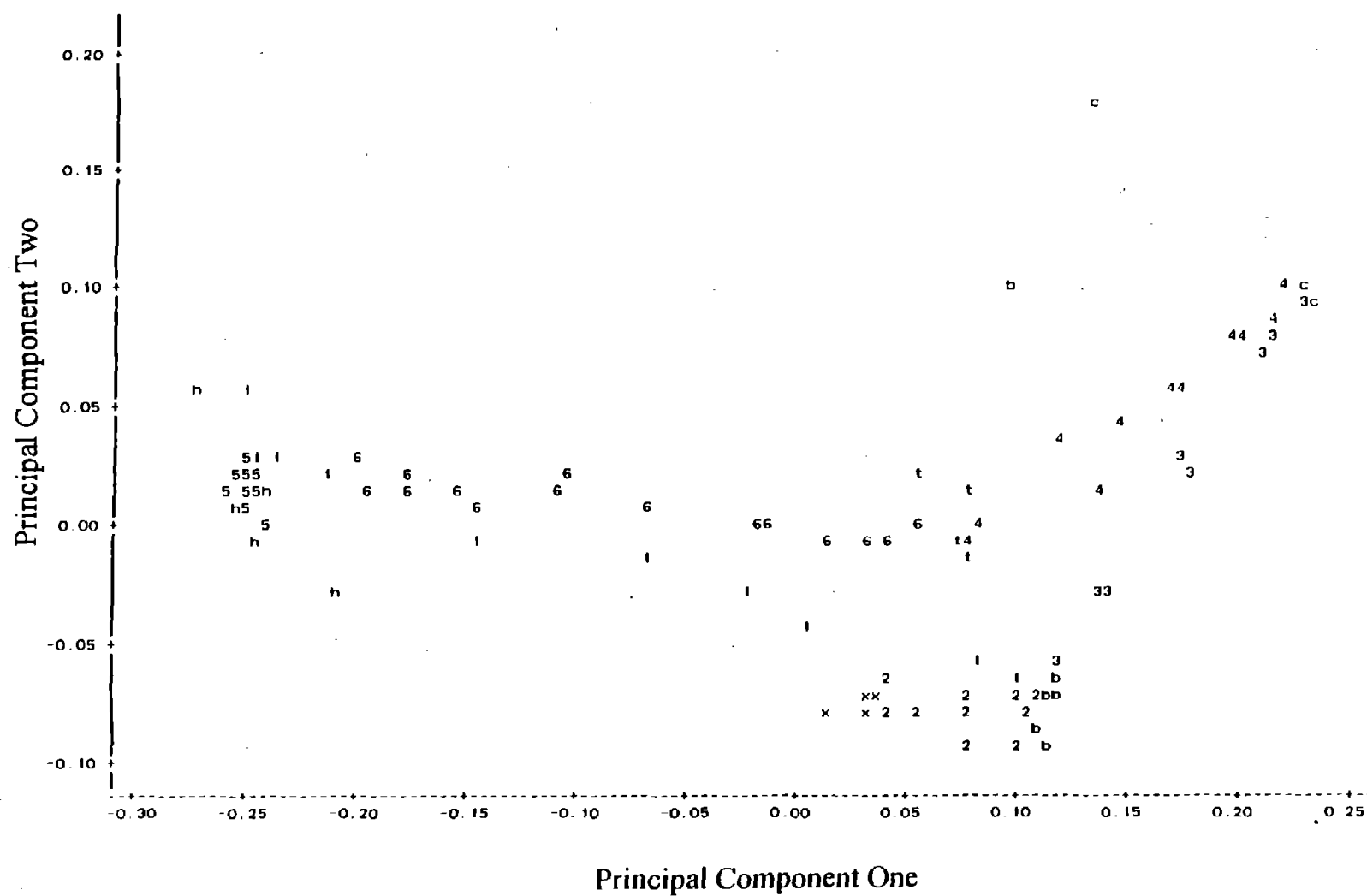


Figure 8. PCA plot of the sensor response vectors to TCE and chloroform and their binary mixtures. Legend: c (chloroform), t (TCE), and the numbers designate the binary mixtures shown in the inset.

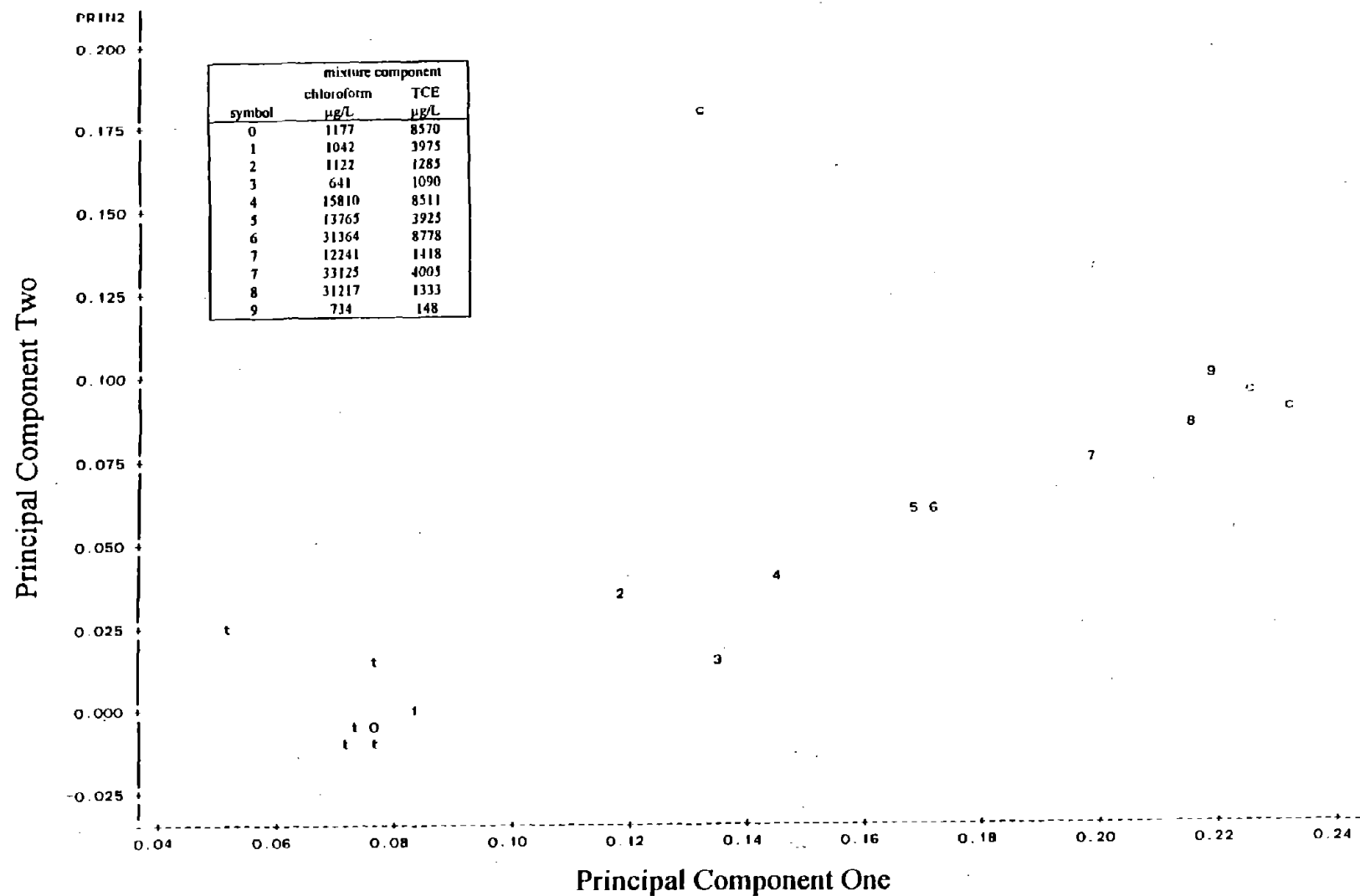


Figure 9. PCA plot of the sensor response vectors to hexane, isooctane, and their binary mixtures. Legend: h (hexane), i (isooctane), and the numbers designate the binary mixtures shown in the inset.

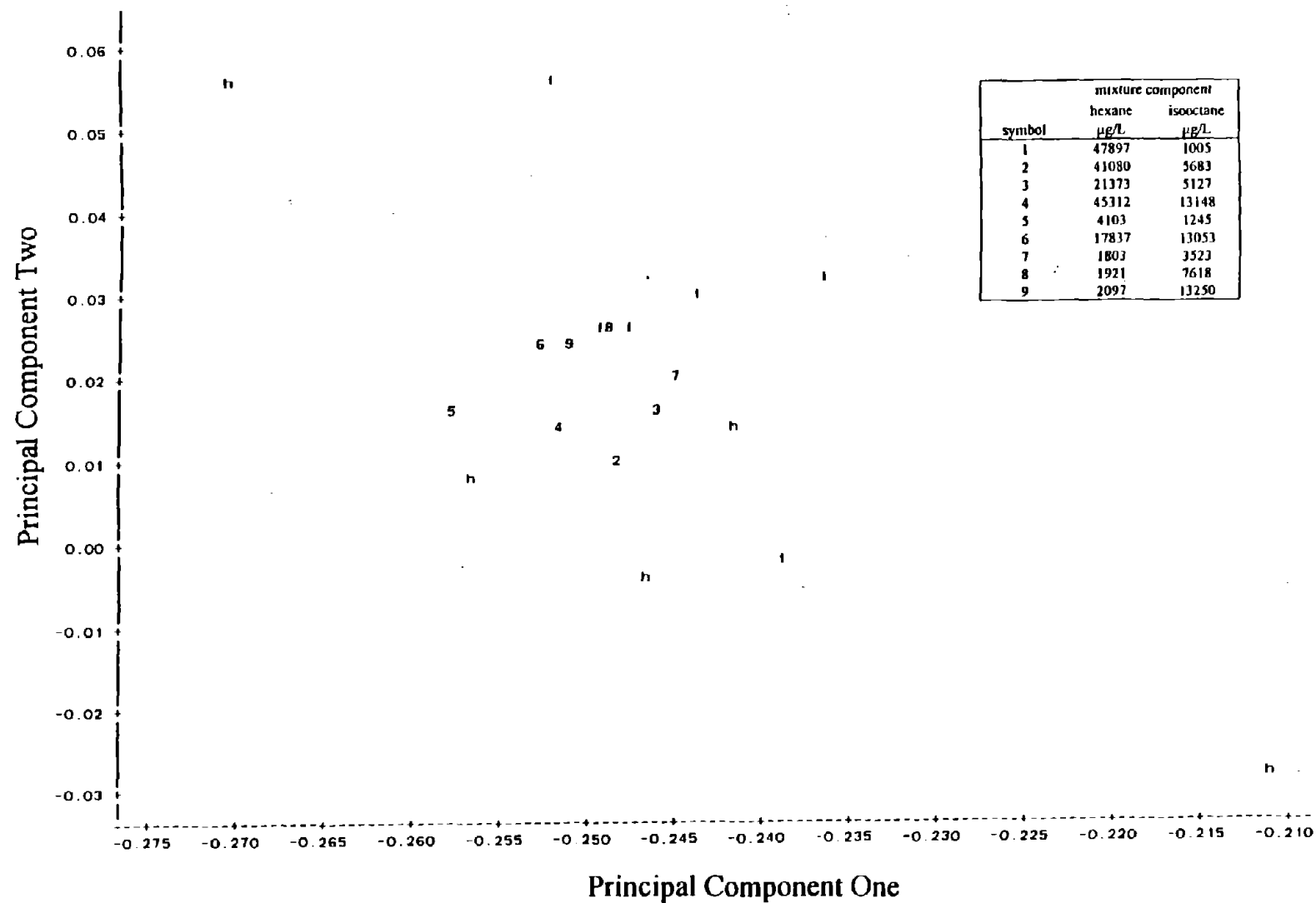


Table 10. Results of classification and quantification of experimental responses to individual vapors and binary vapor mixtures using optimized array and EDPCR (predicted) analysis.

experimental conc.		predicted conc.		pred./exp. conc.	
vapor 1	vapor 2	vapor 1	vapor 2	vapor 1	vapor 2
benzene	isooctane	benzene	isooctane	benzene	isooctane
940	386	930	552	0.99	1.43
4901	426	4867	689	0.99	1.62
9761	351	9864	558	1.01	1.59
7407	9862	7100	10072	0.96	1.02
1090	4205	*a	3296	-	0.78
834	10433	741	9714	0.89	0.93
4622	4241	4780	3967	1.03	0.94
benzene	m-xylene	benzene	m-xylene	benzene	m-xylene
1085	59	1109	48	1.02	0.81
881	59	718	63	0.81	1.07
6110	63	5500	90	0.90	1.43
20000	62	18314	167	0.92	2.69
905	399	*b	425	-	1.07
5814	433	5052	541	0.87	1.25
16865	409	16571	490	0.98	1.20
825	1439	773	1574	0.94	1.09
5775	1498	5511	1632	0.95	1.09
16236	1554	17621	1589	1.09	1.02
chloroform	benzene	chloroform	benzene	chloroform	benzene
2201	20481	2422	21902	1.10	1.07
6964	632	7629	627	1.10	0.99
9425	5288	10420	5387	1.11	1.02
1985	5686	2440	5659	1.23	1.00
8585	20350	9835	21349	1.15	1.05
38314	5304	41946	4272	1.09	0.81
33474	626	35935	*c	1.07	-
33029	22598	38976	22392	1.18	0.99
chloroform	TCE	chloroform	TCE	chloroform	TCE
1122	1285	1186	1093	1.06	0.85
1042	3975	611	3723	0.59	0.94
1177	8570	*d	8193	-	0.96
15810	8511	15545	7727	0.98	0.91
31364	8778	33318	8122	1.06	0.93
33125	4005	35293	3397	1.07	0.85
31217	1333	33041	1083	1.06	0.81
12241	1418	12173	1167	0.99	0.82
13765	3925	13554	3433	0.98	0.87
641	1090	911	778	1.42	0.71
734	148	1001	*e	1.36	-

