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Solubility Interactions and the Design of Chemically Selective Sorbent Coatings for Chemical Sensors and Arrays

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13. ABSTRACT (Maximum 200 words) In designing microsensors for vapor detection, interactive coating materials must be chosen which will collect and concentrate analyte molecules at the sensor's surface. The sensitivity and selectivity of each individual sensor is controlled by tailoring the chemical and physical properties of the coating material to maximize particular solubility interactions. The selection of coatings for the complete sensor array is logically made through a systematic variation of the solubility properties of the coating materials, so that each sensor is selective for a different balance of solubility interactions. Parameters and methodologies for characterizing analyte solubility properties, sensor coating material solubility properties, and their interactions, are presented. Specific functional groups are recommended for inclusion in sensor coating materials in order to maximize particular interactions. In addition, the treatment of coating material properties is integrated with consideration of the factors which influence chemical selectivity in sensor arrays. Methods for intelligently choosing coatings for sensor arrays, and for optimizing sensor arrays for particular analytes, are considered.				
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$$\Delta f = k F^2 \Delta m / A \quad (1)$$

$$\Delta f_s = (k_1 + k_2) F^2 h \rho - k_2 F^2 h (4 \mu / V_R^2) [(\lambda + \mu) / \lambda + 2\mu] \quad (2)$$

$$\delta_T^2 = \delta_d^2 + \delta_o^2 + 2 \delta_{ind} \delta_d + 2 \delta_a \delta_b \quad (3)$$

$$K = C_s / C_v \quad (4)$$

$$\Delta G_s^0 = - R T \ln K \quad (5)$$

$$\Delta f_v = \Delta f_s C_v K / \rho \quad (6)$$

$$\log K = c + d \delta_2 + s \pi_2^* + a \alpha_2^H + b \beta_2^H + 1 \log L^{16} \quad (7)$$

$$\log K = c + r R_2 + s \pi_2^* + a \alpha_2^H + b \beta_2^H + 1 \log L^{16} \quad (8)$$

$$\log K = -1.02 - 0.42 R_2 + 0.82 \pi_2^* + 1.85 \alpha_2^H + 4.90 \beta_2^H + 0.75 \log L^{16} \quad (9)$$

$$MR_x = 10 [(n^2-1) / (n^2+2)] V_x \quad (10)$$

$$R_2 = MR_x - MR_x \text{ for an alkane of the same } V_x \quad (11)$$

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SOLUBILITY INTERACTIONS AND THE DESIGN OF CHEMICALLY SELECTIVE SORBENT COATINGS FOR CHEMICAL SENSORS AND ARRAYS

INTRODUCTION

A continual challenge in the field of chemical detection is the development of approaches to designing microsensors and microsensor-based detectors with high selectivity. This challenge results from the variety of analytes to be detected, the many types of materials which can be used to interact with the chemical environment, and the numerous transducers which can be used to convert physico-chemical interactions to electrical or optical signals. No single science exists to unite all sensor technologies with a common set of principles and a common approach to achieving selectivity.

Nevertheless, in the area of vapor detection, sorption phenomena and solubility interactions can be identified as common features of many sensors. By understanding these two disciplines, interactive materials can be chosen which will selectively collect and concentrate analyte molecules at the sensor's surface, thus improving sensitivity and selectivity. This principle is illustrated in Figure 1 for a sensor which absorbs vapor into a chemically selective coating on the sensors surface. The transducer converts a vapor-induced physical change in the coating material into an optical or electronic signal. The most straightforward examples of this principle are sensors based on a variety of acoustic wave devices, which will be referred to collectively as piezoelectric sorption detectors.¹⁻¹³ The transducer acts as a microbalance which measures the mass increase of the coating when a vapor is sorbed.