*a 157 µg/L m-xylene

*b 573 µg/L TCE

*c classified as solely chloroform

*d classified as solely TCE

*e classified as solely chloroform

Table 10. (continued)

experimental conc.		predicted conc.		pred./exp. ratio	
vapor 1	vapor 2	vapor 1	vapor 2	vapor 1	vapor 2
hexane	isooctane	hexane	isooctane	hexane	isooctane
4103	1245	3530	1397	0.86	1.12
1803	3523	4384	2821	2.43	0.80
1921	7618	3248	6954	1.69	0.91
2097	13250	8948	11114	4.27	0.84
47897	1005	54330	*f	1.13	-
21373	5127	18168	5586	0.85	1.09
41080	5683	40344	4983	0.98	0.88
45312	13148	49989	11792	1.10	0.90
17837	13053	8841	14893	0.50	1.14
TCE	isooctane	TCE	isooctane	TCE	isooctane
788	1631	955	1546	1.21	0.95
804	2398	883	2479	1.10	1.03
784	2405	*g	*h	-	-
725	4771	914	4641	1.26	0.97
687	4762	1011	4544	1.47	0.95
813	7481	1021	7250	1.26	0.97
822	7404	1000	7474	1.22	1.01
812	10430	1104	10977	1.36	1.05
778	10278	907	11104	1.17	1.08
1810	1740	1961	*i	1.08	-
1792	1776	2036	*j	1.14	-
2939	1732	3249	*k	1.11	-
2995	1722	3285	*l	1.10	-
5410	1700	5771	1518	1.07	0.89
5182	1704	5559	*m	1.07	-
9293	1645	9940	1363	1.07	0.83
9196	1638	9786	1402	1.06	0.86
benzene	none	benzene		benzene	
496		*n		-	
2061		2071		1.00	
3932		3943		1.00	
11788		10935	*o	0.92	
11788		11167		0.95	
19812		20178	*p	1.02	
chloroform	none	chloroform		chloroform	
291		470		1.62	
3090		3151		1.02	
6751		6816		1.01	
20659		20626		1.00	

*f classified as solely isooctane

*g 1427 µg/L benzene

*h 14578 µg/L hexane

*i 7991 µg/L hexane

*j 7596 µg/L hexane

*k 7643 µg/L hexane

*l 7612 µg/L hexane

*m 8319 µg/L hexane

*n 340 µg/L TCE

*o 521 µg/L chloroform

*p 34 µg/L m-xylene

Table 10. (continued)

experimental conc.		predicted conc.		pred./exp. ratio	
vapor 1	vapor 2	vapor 1	vapor 2	vapor 1	vapor 2
TCE	none	TCE		TCE	
283		*q	*r	-	
1295		1419		1.10	
1325		1417		1.07	
2404		2488		1.03	
3796		3725		0.98	
6412		6349		0.99	
7673		7407	*s	0.97	
12892		12951		1.00	
isooctane	none	isooctane		isooctane	
1282		1269		0.99	
2544		2505		0.98	
4639		4592		0.99	
6806		6701		0.98	
14668		14449	*t	0.99	
m-xylene	none	m-xylene		m-xylene	
37		62		1.68	
167		178		1.07	
486		488		1.00	
964		933	*u	0.97	
1723		1719		1.00	
hexane	none	hexane		hexane	
3769		3838		1.02	
11233		6363	*v	0.57	
24409		16240	*w	0.67	
53636		53353		0.99	
3879		*x		-	

*q 553 µg/L chloroform

*r 1477 µg/L hexane

*s 347 µg/L benzene

*t 1383 µg/L hexane

*u 209 µg/L TCE

*v 1035 µg/L isooctane

*w 1858 µg/L isooctane

*x 726 µg/L isooctane

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.

One additional set of experiments was performed to examine whether hydrogen-bonding vapors would also exhibit response additivity. To this end, vapors of 1-butanol and 2-methoxyethanol (2-ME) were generated individually and as mixtures in various relative concentrations. Table 11 shows that the mixtures did exhibit response additivity, indicating no significant vapor-vapor interactions within the coating films. Table 12 shows that concentration determinations using EDPCR were quite accurate for both the individual vapors and the mixture components. Misclassifications were rare and, as with the previous set of vapors, involved low concentrations of one component.

Coating Selection for Individual Binary Mixtures. In the preceding analyses, we considered the case where any of six vapors might be present in the environment either individually or in binary mixtures. If the number of possible vapors that can be present in the environment is reduced, the optimal coating set may change and the performance of the sensor array will generally improve. In certain practical situations, one might have as few as two vapors associated with a given industrial process, where either vapor might be present alone,

Table 11. Ratios of responses to mixtures of 1-butanol and 2-ME: actual responses are divided by the responses expected assuming additivity of responses for the vapor components.

mixture component		coating			
1-butanol	2-ME	PIB	PDPP	DEGA	PCP
$\mu\text{g/L}$	$\mu\text{g/L}$				
517	1140	0.96	1.08	1.09	1.10
536	884	0.94	1.06	1.09	1.06
511	532	0.90	1.12	1.14	1.05
484	2450	0.92	1.04	1.05	1.04
1300	579	0.90	1.07	1.05	1.04
1210	943	0.91	1.02	1.03	1.05
1150	2080	0.91	1.00	1.01	1.02
2360	515	0.94	1.01	1.06	1.05
2370	1340	0.95	0.97	1.05	1.05
2240	2210	0.95	1.04	1.07	1.08

Table 12. Results of EDPCR classification and quantification of experimental responses to 1-butanol and 2-ME individually and in binary mixtures using optimized array.

experimental conc.		predicted conc.		pred./exp. ratio	
vapor 1	vapor 2	vapor 1	vapor 2	vapor 1	vapor 2
1-butanol	2-ME	1-butanol	2-ME	1-butanol	2-ME
517	1140	770	1057	1.49	0.93
536	884	733	795	1.37	0.90
511	532	682	451	1.33	0.85
484	2453	*a	2831	-	1.15
1297	579	1594	394	1.23	0.68
1208	943	1485	769	1.23	0.82
1153	2077	1084	2104	0.94	1.01
2360	515	2577	426	1.09	0.83
2374	1338	2387	1396	1.01	1.04
2235	2205	2141	2459	0.96	1.12
1-butanol	none	1-butanol	1-butanol		
606		603	1.00		
609		583	0.96		
1015		1003	0.99		
2185		2156	0.99		
4087		4110	1.01		
2-ME	none	2-ME	2-ME		
304		292	0.96		
574		559	0.97		
1176		916	*b	0.78	
1326		1332	1.00		
1417		1395	0.98		
1681		1647	0.98		
2181		2170	0.99		
2864		2795	0.98		
4102		4184	1.02		

*a classified as solely 2-ME

*b 388 µg/L 1-butanol

or where both vapors are present at different concentrations. This represents a simpler case than that dealt with above.

To explore how this might affect the selection of optimal coatings and the identification and quantification problems, the preceding analyses were repeated for the cases where only a given pair of vapors was allowed to be present (individually or as binary mixtures of various concentrations). Table 13 summarizes the results in terms of the optimal coating sets and the expected rates of misclassification. All 15 possible binary vapor combinations were considered for all 126 possible combinations of four coatings from a total of nine (only PIB, PDPP, DEGA, PCP, ABC, PECH, OV-25, OV-275, and APL were considered). As shown in Table 13, very high correct classification rates were obtained. The optimal set of coatings varies with the exposure situation, as does the correct classification rate. The lowest classification rates were associated with mixtures of TCE and benzene, TCE and xylene, and chloroform and benzene. Surprisingly, the discrimination of hexane and isooctane was not problematic. These analyses indicate that any of a number of coating sets will perform quite well for a given potential exposure situation, which is to be expected when using four sensors to determine one or two vapors. The error rates appear to be somewhat low, and these simulations need to be repeated with higher assumed error (i.e., 2.5% is likely to be too conservative). In certain cases, the optimal coating set determined for all possible combinations (i.e., PIB, PDPP, DEGA, and PCP, from Table 7) was also the optimal coating set for the individual pairs. In all cases this set ranked quite highly, but in certain cases (e.g., benzene + TCE and benzene + xylene) it did not rank among the top coating sets. Experimental verification of these results is currently in progress.

Coating Selection for Ternary Mixtures. In an extension of the analyses performed to select optimal coatings for binary mixtures, we examined the use of EDPCR and Monte Carlo simulations for selecting coatings for each of several ternary mixture determinations. Calibrations for the individual vapors (Table 3) were used in conjunction with Eq. 4 to simulate individual-vapor, binary-mixture, and ternary-mixture responses at various concentrations. The random noise level was assumed to be 15 Hz, and two levels of slope noise, 2.5% and 5%, were used. As before, 100 simulations were run for each of the 126 possible sets of four coated sensors. The coating selections were ranked according to the rates of misclassification.

Table 14 presents the results and shows again that the optimal coating set and the correct classification rate vary with the exposure situation. The assumed level of error obviously affects the correct classification rate and also affects the coating selection, although only marginally in most cases. That is, the optimal coatings chosen assuming 2.5% error are

Table 13. Optimal coating selections and classification rates for simulated binary mixtures.

vapor mixture	optimal coatings	Rate of Correct Classification (%)	Classif. Rate for PIB,PDPP,DEGA,PCP
chloroform hexane	110 coating sets	>99.0	100
chloroform benzene	PIB,DEGA,ABC,OV25	96.0	94.2
	PDPP,DEGA,ABC,APL	95.3	
	DEGA,ABC,OV25,OV275	95.3	
	PIB,DEGA,OV25,OV275	95.2	
	PDPP,DEGA,PECH,OV25	95.2	
chloroform TCE	PIB,PDPP,DEGA,OV275	97.7	95.3
	PIB,DEGA,OV25,OV275	97.7	
	PIB,PCP,ABC,OV275	97.2	
	PIB,DEGA,PCP,OV275	97.0	
	PCP,ABC,OV25,OV275	97.0	
chloroform isooctane	116 coating sets	>99.0	99.8
chloroform xylene	9 coating sets	>99.0	97.8
hexane benzene	87 coating sets	>99.0	99.8
hexane TCE	76 coating sets	>99.0	99.3
hexane isooctane	79 coating sets	>99.0	99.7
hexane xylene	85 coating sets	>99.0	99.7
benzene TCE	PIB,PCP,OV275,APL	94.8	90.7
	PIB,PECH,OV25,OV275	94.7	
	PIB,DEGA,ABC,OV275	94.7	
	PIB,PCP,PECH,OV275	94.5	
	PIB,DEGA,PECH,OV275	94.5	

Table 13. (cont.)

vapor mixture	optimal coatings	Rate of Correct Classification (%)	Classif. Rate for PIB,PDPP,DEGA,PCP
benzene isooctane	106 coating sets	>99.0	100
benzene	PIB,DEGA,OV275,APL	97.5	90.7
xylene	PIB,DEGA,PCP,OV275	97.3	
	PIB,PECH,OV275,APL	97.2	
	PCP,PECH,OV275,APL	97.2	
	PIB,PCP,OV275,APL	97.0	
TCE isooctane	98 coating sets	>99.0	99.7
TCE	PIB,DEGA,PCP,OV275	96.0	94.7
xylene	DEGA,PCP,ABC,OV275	95.5	
	PIB,DEGA,PCP,PECH	95.3	
	DEGA,PCP,PECH,OV275	95.0	
	DEGA,PECH,OV25,OV275	95.0	
isooctane xylene	84 coating sets	>99.0	99.7

typically among the top five or ten coatings assuming 5% error. Certain coating sets are seen to appear in several lists, indicating generally utility. Best classification rates are obtained for mixtures containing vapors with the most differences in polarity (e.g., methanol, isooctane and xylene). In all cases a high rate of correct classification is achieved.

For the mixture of styrene, methylene chloride and 2-butanone, which are solvents commonly encountered together in the reinforced plastics industry, errors were found to be primarily associated with 2-butanone being misidentified as methylene chloride. The normalized response patterns for these three vapors are shown in Fig. 10. Keep in mind that the sensitivity to methylene chloride is quite low, meaning that detection of this vapor will not be possible at low concentrations. It follows that identification of styrene and 2-butanone would be increased under these conditions (simulations involved tests of methylene chloride concentrations that were high enough to give measurable signals in at least one of the sensors).