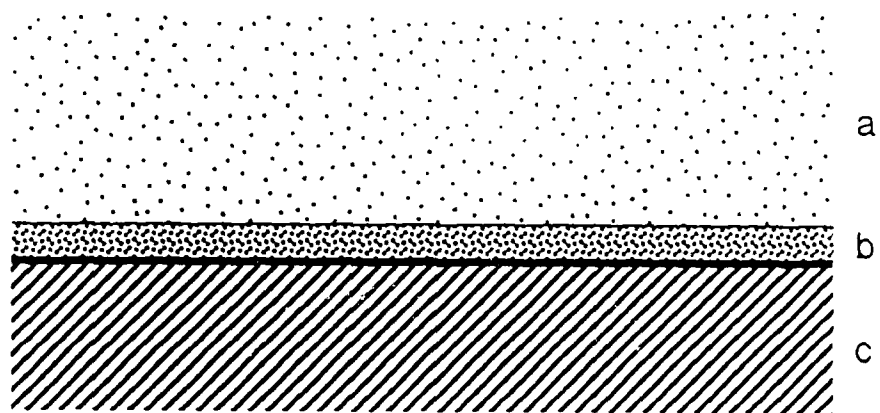


Figure 1. Schematic illustration of the absorption of a vapor (a) into a sorbent stationary phase (b) on a solid surface (c).

Optimizing a single sensor for the analyte of interest represents the first step in detector development. In many cases this may be sufficient for the analytical problem at hand. However, complex environments can be very demanding with regard to chemical selectivity. This is particularly true when it is necessary to detect the analyte at trace concentrations in field environments where potential interferents (such as humidity) may be present at orders of magnitude higher concentrations. In such cases, the use of pattern recognition techniques in combination with an array of chemical sensors offers improved selectivity, and the opportunity to use a single detector system to analyze for more than one analyte.¹⁴⁻²⁵ In this fairly general approach to enhancing chemical selectivity, the pattern recognition algorithm evaluates the pattern of responses from the sensor array to determine if the vapor of interest is present. The bar graphs in Figure 2 illustrate how different vapors give rise to different patterns when detected by an array of sensors.

The success of the array detector approach depends on the amount and quality of information being provided by the sensors. To be useful, each sensor must give unique information. In other words, sensors(or sensor coatings) must be chosen carefully. Each sensor must be selective for different vapors than the other sensors in the array. This requirement brings us full circle, since we must again focus on the selectivity of individual sensors. However, in addition to a sensor which is sensitive and selective for the target analyte, one must also design sensors which will be selective for known and possibly unknown potential interferences. In this context, it is particularly important to develop a comprehensive approach to chemical selectivity so that an array can gather as much information as possible about any vapor which may sorb and produce sensor signals.

The approach taken in this article will be to focus on a solubility model for absorption as it applies to piezoelectric sensors for organic vapors . We will show how a detailed understanding of sorption and solubility interactions can be applied to the design of sensors for a sensor array. The sensitivity and selectivity of each individual sensor is controlled by tailoring the chemical and physical properties of the coating material to maximize particular solubility interactions. The selection of coatings for the complete array is logically made through a systematic variation of the solubility properties of the coating materials, so that each sensor is selective for a different balance of solubility interactions.