Table 14. Optimal coating selections and classification rates using EDPCR for selected ternary mixtures assuming either 2.5% or 5% error in Monte Carlo simulations.

vapor mixture	assumed error (%)	optimal coatings	Rate of Correct Classification (%)
styrene	2.5	ABC,PECH,OV275,APL	95.7
2-butanone	2.5	DEGA,PCP,ABC,OV275	95.6
methylene chloride	2.5	PIB,PECH,OV275,APL	95.4
	2.5	DEGA,PECH,OV275,APL	95.2
	5.0	DEGA,PECH,OV275,APL	90.7
	5.0	PIB,PECH,OV275,APL	90.4
	5.0	PCP,PECH,OV275,APL	90.2
	5.0	DEGA,PCP,ABC,OV275	90.1
methanol	2.5	PIB,PDPP,OV275,APL	100
isooctane	2.5	PDPP,PECH,OV275,APL	99.9
xylene	2.5	PIB,PDPP,DEGA,PCP	99.9
	2.5	PIB,DEGA,PECH,OV275	99.8
	5.0	PDPP,PECH,OV275,APL	98.8
	5.0	PIB,DEGA,PECH,OV275	98.6
	5.0	PIB,PCP,PECH,OV275	98.6
	5.0	PIB,ABC,PECH,OV275	98.5
chloroform	2.5	PIB,ABC,OV275,APL	93.6
methylene chloride	2.5	PIB,DEGA,ABC,OV275	93.0
TCE	2.5	PIB,DEGA,OV275,APL	92.8
	2.5	PIB,PDPP,ABC,OV275	92.8
	5.0	PIB,PCP,ABC,OV275	89.1
	5.0	PIB,ABC,PECH,OV275	88.3
	5.0	PIB,ABC,OV275,APL	88.2
	5.0	PIB,DEGA,OV275,APL	87.8
styrene	2.5	PIB,DEGA,ABC,OV275	92.8
xylene	2.5	PIB,ABC,OV275,APL	92.2
benzene	2.5	PIB,ABC,PECH,OV275	92.2
	2.5	ABC,PECH,OV275,APL	92.0
	5.0	DEGA,ABC,OV275,APL	86.8
	5.0	PIB,ABC,OV275,APL	86.6
	5.0	PIB,DEGA,ABC,OV275	85.6
	5.0	PIB,DEGA,PECH,OV275	84.7

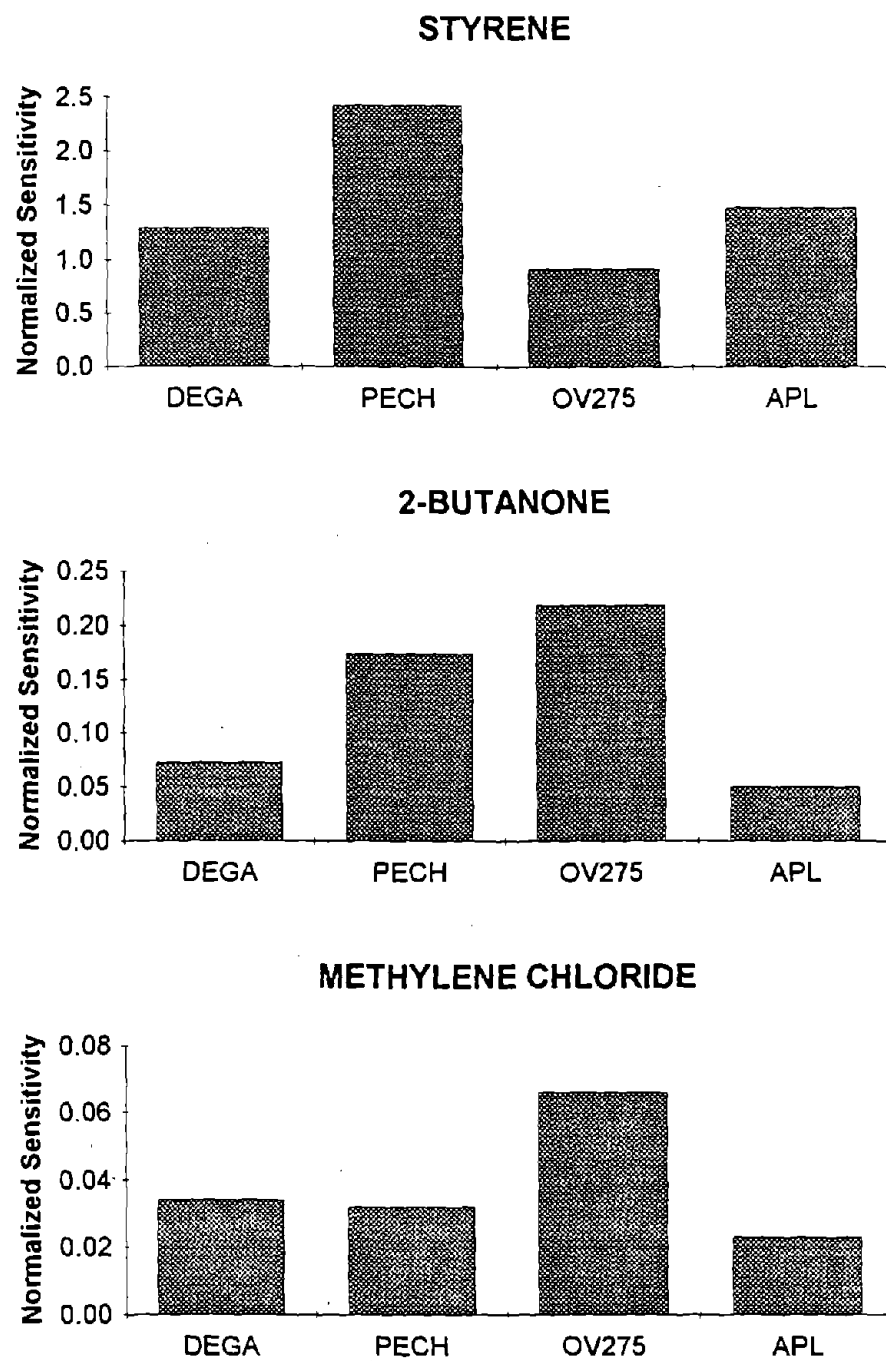


Figure 10. Response patterns for styrene, 2-butanone and methylene chloride with the optimal array for this ternary mixture (y-axis is sensitivity in units of $\text{Hz}/(\mu\text{g/L})$).

These results indicate that successful identification and quantification of ternary mixtures will be possible with a simple four sensor array for many industrially relevant situations.

Use of LSER Model in the Context of Optimal Coating Selection. Finally, it was of interest to determine whether the LSER model, described in Chapter 3, would be of use in selecting coatings. That is, we wanted to determine whether it would be possible to select coatings without having to perform calibrations for each vapor/coating pair. To this end, responses from the first 14 vapors listed in Table 1 were used to establish solvation parameter coefficients for the nine coatings. These were then used to generate modeled K_e values for each solvent/coating pair, as described in detail in Chapter 3. The modeled K_e values were then used with EDPCR to select optimal coatings.

Table 15 shows the solvation parameter coefficients for the coatings. The parameters are defined as follows: c = a regression constant, r = polarizability, s = dipolarity, a = hydrogen-bonding acceptance of the coating, b = hydrogen-bonding donation of the coating, l = dispersion interaction. In general the parameters shown in Table 15 show good agreement with values that would be expected based on structural considerations. The more polar species DEGA, ABC, and OV-275 show higher coefficients for the a parameter relative to the moderately polar coatings PDPP, PCP, PECH and OV-25 and the non-polar PIB and APL. If one considers the polarizability and dipolarity/polarizability parameters together (in Chapter 3 we noted that these terms can be highly correlated) then as expected the non-polar coatings have significantly lower degrees of polarizability and dipolarity compared to the remaining coatings. A few anomalies similar to those noted for the coatings discussed in Chapter 3 are also seen in this data set. All of the coatings have positive b values which indicate hydrogen bond donation. Of the coatings listed, only DEGA has a hydrogen atom capable of readily being donated. However, as noted previously this unexpected b value may be due to vapor adsorption at the sensor substrate or due to water vapor sorbing into the coating and providing a source of hydrogen-bond donor species.

In Table 16 the ratios of modeled K_e values to experimental values is shown. Although there are some notable exceptions (overpredicted values for 1,4-dioxane and underpredicted values for pyridine) the overall predictive accuracy is quite good. The modeled K_e values are within a factor of three of the experimental values in all cases, 98% of modeled values are within a factor of two from the experimental values, and 64% of the modeled values are within $\pm 25\%$ of the experimental values.

Using modeled values of K_e in the EDPCR approach to coating selection yielded the results presented in Tables 17-20 for each of the four ternary mixtures discussed

Table 15. Coating solvation parameter coefficients determined in this study.^a

coating	c	r	s	a	b	l	sd	R ²
PIB	0.427 (0.161)	0.414 (0.154)	-	-	0.690 (0.169)	0.796 (0.054)	0.145	0.965
PDPP	-0.229 (0.198)	0.448 (0.229)	0.683 (0.310)	1.31 (0.38)	0.802 (0.301)	0.881 (0.065)	0.128	0.976
DEGA	-0.572 (0.322)	0.826 (0.373)	1.44 (0.50)	2.96 (0.63)	1.11 (0.49)	0.707 (0.105)	0.226	0.955
PCP	0.054 (0.292)	1.01 (0.206)	-	1.67 (0.55)	2.12 (0.23)	0.724 (0.097)	0.209	0.948
ABC	-0.125 (0.210)	0.903 (0.244)	0.730 (0.329)	2.28 (0.41)	1.41 (0.32)	0.747 (0.068)	0.148	0.976
PECH	-0.200 (0.173)	0.476 (0.200)	0.998 (0.270)	1.79 (0.34)	1.22 (0.26)	0.817 (0.056)	0.121	0.984
OV-25	0.299 (0.089)	-	0.974 (0.085)	0.699 (0.165)	0.350 (0.094)	0.790 (0.029)	0.064	0.993
OV-275	0.140 (0.130)	0.344 (0.150)	1.58 (0.20)	2.45 (0.25)	0.946 (0.197)	0.526 (0.042)	0.091	0.990
APL	0.009 (0.081)	0.189 (0.057)	-	0.711 (0.151)	0.241 (0.065)	0.933 (0.027)	0.058	0.994

^a sd = overall standard deviation. R² = multiple correlation coefficient. Values in parentheses are standard errors. Hyphen = not statistically significant.

Table 16. Ratios of K_e values (LSER model:experimental).

vapor	PIB	PDPP	DEGA	PCP	ABC	PECH	OV-25	OV-275	APL
chloroform	1.14	1.19	0.89	0.95	1.00	1.09	1.16	1.25	1.18
hexane	1.63	1.63	2.91	1.30	1.38	1.48	0.96	0.81	0.98
benzene	1.27	0.98	1.29	1.42	1.21	0.97	0.94	1.04	1.08
TCE	0.89	0.76	0.53	0.98	0.74	0.81	0.82	0.79	0.92
isooctane	0.69	0.92	0.72	0.71	1.02	1.04	1.17	1.25	1.04
m-xylene	0.92	1.21	1.32	1.08	1.21	1.12	1.08	1.10	0.97
cyclohexanone	1.36	1.13	1.30	0.87	1.10	1.06	1.02	0.89	1.10
1-butanol	0.80	1.20	1.17	1.74	1.17	1.26	0.97	0.96	0.95
styrene	1.04	1.11	1.28	1.34	1.06	0.99	0.94	0.98	0.97
1,4-dioxane	1.90	1.66	1.28	2.69	1.93	1.68	1.42	1.57	1.37
amyl acetate	0.71	0.73	0.60	0.69	0.74	0.77	0.90	0.85	0.97
pyridine	0.60	0.70	0.53	0.40	0.57	0.84	0.89	0.82	0.81
1-hexene	0.82	0.70	0.52	1.26	0.69	0.71	0.96	1.00	0.93
chlorobenzene	0.90	0.87	1.03	0.85	0.93	0.95	1.06	1.04	0.98
methanol	0.63	0.77	0.88	0.66	0.83	0.76	0.96	0.96	0.97
2-butanone	1.43	1.11	1.34	1.08	0.97	0.97	0.91	0.88	0.87
butyl acetate	0.94	0.78	1.00	0.77	0.88	0.81	0.89	1.06	0.95
methylene chloride	1.31	1.12	1.09	0.91	1.25	1.25	1.04	1.00	1.07

above (see Table 14). An error rate of five percent was assumed. The left sides of Tables 17-20 show the coating selections based on experimental data and the right sides show the coating selections based on the LSER modeled data. The top portion of each table lists the 15 top ranked coating combinations, while the lower portion shows the 15 lowest ranked coating combinations (rankings 112-126). The coatings are designated by number, where 1=PIB, 2=PDPP, 3=DEGA, 4=PCP, 5=ABC, 6=PECH, 7=OV-25, 8=OV-275, and 9=APL. For example, for the mixture of styrene, 2-butanone and methylene chloride (Table 17) the first ranked set of coatings from the experimental data consists of 3,6,8, and 9 (DEGA, PECH, OV-275, and APL). Of the 100 simulations performed, the average correct classification rate from the experimental data was 90.7% with a standard deviation of 6.4%. The experimental ranking of this coating set is #1 and the LSER ranking of the same coating set is #9. That is, with the LSER based simulations eight coating sets had better correct classification rates than the set 3,6,8, and 9.

On the right hand sides of Tables 17-20 the LSER based coating rankings are shown in descending order along with the corresponding classification rates and the experimental rankings for the same coating sets. In general, the agreement between the coating combinations selected from the experimental and LSER based data are quite good. In Table 17, the top five experimental combinations are within the top 11 LSER modeled combinations, and the top five LSER modeled selections fall within the top 29 of the experimental selections. For both data sets, considering the 15 lowest ranked coatings, no individual combination is ranked above 52 from the alternate data set. Thus, both sets are similar in their ability to identify poor coating sets as well.

The coating selections for the next ternary vapor mixture (i.e., methanol, isooctane, and m-xylene) are shown in Table 18. As shown, there is very good agreement between the experimental and LSER modeled rankings. Of the top ten coatings in either data set, the alternate data set ranking is within the top 25. Of the lowest ranked 15 coatings from either set, the ranking from the alternate set is no higher than 48.

For the next ternary mixture, consisting of chloroform, TCE, and methylene chloride (Table 19), the agreement between the experimental and LSER modeled results is also quite good, with the top 5 coating rankings in either set being ranked no lower than 9 by the alternate method. The bottom ranked 15 coatings of either method were ranked no higher than 48 by the alternate method.

The results of the final mixture (Table 20) are also quite good, with the top five coating sets from either set being ranked no lower than 12 by the alternate method and the lowest ranked coatings from both methods in general agreement (one exception occurs in that the 114th coating combination from the LSER data is ranked 17 using the experimental data).