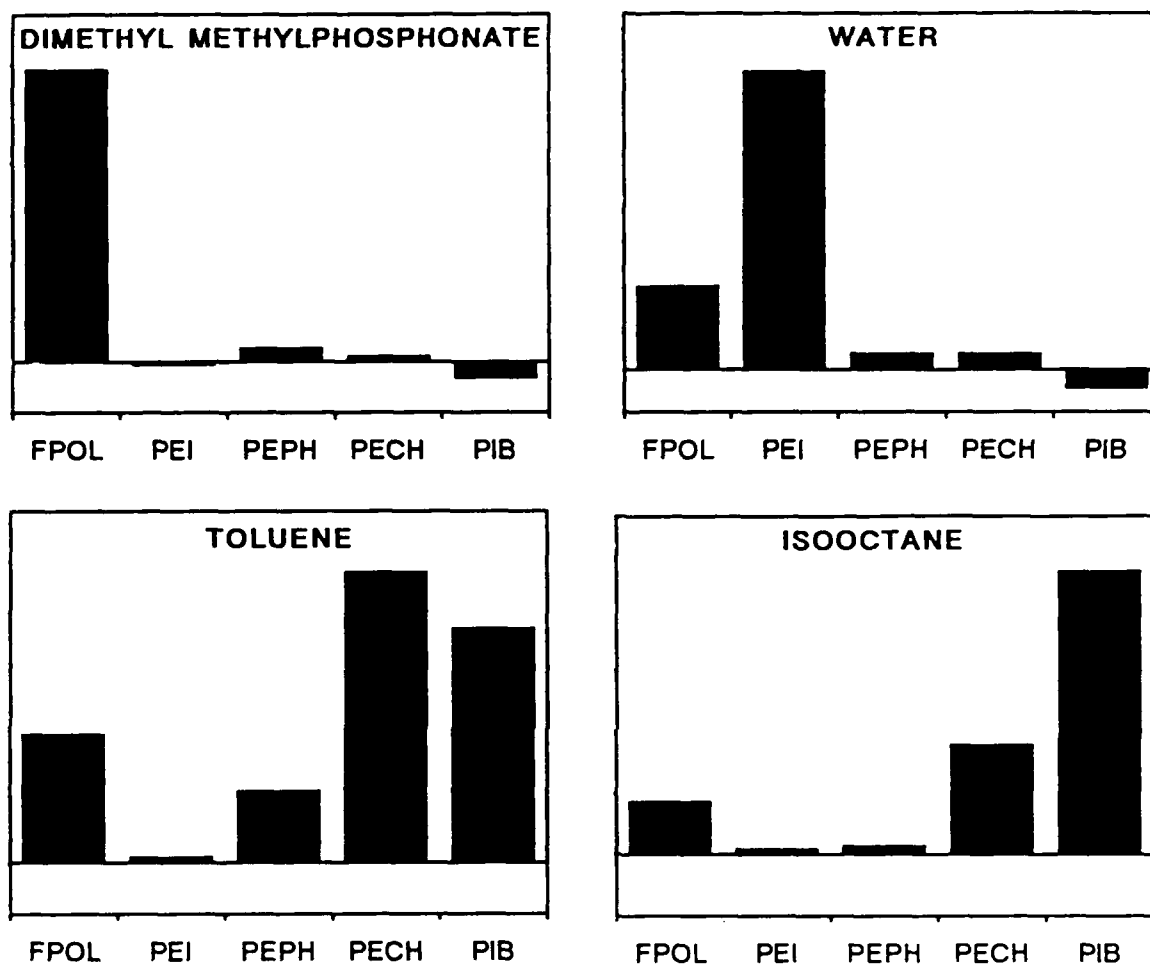


Figure 2. Bar graphs illustrating how different vapors give rise to different patterns when detected by a sensor array, using data from reference 15. Each graph illustrates the relative responses of five dual delay line SAW vapor sensors to a single vapor, normalized to the highest response. The coating materials on the sensors are fluoropolyol(FPOL), poly(ethylenimine)(PEI), poly(ethylene phthalate)(PEPH), poly(epichlorohydrin)(PECH), and poly(isobutylene)(PIB).

The emphasis will be on bulk absorption (as opposed to surface adsorption) of neutral organic vapors into soft coating materials containing neutral organic functional groups. In addition, the discussion will be limited to reversible sensors. The issue of reversibility is closely related to the issue of chemical selectivity. Weak interactions between the vapor and sensor coating will produce sensors with good reversibility and little hysteresis. However, such sensors may not have sufficient sensitivity and selectivity to be widely useful. Very strong interactions may improve the sensitivity and selectivity, but can result in sensors which are irreversible or only slowly reversible. Thus, if reversibility is important, a balance must be struck between selectivity on the one hand, and reversibility on the other. This balance can be achieved by using sensor coatings which interact with vapors via solubility interactions.

Several articles and reviews have appeared which discuss piezoelectric chemical sensors, and in some cases, chemical selectivity.^{2-5,8-13,26-27} These provide comprehensive literature references, and some give lists of sensor coating materials organized according to the analytes which are detected. We do not duplicate these efforts here. Our account discusses solubility in greater detail than any previous treatment of chemical sensors. Parameters and methodologies for characterizing analyte properties, sensor coating material properties, and their interactions, are presented. Specific functional groups are recommended for inclusion in sensor coating materials in order to maximize particular interactions. In addition, we integrate the treatment of coating material properties with consideration of the factors which influence chemical selectivity in sensor arrays. Methods for intelligently choosing coatings for sensor arrays, and for optimizing sensor arrays for particular analytes, are considered.

PIEZOELECTRIC SORPTION DETECTORS

The concept of a piezoelectric sorption detector was first introduced by King in 1964, using bulk acoustic wave quartz crystals.¹ Detectors based on such crystals are frequently referred to as quartz crystal microbalances, or QCM.²⁻⁵ A variety of other acoustic waves and device configurations have since been utilized to create piezoelectric chemical sensors. These include surface acoustic wave (SAW) devices,⁶⁻¹³ flexural plate wave devices,²⁸⁻³¹ and horizontally polarized shear wave devices.^{32,33} Some of these devices are illustrated in Figure 3. In each case, metal transducers on the piezoelectric substrate convert rf electrical energy into mechanical energy in the form of an acoustic wave. For sensor applications, the device is usually placed in an oscillator circuit where it functions as the resonant element, and the frequency is monitored. Shifts in the frequency are observed when the mass on the surface changes, e.g. by sorption of vapor into a surface coating as illustrated in Figure 1.