Table 17. Coating set rankings based on correct classification rates of the vapors styrene, 2-butanone, methylene chloride, and their binary and ternary mixtures from simulations based on experimental and LSER modeled response data.

experimental					LSER modeled				
coating set	% corr.	% sd	rank exper.	rank model	coating set	% corr.	% sd	rank model	rank exper.
3 6 8 9	90.7	6.4	1	9	4 5 8 9	91.7	5.7	1	11
1 6 8 9	90.4	4.3	2	10	1 4 8 9	91.3	5.2	2	12
4 6 8 9	90.2	6.3	3	3	4 6 8 9	90.9	6.2	3	3
3 4 5 8	90.1	4.9	4	11	2 4 8 9	90.7	5.2	4	13
2 6 8 9	90.1	5.1	5	6	4 7 8 9	90.0	4.8	5	29
5 6 8 9	90.0	5.6	6	8	2 6 8 9	89.4	5.1	6	5
2 3 6 8	89.3	5.5	7	37	3 4 8 9	89.0	5.1	7	34
3 5 8 9	89.3	5.8	8	20	5 6 8 9	88.9	5.7	8	6
2 5 6 8	89.0	5.3	9	27	3 6 8 9	88.8	6.5	9	1
1 3 4 8	88.9	2.9	10	16	1 6 8 9	88.6	5.0	10	2
4 5 8 9	88.8	7.8	11	1	3 4 5 8	88.3	5.2	11	4
1 4 8 9	88.7	4.5	12	2	1 2 4 8	88.1	4.1	12	21
2 4 8 9	88.7	4.7	13	4	6 7 8 9	88.0	6.1	13	15
2 5 8 9	88.7	6.5	14	19	2 4 7 8	88.0	5.7	14	35
6 7 8 9	88.4	6.2	15	13	2 4 6 8	87.9	5.6	15	19
4 5 6 9	77.7	3.1	112	117	2 3 5 6	75.5	2.9	112	107
2 4 5 9	77.5	3.9	113	101	1 2 3 9	75.4	4.2	113	121
2 4 6 9	77.5	6.8	114	69	1 3 5 7	74.7	9.4	114	55
1 2 4 6	76.7	6.5	115	100	1 2 5 7	74.5	10.1	115	97
1 7 8 9	76.5	13.1	116	52	1 2 3 8	74.2	10.9	116	54
1 2 7 9	76.3	7.2	117	76	4 5 6 9	73.9	6.2	117	112
1 2 7 8	75.5	12.8	118	122	1 3 5 6	73.3	6.3	118	81
1 2 4 9	75.2	9.1	119	73	1 4 5 6	72.4	8.6	119	106
1 2 4 5	74.7	6.4	120	99	1 2 5 6	72.3	5.1	120	126
1 2 3 9	73.9	8.1	121	113	1 2 5 9	72.2	2.4	121	125
1 2 6 9	72.8	9.7	122	108	1 2 7 8	72.2	14.6	122	118
2 5 6 9	72.6	10.1	123	105	1 3 7 8	70.5	12.5	123	60
1 5 6 9	70.8	13.5	124	125	1 2 3 5	70.4	6.2	124	99
1 2 5 9	69.2	9.5	125	121	1 5 6 9	69.6	9.5	125	124
1 2 5 6	64.8	16.7	126	120	1 2 3 7	67.5	11.6	126	103

^a 1=PIB, 2=PDPP, 3=DEGA, 4=PCP, 5=ABC, 6=PECH, 7=OV-25, 8=OV-275, 9=APL

Table 18. Coating set rankings based on correct classification rates of the vapors methanol, isooctane, m-xylene, and their binary and ternary mixtures from simulations based on experimental and LSER modeled response data.^a

experimental					LSER modeled				
coating set	% corr.	% sd	rank exper.	rank model	coating set	% corr.	% sd	rank model	rank exper.
2 6 8 9	98.8	1.9	1	1	2 6 8 9	99.4	1.0	1	1
1 4 6 8	98.6	1.7	2	9	2 3 8 9	98.9	1.1	2	17
1 3 6 8	98.6	1.8	3	6	2 5 8 9	98.8	1.2	3	19
1 2 5 8	98.5	2.1	4	11	5 6 8 9	98.7	1.6	4	9
1 5 6 8	98.5	1.7	5	5	1 5 6 8	98.7	1.1	5	5
1 2 6 8	98.4	2.1	6	12	1 3 6 8	98.7	1.7	6	3
1 6 7 8	98.3	1.7	7	10	2 7 8 9	98.7	1.7	7	24
1 2 3 5	98.2	2.6	8	18	1 6 8 9	98.7	2.0	8	11
5 6 8 9	98.2	2.0	9	4	1 4 6 8	98.6	1.2	9	2
1 2 7 8	98.2	2.2	10	25	1 6 7 8	98.5	1.1	10	7
1 6 8 9	98.2	2.6	11	8	1 2 5 8	98.5	1.7	11	4
1 2 3 8	98.1	2.4	12	14	1 2 6 8	98.3	1.8	12	6
4 6 8 9	98.0	1.9	13	15	5 6 7 8	98.3	1.4	13	29
3 6 8 9	98.0	2.4	14	17	1 2 3 8	98.3	1.8	14	12
3 5 6 9	97.9	2.9	15	29	4 6 8 9	98.2	1.4	15	13
3 4 6 8	91.8	3.3	112	110	1 4 5 9	91.6	7.7	112	110
3 4 7 8	91.4	7.0	113	48	2 4 6 7	91.5	3.4	113	117
2 4 5 7	91.0	5.1	114	109	2 5 6 7	91.5	2.6	114	124
2 3 4 8	90.9	5.9	115	98	3 5 6 8	91.0	2.9	115	126
2 4 7 8	90.9	5.7	116	64	1 2 6 7	91.0	3.5	116	109
2 4 6 7	90.8	4.3	117	113	2 3 4 6	91.0	4.2	117	107
3 4 5 8	90.8	1.9	118	111	2 3 5 6	90.6	5.4	118	100
4 5 6 7	90.7	4.6	119	120	1 6 7 9	90.6	4.2	119	91
1 3 4 9	90.4	14.0	120	94	4 5 6 7	90.5	3.7	120	119
2 3 4 7	90.4	5.2	121	92	2 4 6 8	89.8	4.9	121	96
3 4 5 6	90.0	3.7	122	123	2 3 4 5	89.2	5.6	122	111
2 4 5 6	89.5	4.7	123	124	3 4 5 6	87.7	4.0	123	122
2 5 6 7	89.2	3.9	124	114	2 4 5 6	87.6	6.0	124	123
1 2 7 9	86.0	3.3	125	126	4 5 6 8	87.5	3.5	125	105
3 5 6 8	80.0	8.2	126	115	1 2 7 9	81.0	7.7	126	125

^a 1=PIB, 2=PDPP, 3=DEGA, 4=PCP, 5=ABC, 6=PECH, 7=OV-25, 8=OV-275, 9=APL

Table 19. Coating set rankings based on correct classification rates of the vapors chloroform, trichloroethylene, methylene chloride, and their binary and ternary mixtures from simulations based on experimental and LSER modeled response data.^a

experimental					LSER modeled				
coating set	% corr.	% sd	rank exper.	rank model	coating set	% corr.	% sd	rank model	rank exper.
1 4 5 8	89.1	3.2	1	1	1 4 5 8	86.0	5.1	1	1
1 5 6 8	88.3	3.0	2	3	1 5 8 9	84.8	5.9	2	3
1 5 8 9	88.2	3.1	3	2	1 5 6 8	84.2	5.5	3	2
1 3 8 9	87.8	4.6	4	5	1 3 4 8	84.2	6.2	4	7
1 3 5 8	87.6	2.9	5	9	1 3 8 9	84.1	6.7	5	4
5 6 8 9	87.2	3.0	6	12	1 4 8 9	83.7	7.3	6	30
1 3 4 8	87.0	5.1	7	4	3 4 8 9	83.6	6.6	7	11
1 3 6 8	86.4	3.4	8	15	1 2 8 9	83.5	7.1	8	66
2 3 8 9	86.3	4.3	9	27	1 3 5 8	83.2	4.1	9	5
3 5 8 9	86.2	3.5	10	11	1 6 8 9	83.0	6.2	10	19
3 4 8 9	85.7	4.9	11	7	3 5 8 9	83.0	5.0	11	10
1 3 7 8	85.6	5.1	12	22	5 6 8 9	82.9	5.1	12	6
5 7 8 9	85.5	3.2	13	37	1 2 3 8	82.5	6.6	13	24
2 5 8 9	85.5	2.9	14	34	2 3 4 8	82.5	7.7	14	23
1 5 7 8	85.4	1.7	15	31	1 3 6 8	82.4	6.0	15	8
1 2 7 9	73.2	11.1	112	73	2 3 5 9	69.1	15.7	112	108
1 3 4 9	73.1	9.9	113	48	2 5 6 7	69.0	4.2	113	98
2 5 6 9	73.0	7.5	114	116	2 4 6 9	68.9	15.0	114	117
2 3 5 6	72.1	6.8	115	119	1 3 4 5	68.7	16.2	115	83
1 2 3 6	71.5	12.0	116	103	2 5 6 9	68.1	14.3	116	114
2 4 6 9	71.1	8.2	117	114	1 2 5 6	68.1	13.3	117	101
3 5 6 9	70.9	8.3	118	111	1 3 4 6	67.1	16.5	118	96
2 3 6 9	70.7	10.8	119	108	2 3 5 6	66.7	13.3	119	115
1 2 4 6	70.0	10.5	120	120	1 2 4 6	66.0	11.8	120	120
4 5 6 7	69.9	11.5	121	101	2 3 4 6	65.6	19.4	121	109
1 2 6 9	69.7	10.4	122	92	3 4 5 6	65.6	15.6	122	124
1 4 6 9	69.6	10.1	123	85	2 3 4 5	65.2	14.5	123	100
3 4 5 6	68.5	6.5	124	122	1 4 5 6	64.2	16.7	124	85
1 2 4 9	65.4	14.7	125	98	1 2 4 5	64.1	14.5	125	79
1 3 6 9	62.4	16.5	126	58	2 4 5 6	62.3	12.7	126	99

^a 1=PIB, 2=PDPP, 3=DEGA, 4=PCP, 5=ABC, 6=PECH, 7=OV-25, 8=OV-275, 9=APL

Table 20. Coating set rankings based on correct classification rates of the vapors benzene, m-xylene, styrene, and their binary and ternary mixtures from simulations based on experimental and LSER modeled response data.^a

experimental					LSER modeled				
coating set	% corr.	% sd	rank exper.	rank model	coating set	% corr.	% sd	rank model	rank exper.
3 5 8 9	86.8	4.5	1	1	3 5 8 9	86.2	4.2	1	1
1 5 8 9	86.6	4.0	2	2	1 5 8 9	84.5	2.1	2	2
1 3 5 8	85.6	2.6	3	8	5 7 8 9	84.1	1.6	3	6
1 3 4 8	85.0	4.2	4	12	5 6 8 9	83.7	2.0	4	8
1 3 6 8	84.7	6.1	5	10	2 3 8 9	83.4	4.7	5	12
5 7 8 9	84.5	2.0	6	3	4 5 8 9	83.0	4.9	6	9
1 3 8 9	84.4	6.7	7	11	3 7 8 9	82.6	2.4	7	13
5 6 8 9	84.4	3.5	8	4	1 3 5 8	82.5	4.1	8	3
4 5 8 9	84.1	5.4	9	6	3 4 8 9	82.5	3.8	9	24
1 2 3 8	83.8	4.9	10	17	1 3 6 8	82.4	5.8	10	5
1 3 7 8	83.5	5.4	11	22	1 3 8 9	82.3	3.9	11	7
2 3 8 9	83.4	4.2	12	5	1 3 4 8	82.0	3.5	12	4
3 7 8 9	83.3	2.6	13	7	1 6 8 9	81.9	4.6	13	25
1 5 6 8	83.3	2.5	14	16	3 6 8 9	81.9	2.5	14	16
1 4 5 8	83.3	2.9	15	25	2 6 8 9	81.7	2.7	15	18
2 3 4 9	70.3	10.2	112	86	1 3 4 6	70.4	7.4	112	121
1 7 8 9	70.2	14.7	113	113	1 7 8 9	70.1	11.9	113	113
1 4 6 9	70.2	11.2	114	81	1 3 5 7	70.0	14.0	114	17
1 2 3 6	70.0	14.1	115	52	1 4 5 6	70.0	7.0	115	104
3 5 6 7	69.6	13.5	116	91	2 3 4 6	69.8	4.9	116	123
3 4 5 6	69.1	9.6	117	123	1 3 4 5	69.1	12.2	117	95
2 5 6 7	68.7	8.1	118	108	1 4 6 7	69.0	7.6	118	73
1 2 6 9	68.4	13.4	119	87	2 3 4 5	69.0	6.0	119	107
2 4 6 9	67.8	12.5	120	106	1 5 6 7	68.9	7.8	120	60
1 3 4 6	67.5	16.1	121	112	3 4 5 7	68.4	13.4	121	72
1 2 4 6	67.3	15.7	122	99	2 4 5 6	68.2	5.3	122	110
2 3 4 6	66.9	9.5	123	116	3 4 5 6	67.3	3.7	123	117
3 4 6 9	66.8	13.2	124	78	1 3 4 7	66.2	14.8	124	45
1 2 4 9	65.3	12.6	125	82	1 4 5 7	62.3	14.5	125	57
2 3 5 6	64.9	11.0	126	126	2 3 5 6	57.2	15.0	126	126

^a 1=PIB, 2=PDPP, 3=DEGA, 4=PCP, 5=ABC, 6=PECH, 7=OV-25, 8=OV-275, 9=APL

The analyses presented above indicate the degree of success expected of a four sensor array with the given coatings in selectively identifying the components of binary and ternary vapor mixtures and demonstrate the ability to optimize coating selections for various potential exposure situations. In order to perform these analyses, one would ideally have calibration data for each vapor/coating combination. However, as just demonstrated, analyses performed using modeled responses will also provide useful information in the coating selection process, without the need for experimental data.

Temperature Effects. 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 differ slightly in their temperature responses. Second, temperature changes will also affect vapor sorption equilibria. A negative Arrhenius temperature dependence is generally observed for vapors partitioning into organic polymers [8,16,17] 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 PIB, PDPP, DEGA, PCP. 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 21. Arrhenius plots of the data in Table 21 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 11).

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 22 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 22, this would be sufficient to differentiate TCE from either benzene or isooctane,

Table 21. Responses of coated sensors to selected vapors as a function of temperature.

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

Table 22. Slopes of Arrhenius plots shown in Figure 11.

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

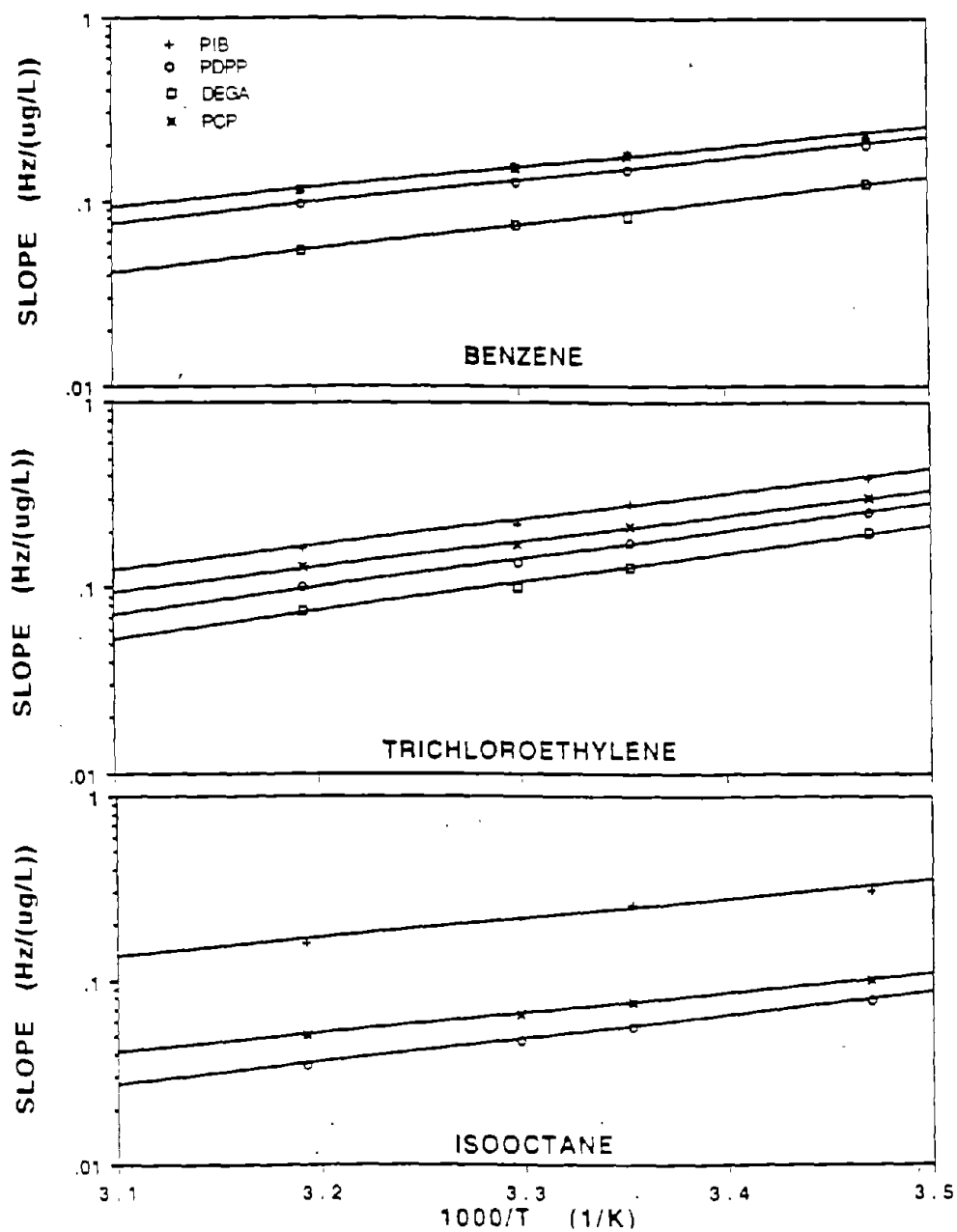


Figure 11. Arrhenius plots of vapor sensitivities for each of four coatings

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 merely monitoring the temperature 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.

Relative Humidity Effects. 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 [17-19], the latter has not received much attention. Recall from Chapter 3 that the response to butanol was influenced strongly by humidity with both highly polar and non-polar coatings. 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 N₂ and to air at RHs ranging from 20 to 85%. Responses were rapid and reversible in all cases. Fig. 12 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.

Effects of water vapor on sensor responses to benzene and TCE were tested by comparing sensitivities in dry N₂ 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.

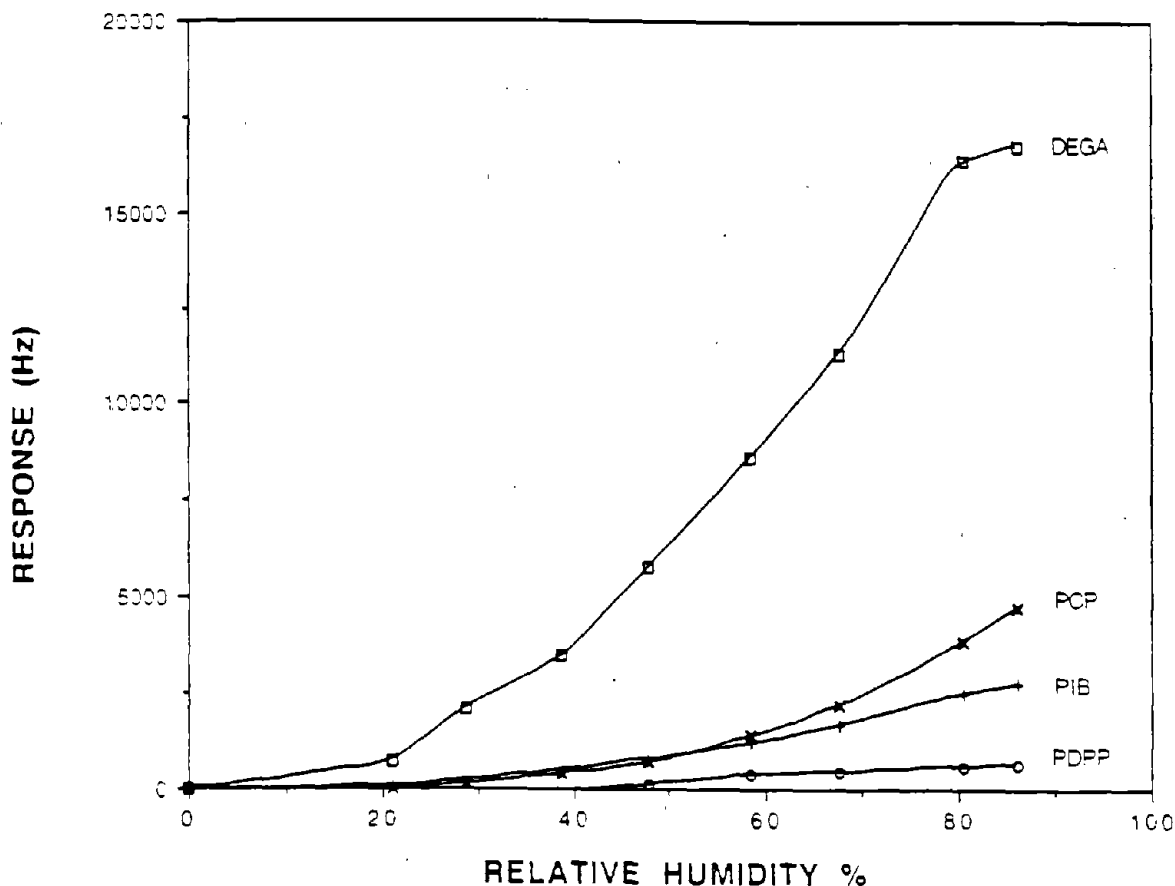


Figure 12. Sensor responses to water vapor from 0-85% RH.

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. [9] to account for variations in the responses of coated SAW devices whose substrates had been cleaned by different methods.

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.

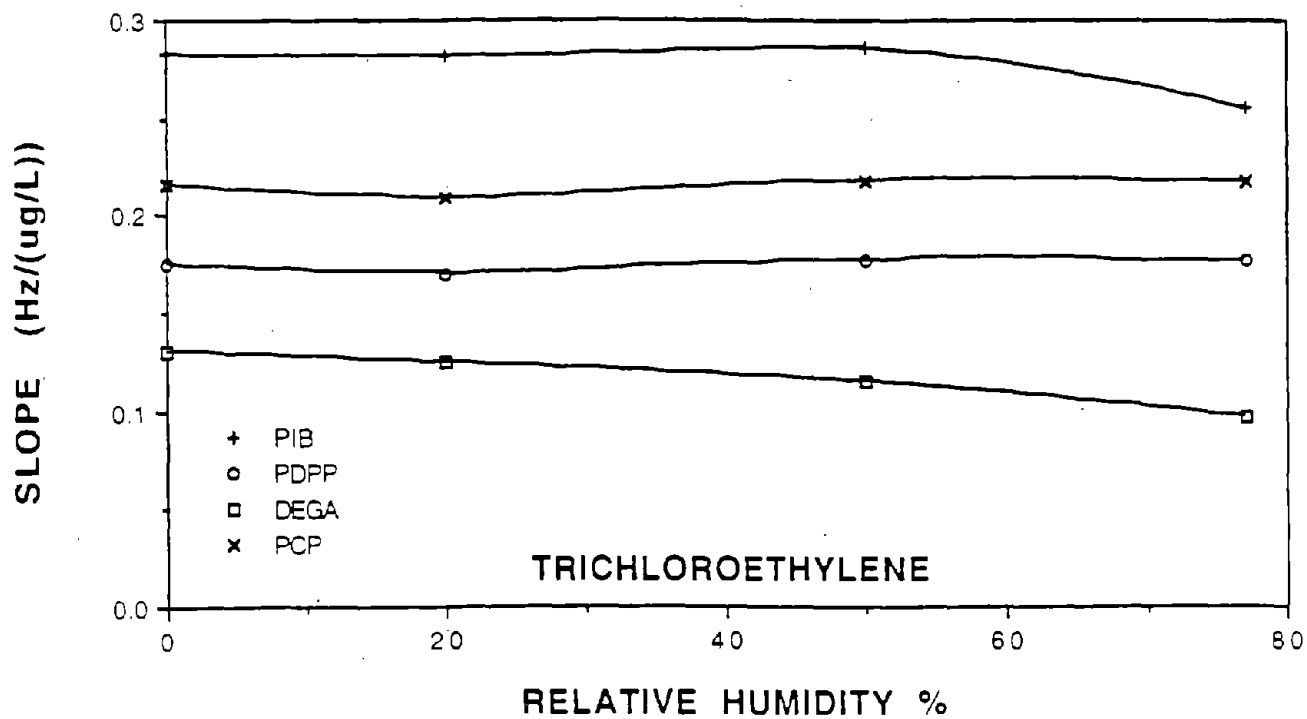
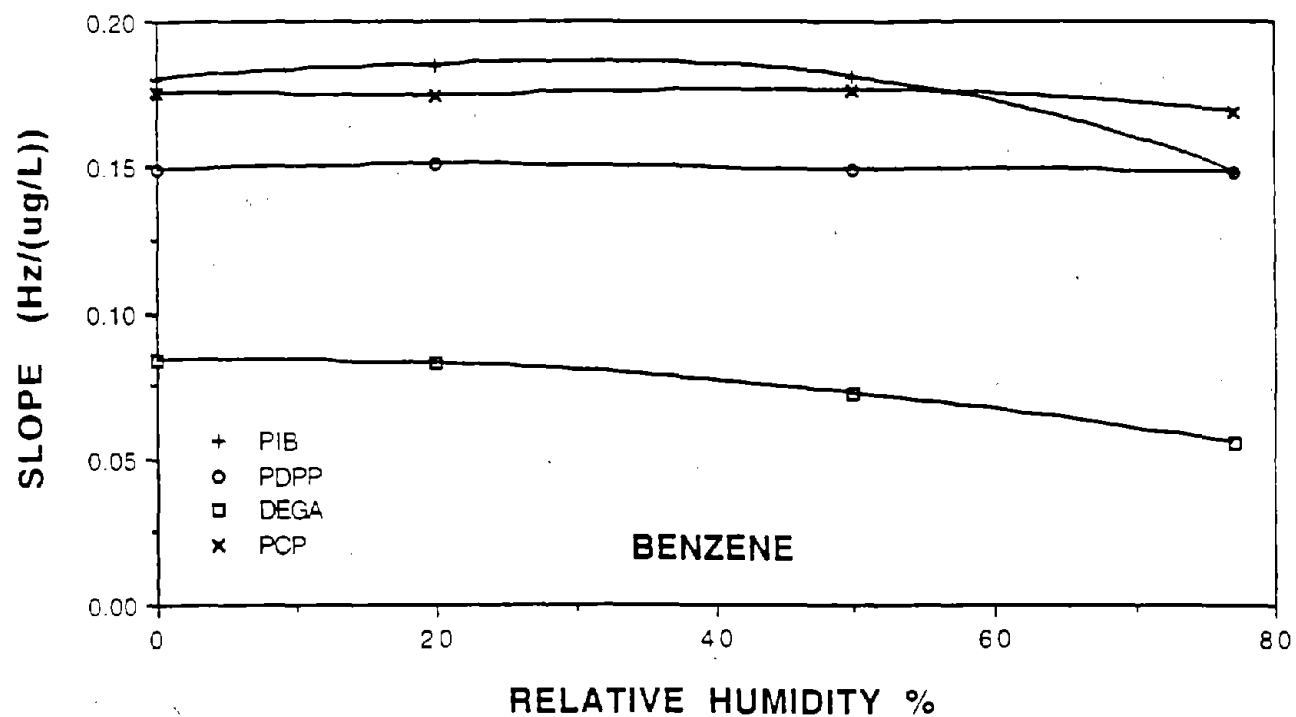


Figure 13. Vapor sensitivities as a function of relative humidity.