Detailed descriptions of the operation of these types of devices have been published in references noted above. Those features which are relevant to the selection of coating materials and quantifying sorption will be presented here. Discussion will focus primarily on the QCM and SAW devices.

Perturbations on the mass, Δm , on the surface of a QCM cause shifts in the oscillator frequency, Δf , according to the following relationship:¹⁻²

$$\Delta f = k F^2 \Delta m / A \quad (1)$$

The variable A is the active area of the device, F is the fundamental resonant frequency of the oscillator, and k is a constant related to the crystal material and thickness. This relationship shows that the mass of vapor sorbed by a coating can be measured by the frequency shift. Some care is needed in the application of this relationship to the QCM, however, because of its radial sensitivity function.³⁴

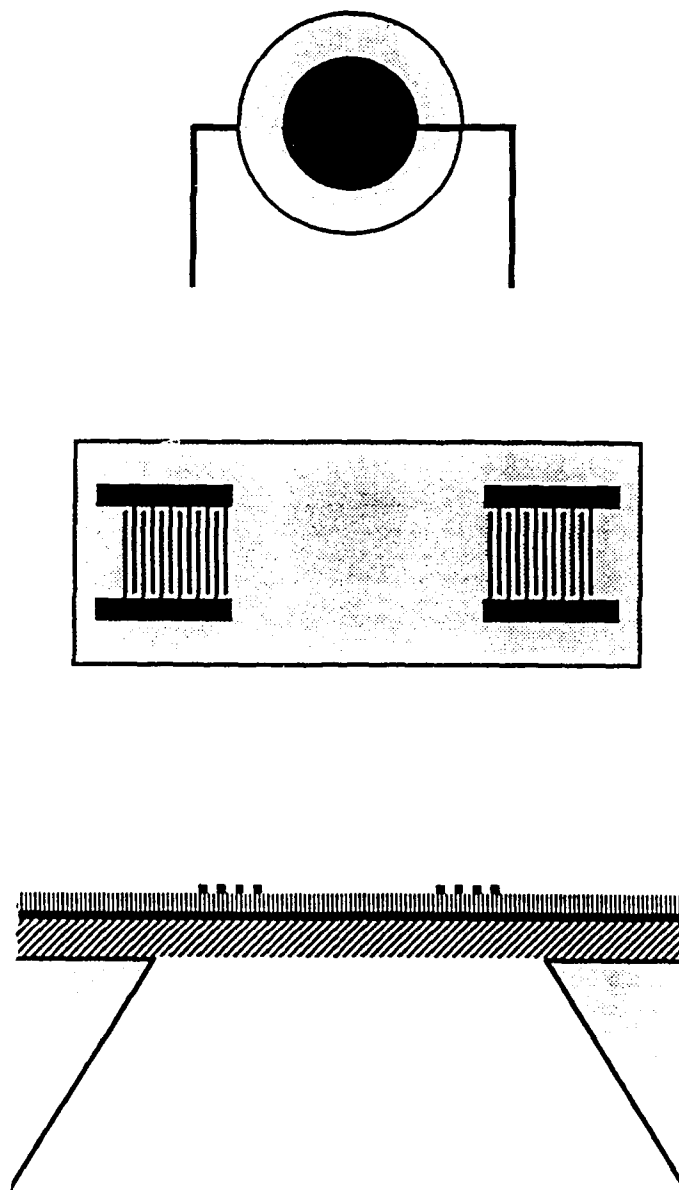


Figure 3. Schematic diagram of selected piezoelectric transducers. Shown from top to bottom: a quartz crystal microbalance and lead wires, as seen from the top, consisting of a quartz disc with metallized transducers; a surface acoustic wave delay line, as seen from the top, consisting of a quartz plate with metallized interdigital transducers; and the membrane portion of a flexural plate wave device, as seen from the side in cross-section, consisting of aluminum transducers, a ZnO layer, an aluminum ground plane, and a silicon nitride layer supported on the sides by the silicon substrate.