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, air 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, 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 organic vapors 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.

Summary and Conclusions

The laboratory research in this project demonstrated the potential for coated SAW sensor arrays in monitoring organic vapors for industrial hygiene exposure assessment applications. For the six vapors examined, relatively simple and rapid sensor measurements provided compound-specific concentrations of organic vapors when present alone or in simple mixtures. In particular, this study has shown 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 computationally efficient. It uses both sensor response patterns and predicted concentrations in the identification process.

* Optimal selection of coatings (using EDPCR and a Monte Carlo simulation of responses to account for random errors) increases the ability of the array to discriminate among vapors. Correct identification and quantification of binary and ternary 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 organic vapors can be significant for highly polar sensor coatings and must be compensated or controlled for during calibration and field operation. Thermostatting the array may provide a viable means for limiting these effects in field monitoring applications (i.e., if the sensor temperatures can be maintained at an elevated temperature, then the effective concentration of water vapor partitioning into the sensor coatings will be reduced)..

* Sensor responses to organic vapors 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 of the array.

* Medium-term (2-8 months) aging effects are small, reducing the need for recalibration of the sensors.

* Coating-to-coating response reproducibility was less than optimal in certain cases, with variations as high as 30% 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 vapors 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.

*Limits of detection are a function of the complexity of the exposure situation. That is, the ability to identify and quantify a given vapor in a mixture will depend on the nature and number of other vapors present. This work showed that low concentrations of vapors in vapor mixtures are often misclassified or undetected. Further work is needed to define the limits of detection in this context.

*Certain vapor mixtures were difficult to resolve into the component vapors, suggesting the need for further research on coating development and testing to address problematic mixtures. The use of coatings that differentiate between vapors on the basis of size and shape, in addition to functional-group interactions, may provide a solution to this problem (see Chapter 5).

Use of coated-SAW sensor arrays coupled with EDPCR analysis has the capacity to provide improvements in organic vapor monitoring capabilities over those provided by currently available portable instrumentation. 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 vapors, 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 instruments.

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. Thermostating 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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CHAPTER 5

An Investigation of Nematic Liquid Crystals as SAW Sensor Coatings for Discrimination Between Isomeric Aromatic Organic Vapors

Synopsis

This chapter describes the use of thermotropic nematic liquid crystals (LC) as surface-acoustic-wave (SAW) vapor sensor coatings. Responses to four pairs of isomeric aromatic organic vapors were measured using two LC coatings and four isotropic polymer coatings. In most cases, the LC coatings showed higher sensitivity toward the more rod-like isomer within a pair due to the anisotropic nature of the deposited LC films. However, the importance of vapor-coating functional-group interactions as mediating factors in the sensor responses was evident in several cases. Incorporation of an LC coating into a four-sensor array improved the discrimination between isomers relative to an array employing only isotropic coatings. A persistent decline in the sensor baseline signal and vapor sensitivity observed over time with both LC coatings could be attributed to evaporative loss and/or changes in the elastic stiffness of the coatings.

Introduction

The development and characterization of surface coatings continues to be a major focus of research on coated bulk-acoustic-wave (BAW), surface-acoustic-wave (SAW) and related piezoelectric vapor sensors [1-4]. The type of coating material employed and the nature of the interactions that occur between the coating and the analyte vapor(s) are key determinants of sensor sensitivity and selectivity. With sorptive coatings, such as high-boiling liquids and rubbery polymers, responses vary directly with the extent of equilibrium vapor partitioning into the bulk of the coating. As a result, sensitivity is generally higher for less volatile vapors and for vapors capable of stronger intermolecular interactions with the coating [5]. The coating-vapor interaction strength, in turn, is determined principally by the relative polarities, polarizabilities, and hydrogen-bond donor/acceptor properties of the functional groups present in the interacting species [5-7]. Selective measurement of certain vapors is possible by employing an array of sensors overlaid with different functionalized coating materials and then analyzing the response pattern obtained upon vapor exposure [8-10]. However, isomeric or structurally homologous vapors, which have very subtle differences in chemical properties, would not likely to be reliably discriminated from each

other using conventional isotropic coating materials. Evidence of this was apparent in the data presented in Chapter 4

The use of coating materials capable of differentiating between vapors on the basis of molecular size and shape constitutes an alternative approach to achieving selectivity with BAW or SAW sensors and sensor arrays. Examples include zeolites, cyclodextrins, cyclophanes, calixarenes, and other so-called cavitands that are characterized by the presence of well-defined cavities or pores. Gases and vapors not able to fit within the cavities are not sorbed as strongly. Although a number of preliminary reports have appeared on the behavior of such materials as acoustic-wave sensor coatings [11-15], a systematic study demonstrating size/shape selectivity, while accounting for differences in vapor volatility and functional-group interactions with the coating material, has yet to be performed.

In this chapter, we present results of an initial investigation of thermotropic nematic liquid crystals (LC) as SAW sensor coatings for discriminating between isomeric and structurally similar organic vapors. LCs are materials that exhibit properties intermediate between those of crystalline solids and isotropic liquids, either over a range of temperatures (as in thermotropic LCs) or due to the presence of solvent (as in lyotropic LCs) [16]. LCs can also be classified by the nature of their structural anisotropy: *nematic* LCs are characterized by anisotropic domains wherein the molecules are aligned parallel to one another; *smectic* LCs also exhibit domains of parallel alignment in addition to a well-ordered layered structure; and *cholesteric* LCs have a spiral anisotropy due to the presence of chiral centers in the constituent molecules.

The LC anisotropy gives rise to solvent properties that differ from those of isotropic liquids [16]. With nematic LCs, for example, solute vapors having more rod-like or planar shapes are often preferentially dissolved. This feature has been exploited in gas chromatography by using LC stationary phases to separate structural isomers (e.g., substituted aromatic compounds) that could not be resolved using standard isotropic stationary phases [17-19].

The first report on the use of LCs as acoustic-wave sensor coatings was published by Mierswinski and Witkiewicz [20]. In that study, responses from an 8-MHz quartz BAW resonator coated with each of four different nematic LCs were examined upon exposure to several vapors. Included in the set of vapors were the o- and p-isomers of diethylbenzene. For most of the vapors, sensor responses varied inversely with vapor boiling point as expected for isotropic coatings. In contrast, the responses for p-diethylbenzene were from 1-21 percent greater than those for o-diethylbenzene, even though these isomers have the same boiling point. The differences in responses between these isomers were attributed to

the preferential solubility of the more rod-like p-isomer in the LC coatings due to the LC anisotropy. Unfortunately, no data were provided on the responses to these isomers using isotropic coatings, and the possibility that the response differences could be accounted for wholly or partly by slight differences in polarity or polarizability between the isomeric vapors was not considered.

In the work described here, SAW sensor responses to several pairs of isomeric aromatic organic vapors are examined using LC coatings and then compared to those obtained using isotropic coatings that span a wide range of structures and polarities. One of our goals was to determine whether partial selectivity for p- or 4-substituted isomers would be observed consistently across different classes of aromatic compounds. In addition, we wanted to assess the relative contributions of structural anisotropy and functional-group interactions to SAW sensor responses using LC coatings. Finally, it was of interest to determine whether inclusion of LC coatings in a SAW sensor array would significantly improve the selective identification of isomeric vapors compared to an array employing only isotropic coating materials.

SAW Sensor Response Equations. Eq. 1 gives an approximate expression for the change in the frequency of a SAW oscillator, Δf_c , upon deposition of a thin, non-conducting, perfectly elastic, isotropic coating film [21,22],

$$\Delta f_c = (k_1 + k_2)f_o^2 h \rho_c - k_1 f_o^2 h 4\mu [(\lambda + \mu)/(\lambda + 2\mu)] / V^2 \quad (1)$$

where k_1 and k_2 are substrate constants ($-8.7 \times 10^{-8} \text{ m}^2/\text{kg}\cdot\text{sec}$ and $-3.9 \times 10^{-8} \text{ m}^2/\text{kg}\cdot\text{sec}$, respectively, for ST-quartz) [10], f_o is the frequency of the uncoated device (Hz), h is the coating film thickness (m), ρ_c is the density of the coating material (kg/m^3), V is the acoustic wave velocity ($3158 \text{ m}/\text{sec}$ for ST-quartz), and λ and μ are, respectively, the Lamé constant and shear modulus of the film (N/m^2) (note: in contrast to Eq. 1 in Chapter 4, this expression shows the contribution of modulus effects to the frequency shift of the oscillator explicitly).

The quantity $h\rho_c$ is equivalent to the mass per unit area of the film and the first term on the right-hand side of Eq. 1 reflects the component of the sensor response arising from the addition (or loss) of mass from the surface of the sensor. Since k_1 and k_2 are negative, increases of mass lead to decreases in the output frequency. The second term on the right hand side of Eq. 1 depends primarily on the elastic stiffness or, more specifically, the shear modulus of the coating film, μ . The effective value of μ is frequency dependent and will therefore increase with the operating frequency of the SAW sensor [10,23,24]. For

coatings whose shear moduli are in the range of $10^7 - 10^9 \text{ N/m}^2$, the magnitude of the second term of Eq. 1 will be about 1-10 percent of that of the first term. However, since k_1 is negative, the second term will lead to a positive shift in frequency, counteracting the effect of mass loading. The net value of Δf_c will then depend on the relative contributions of the first and second terms of the equation. The observation that Δf_c is invariably negative upon coating deposition indicates that the effect of mass loading predominates over that of elastic stiffness.

An equation similar to Eq. 1 can be used to describe the change of frequency upon exposure of a coated SAW sensor to a vapor [24,25]. For sorptive polymer coatings, vapor exposure causes an increase in the coating mass and a decrease in elastic stiffness (i.e., softening). In this case, the second term on the right hand side of Eq. 1 is positive and mass loading, softening, or a combination of the two will cause a negative shift in sensor frequency.

It has been shown, however, that the following simplified equation can describe quite accurately the responses of polymer-coated SAW oscillators to organic vapors [5,24]:

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

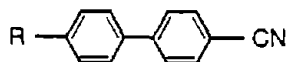
where Δf_v is the frequency shift observed upon exposure to a vapor, C_v is the atmospheric vapor concentration, and K_e is the "effective" partition coefficient. For cases where liquid or rubbery-amorphous polymer coatings are used, responses to most vapors are linear over a considerable range of concentration and K_e can be used as a summary measure of sensitivity. Values of K_e are typically higher than the partition coefficients determined from gas chromatographic measurements [5,24] presumably because sensor responses are a function of changes in both the mass and modulus of the coating upon vapor sorption. Thus, while K_e is not a true partition coefficient it nonetheless serves as a useful index with which to compare sensor responses to different vapors.

Experimental

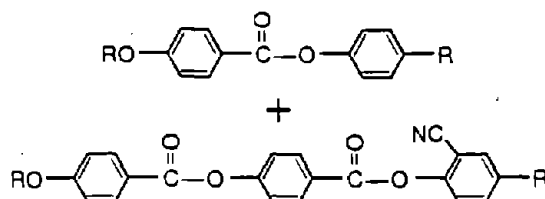
Two commercially available LC coating materials, referred to as E38 and ZLI-389 (EM Industries, Hawthorn, NY), were investigated. E38 is a proprietary mixture of 4-cyano-4'-n-alkylbiphenyls ($\rho = 1.005 \text{ g/cm}^3$) that exhibits a stable nematic phase between -9 and 85°C . ZLI-389 is a proprietary mixture of two types of aromatic esters ($\rho = 1.077 \text{ g/cm}^3$) with a nematic range between -20 and 60°C . Aside from their commercial availability, these particular LCs were chosen for study because they have nematic ranges

that bracket normal ambient temperatures and, unlike many common LCs, they are chemically stable in the presence of atmospheric oxygen and water vapor. Their basic structures are shown below.

E38



ZLI-389



The following isotropic coatings were also examined: poly(bis(cyanoallyl)siloxane) ($\rho = 1.001 \text{ g/cm}^3$, OV-275), poly(methylphenylsiloxane) (25% methyl, $\rho = 1.15 \text{ g/cm}^3$, OV-25), poly(phenylether) six-rings ($\rho = 1.22 \text{ g/cm}^3$, PPE), Apiezon-L (a branched hydrocarbon grease, $\rho = 0.892 \text{ g/cm}^3$, APL) (Anspec, Ann Arbor, MI), and poly(isobutylene) ($\rho = 0.918 \text{ g/cm}^3$, PIB) (Aldrich, Milwaukee, WI). Solutions of the coatings were prepared in one of several organic solvents and applied to the sensors using an airbrush. For each coating material, the deposition process was monitored via the sensor frequency shift and concluded when Δf_c reached approximately 200 kHz (note: as in the preceding chapters, the actual quantity measured was the difference frequency between the coated device and an uncoated reference device, and since the frequency of the coated sensor was initially lower than that of the reference sensor, decreases in the coated sensor frequency correspond to increases in the difference frequency).

The solvents examined are listed in Table 1 along with their respective boiling points [26]. All solvents were obtained from Aldrich and were greater than 98 percent pure, with the exception of the lutidine (i.e., dimethylpyridine) isomers which were 96 percent pure.

A dual 158-MHz delay-line oscillator configuration, consisting of a coated oscillator and a sealed uncoated reference oscillator, was employed. The oscillators and associated circuitry (i.e., mixers, amplifiers, frequency counters, etc.) were obtained from Microsensor

Systems Inc., Bowling Green, KY. A few initial measurements were collected with an individual sensor pair while the majority were collected with an array of four sensor pairs. In all cases, difference frequencies were collected at 2-sec intervals and logged on a personal computer via an RS-232 interface. Coated sensors were fitted with nickel-plated lids each having a vapor inlet and outlet port. The lids were held in place with clamps and a Teflon[®] gasket was used to seal the lids to the T-08 headers on which the sensors were mounted. Sensor temperatures were maintained at 25 ± 0.1 °C by contacting the lids either with heating tape or with an aluminum block through which thermostatted water was circulated. The temperature was monitored with a thermocouple threaded inside of one of the sensor lids.

Dynamic test atmospheres of each vapor were generated by bubbling nitrogen through the liquid solvent and then diluting with a stream of filtered clean air controlled to 25°C and 50% relative humidity (Model HCS-302 Flow-Humidity-Temperature Controller, Miller-Nelson Research, Carmel Valley, CA). Vapor concentrations were monitored continuously with an infrared gas analyzer (MIRAN 1A, Foxboro, Bridgewood, MA) placed in-line upstream from the sensors. The sensors were connected to the system via stainless steel or Teflon[®] tubing and a four-port valve was used to expose the sensor(s) alternately to clean air and air containing the test vapor. The flow rates over the sensors were maintained at approximately 0.080 L/min and were monitored with downstream rotameters.

Each measurement sequence consisted of an initial exposure to clean humidified air to establish a stable baseline frequency followed by duplicate 40-sec exposures to a pre-set concentration of the test vapor. Each vapor exposure was separated by a 40-sec exposure to clean air. Responses and recoveries were quite rapid, with stable readings being attained within 10-20 sec of introduction or removal of the vapor stream. Readings from the last 10 sec of each exposure period were averaged and the baseline subtracted to obtain the net sensor response at a given vapor concentration. Each vapor was tested at four different concentrations over a 4-10 fold range. Pairs of isomeric vapors were tested over similar concentration ranges.

Results and Discussion

Responses to Isomeric Vapors. Sensor responses to the vapors were linear for all coatings over the concentration ranges tested, yielding calibration plots with linear regression correlation coefficients (r^2) > 0.99. Values of K_e were calculated for each vapor/coating combination from the average of the responses at each concentration (Eq. 2).

K_e values for the isotropic coatings ranged from about 2,000 to 25,000 and calculated limits of detection (LOD) ranged from 10 to 110 $\mu\text{g/L}$ (the LOD is defined here as the concentration producing a signal-to-noise ratio of three, where a noise level of 15 Hz is assumed). Specific values of K_e and LOD for each isotropic coating/vapor combination have been published elsewhere [5]. For the LC coatings, initial K_e values (see below) ranged from 3,600 to 21,000 and LODs ranged from about 10 to 60 $\mu\text{g/L}$. Intercoating reproducibility, as determined from the average K_e values for m-xylene from fresh replicate coating films ($n = 2-5$), was within the range of $\pm 15\%$ for the LC coatings.

Since our primary interest is in the relative responses to the various isomers, the average K_e value for each rod-like (i.e., p- or 4-substituted) isomer was divided by that for the corresponding non-rod-like (i.e., o-, m-, or α -substituted) isomer for each coating (note: for the lutidines, the 2,5-isomer is considered to be more rod-like than the 2,4 isomer). Table 1 presents the ratios of the K_e values for each isomer pair on the isotropic and LC coatings. For sensor responses determined more than once with the same deposited coating film or with different films of that material, the average K_e ratio, standard deviation and number of determinations are provided in Table 1. The calculation of any particular ratio was always based on isomer responses collected on the same day.

For the xylenes, the p-isomer:m-isomer response ratios observed with the isotropic coatings ranged from 0.97 to 1.08, while that for E38 was 1.16. The ratio for the other LC coating, ZLI-389, was 1.05 which is within the range observed with the isotropic coatings. Although the ratios for the isotropic coatings are all close to one, the fact that three of the five isotropic coatings gave response ratios greater than one belies the fact that the boiling point for the p-xylene is slightly lower than that of m-xylene. The significantly larger ratio observed for E38 suggests at least some degree of structural anisotropy in the deposited coating film. The failure to observe a larger response ratio with ZLI-389 may be due to the lack of anisotropic alignment in the deposited film, the disruption of alignment upon vapor sorption, and/or the predominance of chemical (i.e., functional-group) factors over shape factors in the overall coating-vapor interaction.

For the chlorotoluenes, the 4-isomer:2-isomer K_e ratios range from 0.91-1.09 on the isotropic coatings, whereas both of the LC coatings give ratios of about 1.2. In this case, a higher response was expected for the higher boiling 4-isomer. The similarity of the ratios for the LC coatings is curious in light of the data for the xylenes: since the chlorine atom is similar in size to the methyl group, the response ratios for the chlorotoluenes with

Table 1. K_e ratios for isomeric aromatic organic vapors for each SAW sensor coating.

vapor pair	coating							
	BP (°C)	APL	PIB	OV-25	PPE	OV-275	ZLI-389	E-38
p-xylene/m-xylene	138/139	1.04	0.97	1.04	0.97	1.08	1.05	1.16
standard deviation		0.02	nd	nd	nd	0.03	0.01	0.04
n		5	1	1	1	2	3	8
4-methylstyrene/ α -methylstyrene	169/163	1.25	1.06	1.04	1.01	1.26	1.49	1.65
standard deviation		0.05	nd	nd	nd	0.02	0.03	0.02
n		2	1	1	1	2	3	3
4-chlorotoluene/2-chlorotoluene	162/159	1.02	0.91	0.97	1.04	1.09	1.23	1.21
standard deviation		0.02	nd	nd	nd	0.10	0.04	0.03
n		2	1	1	1	2	3	2
2,5-lutidine/2,4-lutidine	157/159	0.90	0.87	0.96	0.90	0.86	0.95	0.91
standard deviation		0.01	nd	nd	nd	0.01	0.05	0.04
n		2	1	1	1	2	3	3

n = number of determinations, nd = not determined.

ZLI-389 were expected to be comparable to those for the xylenes. This provides further evidence of the importance of factors other than shape in affecting responses with this LC coating.

For the methylstyrene isomers the isotropic coatings consistently gave 4-isomer: α -isomer ratios greater than one (range = 1.01-1.26), accordant with the order of boiling points. Once again, however, the LC coatings gave ratios significantly larger than those for the isotropic coatings (1.49 and 1.65 for ZLI-389 and E38, respectively). That the larger ratios observed with the LC coatings are attributable principally to differences in shape between these isomers is supported by photoelectron spectroscopic data showing that in α -methylstyrene the ring carbon atoms and pendant ethylene carbon atoms are not coplanar [27], in contrast to styrene (and, presumably 4-methylstyrene). Thus, the α -methylstyrene would not be expected to fit as well into the parallel LC domains.

Finally, for the lutidines the isotropic coatings gave 2,5-isomer:2,4-isomer response ratios ranging from 0.86 to 0.96, again, consistent with the slightly higher boiling point of the latter isomer. In this case, however, neither LC coating showed preferential response toward the more rod-like 2,5-lutidine, and the response ratios were similar to those for the isotropic coatings (i.e., ZLI-389 = 0.95 and E38 = 0.91). Factors related to chemical interactions with these relatively polar isomers apparently predominate completely over shape factors for both of the LC coatings.

Responses to Other Structurally Similar Vapors. The preceding results indicate that the LC anisotropy can indeed influence the relative responses to isomeric aromatic vapors due to differences in their shapes, but also that functional-group interactions are important mediating factors. To explore this issue further, responses to cyclohexane, cyclohexene and benzene were examined using the same set of coatings as above. These vapors were selected, in part, based on a previous report describing their analysis by gas chromatography using both LC stationary phases and several unspecified isotropic stationary phases [17]. The finding that these vapors eluted in the order given above on LC stationary phases was attributed to the progression in structure from the planar benzene to the non-planar cyclohexane. These results were contrasted to those observed using the isotropic phases, where these vapors eluted in the order of boiling points (i.e., benzene < cyclohexane < cyclohexene).

Table 2 presents the ratios of K_e values for these three vapors on each of the coatings examined here. For the non-polar coatings APL and PIB, the order of K_e values follows that of the vapor boiling points, as expected. For E38, the K_e values increase from cyclohexane to cyclohexene to benzene, consistent with the expectations based on planarity.

Table 2. Normalized K_e values for benzene, cyclohexane and cyclohexene.

vapor	BP (°C)	normalized K_e value					
		APL	PIB	E38	OV-25	PPE	OV-275
benzene	80	0.69	0.75	1.00	1.00	1.00	1.00
cyclohexane	81	0.82	0.84	0.27	0.44	0.26	0.12
cyclohexene	83	1.00	1.00	0.42	0.65	0.52	0.44

However, for the more polar coatings OV-25, PPE and OV-275, the order of K_e values also increases with vapor planarity. Furthermore, larger differences in responses are observed between these vapors with OV-275 than with E38.

Thus shape differences are not necessarily the overriding factors governing the relative sensor responses (and gas chromatographic retention times) with LC materials. Benzene is not only the most planar vapor, but also the most polar and polarizable, followed in order by cyclohexene and cyclohexane. The presence of the cyano and phenyl functionalities in the E38, alone, could account for the greater affinity for benzene than for the other vapors.

Aging Effects. Baseline frequencies and responses to m-xylene were monitored over time to assess coating stability. Table 3 presents some typical Δf_c and K_e values as a function of time for the LC coatings and two of the isotropic coatings. Data were collected for all four coatings simultaneously with the sensor array. Following an initial 5-day test period, the sensor array was allowed to stand at room temperature with the sensors covered for approximately three months and then a final exposure to m-xylene was performed. All K_e values were calculated using the initial value of Δf_c obtained directly after deposition of the coatings. This provides a common reference point for comparing the change of K_e to the change of Δf_c .

For OV-275, Δf_c was essentially constant with time, whereas for both of the LCs Δf_c declined substantially (63 and 51 percent for E38 and ZLI-389, respectively). For APL, Δf_c was quite constant over the initial 5-day period, but was found to have increased slightly (4 percent) prior to the final exposure to m-xylene. The m-xylene K_e value for OV-275 did not change significantly, while that for APL increased by about 15 percent and those for E38 and ZLI-389 decreased by 46 and 34 percent, respectively. Interestingly, the decreases in Δf_c for the LC coatings were consistently larger than the decreases in their K_e values for m-xylene, and the increase in Δf_c for APL was consistently smaller than the increase in K_e .

Table 3. Values of Δf_c (kHz) and K_e for m-xylene over time.^a

coating	day	Δf_c	% change in Δf_c	K_e	% change in K_e
E38	1	206	-	3660 (110)	-
	3	171	-17	3190 (70)	-13
	4	151	-27	2950 (130)	-19
	5	142	-31	2930 (90)	-20
	135	75	-64	1940 (90)	-47
ZLI-389	1	239	-	4430 (70)	-
	3	216	-10	4290 (90)	-3
	4	207	-13	4200 (50)	-5
	5	198	-17	4260 (60)	-4
	135	118	-51	2940 (90)	-34
OV-275	1	196	-	1890 (110)	-
	3	197	1	1950 (80)	3
	4	196	0	1960 (70)	4
	5	196	0	2020 (60)	7
	135	198	1	1990 (90)	5
APL	1	206	-	5120 (110)	-
	3	207	0	5330 (130)	4
	4	208	1	5350 (120)	4
	5	208	1	5650 (120)	10
	135	215	4	5880 (110)	15

^a values in parentheses are standard deviations determined from the K_e values at four exposure concentrations.

The most obvious explanation for the decline in Δf_c and K_e for the LC coatings is evaporation of the coatings from the sensor surface. The fact that the decline of K_e is less than that of Δf_c for both LCs may be due to one component of the LC mixture evaporating to a greater extent than the other(s). If m-xylene were more soluble in the less volatile LC mixture component, K_e would not decline as rapidly as Δf_c .

Other aging mechanisms are also possible. According to Eq. 1, a decrease in the coating thickness, h , such as would occur upon slow evaporation of the coating, would lead to proportional decrease in Δf_c , regardless of the relative contributions of the first and second terms of the equation to Δf_c . Vapor exposure would then yield a proportionally lower K_e value. If, however, the coating evaporation were coupled with an increase in the shear modulus, then K_e might decline to a lesser extent than Δf_c . Even without any loss of coating, a gradual increase in the shear modulus over time would lead to a decrease in the magnitude of Δf_c , and most likely some loss in sensitivity.

The increase in Δf_c for APL can also be explained in terms of modulus changes: a slow relaxation of chain segments in this oligomer could easily account for a decrease in the

modulus, and the disproportionate increase in K_e for APL might be due to an increase in vapor sorption capacity accompanying the increased segmental mobility of the coating film.

The data presented in the previous sections indicate that the LC coatings do possess some degree of anisotropy. However, in the absence of an orienting electric field which would align all molecules in the coating in a common direction, deposited LC coating films most likely consist of a series of small domains where the molecules within each domain have a common average alignment but where successive domains are not necessarily aligned with each other [17]. Over time, the degree of orientation of the domains might increase, leading to an increase in the shear modulus of the coating film (note: although the electric field accompanying wave propagation on the SAW device could contribute to such a change, the oscillation of the field is of too high a frequency to cause synchronous "switching" of the LCs [28]). It is known that vapor solubility in the nematic phase of a substance is less than that in the isotropic phase of the same substance due to both entropic and enthalpic factors [17,19]. Thus, an increase in average alignment within the film would lead to a reduction in K_e .

The plausibility of modulus changes accounting for the observed changes in Δf_c can be assessed by using Eq. 1 to estimate the change of modulus required to account for the observed changes in Δf_c for the LC coatings under the assumption that the entire shift in Δf_c is due to shear modulus changes (note: it is recognized that Eq. 1 is strictly applicable to elastically isotropic coatings, but it should still serve as a useful, if only approximate, model). For E38, for example, the net change in Δf_c over 135 days was -63% or 131 kHz out of the total initial value of 200 MHz. If we assume a coating thickness of 60 nm and a value of 0.84 for the quantity $[(\lambda + \mu)/(\lambda + 2\mu)]$ in Eq. 1 (this quantity is constrained to be between about 0.67 and 1.0), then a modulus change of $6.3 \times 10^9 \text{ N/m}^2$ would be required, regardless of the initial value of the shear modulus.

Although the actual value of the shear modulus of this LC coating is not known, shear moduli derived for several organic polymers from ultrasonic velocity measurements in the low-MHz frequency range [23] suggest that a value somewhere in the range of 10^7 to 10^9 N/m^2 would be expected for the LC coatings at a frequency of 158 MHz. Table 4 summarizes the magnitude of the change in μ required for various possible initial values in this range. For an initial modulus of 10^7 N/m^2 , μ must increase by a factor of more than 600 to account for the shift in Δf_c , whereas for an initial value of 10^9 N/m^2 , only about a 7-fold increase is necessary. Thus, one cannot rule out, a priori, the possibility that the observed decline in Δf_c is entirely due to modulus changes over time.

Additional insight into this issue was obtained from a separate series of exposures to both m- and p-xylene performed with the E38 coating over 26 days. Although the

Table 4. Changes in shear modulus, μ , required to account for the baseline drift of the E38-coated sensor for various initial values of μ (see text).

μ_{initial} (N/m ²)	μ_{final} (N/m ²)	$\mu_{\text{final}}/\mu_{\text{initial}}$
10^9	7.3×10^9	7.3
10^8	6.4×10^9	64
10^7	6.3×10^9	630

sensitivity declined with time, the magnitude of the decline was essentially the same for both vapors. The K_e values obtained with the freshly deposited coating were 4380 and 3660 for p- and m-xylene, respectively, yielding a ratio of 1.20. After 26 days, the respective K_e values had declined to 2720 and 2270, but the ratio remained constant at 1.20. If the decline in K_e were due to modulus changes associated with an increase in parallel alignment of the LC domains, then one would expect to see an increase in the p-xylene:m-xylene response ratio. The fact the response ratios did not change suggests that there was no significant change in alignment or modulus. Thus, the observed declines in Δf_c and K_e are most likely due to evaporative loss with perhaps a small contribution from modulus effects.

Isomer Discrimination with a Sensor Array. Notwithstanding their instability, it was of interest to determine whether inclusion of LC coatings in an array of SAW sensors would improve the capability for differentiating individual isomers from one another. To this end, a comparison was made between response patterns obtained from an array of four SAW sensors employing the isotropic coatings OV-275, PIB, OV-25 and PPE and an array where one of the isotropic coatings was replaced by the LC coating E38. The PPE coating was selected for replacement because it was the most similar to E38 in terms of the absolute and relative magnitudes of responses to the test vapors. Thus, replacing this coating minimized any differences in the overall range of polarities spanned by the two arrays.

The performance of each array was first evaluated using a principal components analysis of the response data after pattern normalizing to remove the effect of concentration (i.e., for each test concentration, the individual sensor response was divided by the sum of responses from all four coatings in the array) [29]. Projection of the resulting response vectors onto the plane defined by the first two principal components provides an indication of the degree to which the responses to each vapor differ from one another.

Figures 1 a and b show the principal components plots for the two arrays being considered. Each point represents the response projection for an individual vapor at a given concentration. For the all-isotropic array, m- and p-xylene cluster quite close together while for the array containing E38 the distance between m- and p-xylene clusters is greatly increased. A similar improvement in separation is observed between 2- and 4-chlorotoluene, and an even greater improvement is seen for the isomeric methylstyrene clusters. For the lutidines, where the K_e ratios were similar for the isotropic and E38 coatings, no increase in separation is observed with the use of the LC in the array. The overall improvement in isomer discrimination with inclusion of the LC coating is apparent, though it is also clear that the isotropic array will show some discrimination between isomers as well.

A more quantitative comparison of the two arrays was then performed using a disjoint principal components regression classification method [30]. In this method the first principal component determined from the array responses to each of the four test concentrations is used to model each vapor. The model created for each vapor is then used in classification procedures. That is, the response vector obtained upon subsequent exposure to a test vapor is compared successively to the principal component vectors of the previously modeled vapors. The test vapor is then identified on the basis of which principal component vector most closely matches that of its response vector.

In lieu of a separate set of response data, a simulated test set was created from the existing calibration set by superimposing Gaussian error (one standard deviation = 5%) on the sensor responses at each concentration and then sampling from the simulated distribution of responses. Each isomer pair was analyzed separately and for each isomer within a pair 40 simulated responses were classified. Error rates were determined from the fraction of incorrect isomer classifications out of the 80 total simulated responses. With the isotropic array error rates of 11, 10, 19 and 14 percent were obtained for the xylenes, chlorotoluenes, methylstyrenes and lutidines, respectively. As acknowledged above (and as shown in Fig. 1a), the isotropic array is capable of providing some discrimination between the isomers, but the error rates are somewhat higher than one would desire. For the array containing the LC coating there were no misclassifications for the first three pairs of isomers, while for the lutidines the error rate was the same as that for the isotropic array (i.e., 14 percent). The latter result was expected since the relative responses to the lutidine isomers for E38 were similar to those for PPE (and the other isotropic coatings). The improvement in classification for the other isomers, however, is significant.

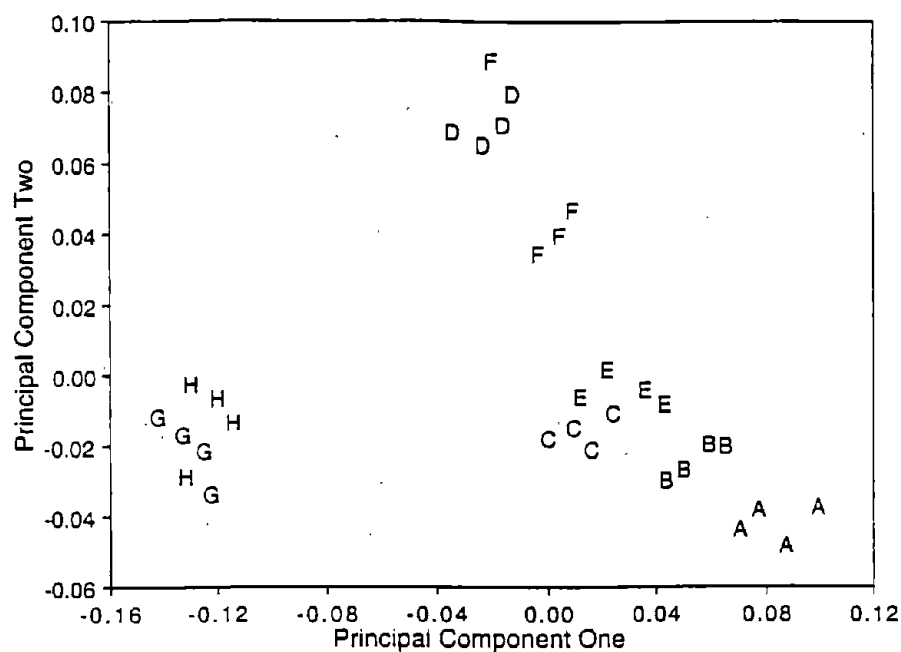
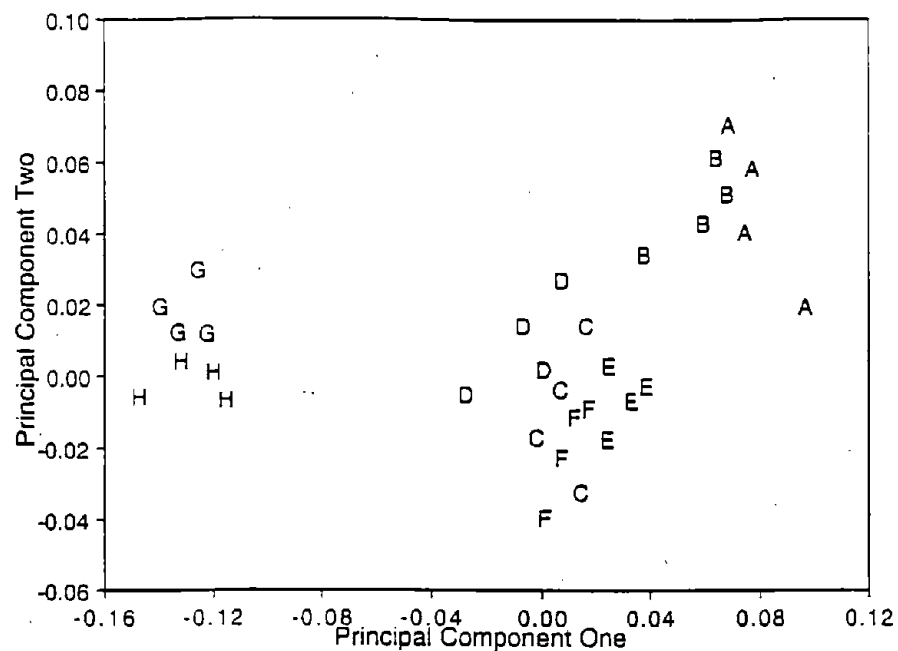


Figure 1. PCA projection plots of response vectors from the four-sensor array with (a) four isotropic coatings (top) and (b) three isotropic coatings and one LC coating (bottom, see text). Legend: a (m-xylene), b (p-xylene), c (α -methylstyrene), d (4-methylstyrene), e (2-chlorotoluene), f (4-chlorotoluene), g (2,4-lutidine), h (2,5-lutidine).

Conclusions

This brief investigation of LC SAW coatings has yielded several noteworthy results. The importance of the structural anisotropy in as-deposited LC coating films was confirmed. However, it was also shown that the two LC materials investigated here exhibited different behavior and that the ability to discriminate between isomers on the basis of shape alone was not universal. That is, the shape discrimination is mediated by the same types of functional-group interactions that govern responses with isotropic coatings. Nonetheless, inclusion of LC coating materials in a SAW sensor array can enhance the ability to selectively identify certain vapors in the presence of their structural isomers compared to an array containing only isotropic coatings.

The finding that the alkyl cyanobiphenyl LC, E38, gave better discrimination than the aromatic ester is consistent with previous findings reported by Mierswinski and Witkiewicz [20] for the one pair of isomers that they examined. It is not clear, however, why this is the case, i.e., whether this is due to a greater degree of anisotropy or to differences in chemical interaction strengths with the vapors. There is some evidence indicating that cyanobiphenyls show a greater degree of alignment than certain other LC materials under the influence of an electric field [16]. Perhaps they also exhibit a greater degree of spontaneous alignment or are influenced more by interactions with the polar quartz surface of the sensor substrate than are LCs of other structures.

The persistent baseline drifts and losses of sensitivity of sensors coated with the LC materials examined here limits their practical utility. The evidence presented here suggests that evaporative loss of the coating is primarily responsible for these effects, but changes in shear modulus arising from changes in the average alignment of the LCs over time may also have contributed. It should be possible to find less volatile nematic LCs that would not have this problem. A number of polymeric LCs with nematic ranges in the ambient temperature range are known [16,33] and would appear worth pursuing in light of the results obtained here.

Certain properties of LC materials, which were not investigated in this study, deserve mention. For example, the application of an orienting electric field as a preconditioning step in order to vary, or optimize, the degree of alignment in the LC coatings may be useful. While this will tend to decrease the average sensitivity to all vapors, it should also increase the selectivity for rod-like or planar molecules. Given the rather high sensitivity exhibited by the LCs used here, some loss in sensitivity could be tolerated in exchange for the improved selectivity expected with more highly oriented

coating films. Another potentially useful feature of LCs is their susceptibility to abrupt phase transitions (i.e., from nematic to isotropic) in the presence of high concentrations of vapor phase solutes [16]. The large changes in sorbed mass and coating stiffness accompanying such transitions would lead to large changes in sensor response and might be used to trigger alarms in automated vapor monitoring systems. These issues are currently being investigated.

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REPORT DOCUMENTATION PAGE	1. REPORT NO.	2.	3. Recipient's Accession No.
4. Title and Subtitle Microsensor Arrays for the Identification of Organic Solvents Vapors			5. Report Date 1993/10/05
7. Author(s) Zellers, E. T.			8. Performing Organization Rept. No.
9. Performing Organization Name and Address Department of Environmental and Industrial Health, School of Public Health, University of Michigan, Ann Arbor, Michigan			10. Project/Task/Work Unit No.
			11. Contract (C) or Grant(G) No. (C) (G) K01-OH-00077
12. Sponsoring Organization Name and Address			13. Type of Report & Period Covered
			14.
15. Supplementary Notes			
16. Abstract (Limit: 200 words) The use of microfabricated surface acoustic wave (SAW) chemical sensor arrays for the measurement of organic solvent vapors in the workplace was described. Performance parameters involved in the use of instrumentation employing SAW chemical sensor arrays were examined in several laboratory investigations. The instrument used in these studies included an array of four sensors coated with each of 16 different isotropic polymer coatings. A new pattern recognition method was developed maximizing the selectivity and accuracy of detection of vapor contaminants as were several predictive models of sensor responses. These models were based on vapor boiling points, coating/vapor solubility parameters, and coating/vapor solvation parameters in conjunction with linear solvation energy relationships. The author concludes that the individual identification and quantification of a large number of vapors in binary and ternary mixtures is possible using a simple four sensor array.			
17. Document Analysis a. Descriptors			
b. Identifiers/Open-Ended Terms NIOSH-Publication, NIOSH-Grant, Grant-Number-K01-OH-00077, End-Date-03-14-1993, Grants-other, Organic-solvents, Air-quality, Air-sampling-techniques, Air-sampling-equipment, Mathematical-models			
c. COSATI Field/Group			
18. Availability Statement	19. Security Class (This Report)	21. No. of Pages 188	
	22. Security Class (This Page)	22. Price	