The response of SAW devices to surface mass changes can be expressed similarly if the surface film is soft and non-conducting. However, changes in the elastic properties of stiff films, or changes in the resistance of conducting films (whose sheet conductivities fall in a particular range) can also perturb the frequency. The influence of the mass and elastic properties of a thin isotropic non-conducting film on the frequency of a SAW device has been expressed according to equation 2, where Δf_s is the change in frequency caused by the film.⁷

$$\Delta f_s = (k_1 + k_2) F^2 h \rho - k_2 F^2 h (4 \mu / V_R^2) [(\lambda + \mu) / \lambda + 2\mu] \quad (2)$$

The values for k_1 and k_2 are material constants for the piezoelectric substrate, F is the fundamental resonant frequency of the oscillator, h is the coating thickness, ρ is the coating density, λ and μ are the Lamé constant and shear modulus of the coating material, and V_R is the Rayleigh wave velocity in the piezoelectric substrate. The first term represents mass effects, since $h \rho$ has the same units as $\Delta m / A$. Thus the first term in equation 2 has the same form as equation 1 for the QCM.

The second term in equation 2 represents the effects of the elastic properties of the surface coating on the frequency of the surface acoustic wave. For soft materials, e.g. $\mu = 10^7$ dynes/cm² (a value typical of elastomeric polymers, i.e. amorphous polymers above their glass transition temperature), the second term is negligible relative to the first. For stiffer materials such as glassy polymers with $\mu = 10^{10}$ dynes/cm² and densities near 1 g/cm³, the second term is 10 to 15% of the value of the first term.

In summary, the important features of piezoelectric detectors are that they are mass-sensitive and that the quantity of vapor sorbed by the chemically selective surface film is measured by the frequency shift. In some cases, such as the SAW device, the frequency can also be influenced by other properties such as changes in stiffness or conductivity, which must be considered in coating material selection. This article will focus on sensor applications of soft, non-conducting materials, such as elastomeric polymers, where mass effects dominate SAW sensor response.

SOLUBILITY, SORPTION, AND LINEAR SOLVATION ENERGY RELATIONSHIPS (LSER)

SOLUBILITY AND ABSORPTION

"Like dissolves like" is the conventional rule of thumb for solubility. Classic textbook examples of solubility such as solutions of toluene in benzene fit this rule. Thermodynamic models for solubility and mixing can easily be derived for such "ideal" systems. More sophisticated treatments recognize that real systems are not ideal, and correction factors such as activity coefficients are introduced to account for deviations from ideality. Nevertheless, such models are still grounded in the concept of ideality.

These models are useful for many purposes, but they do not provide detailed guidance for the design of materials for chemical sensors. The objective in chemical detection is to prepare materials which maximize specific oriented interactions with the sorbed analyte molecules, thus achieving selectivity and sensitivity. Dipole-dipole and hydrogen bonding interactions are examples of orientation-dependent solubility interactions. In ideal solutions, the interactions are limited to non-oriented interactions such as induced-dipole induced-dipole interactions, also known as dispersion interactions. The rule of "like dissolves like" is well suited to ideal solutions, but is contrary to the objectives of chemical detection when the analyte molecule is capable of selective oriented interactions.

Consider, for example, the sorption of a vapor which is a hydrogen bond base. The rule of thumb suggests incorporating similar hydrogen bond basic functional groups into the sensor coating material. However, the incorporation of hydrogen bond acidic groups will interact more strongly and selectively, and will make a better sensor coating material.

This example illustrates why models for solubility which are based on ideal interactions are not adequate for chemical sensors. To fully understand solubility and to unravel multiple solubility interactions which occur simultaneously, one must be able to quantify the strengths of many solubility properties and interactions. These include the solubility properties of the solute molecules (the vapor in this case), the solubility properties of the solvent (the sensor coating or stationary phase), and their interactions. We have selected methodologies utilizing solvation parameters as a multiparametric approach to characterizing and understanding solubility and solubility-related phenomena.^{35,36}

Analysis of the process of absorption in terms of three conceptual steps illustrates the importance of solubility. First, a cavity must form in the solvent. This requires

breaking solvent-solvent interactions, and is endoergic. Second, the monomeric solute fills the cavity with concomitant reorganization of solvent around the cavity. This seems to result in little change in free energy, but possibly substantial changes in enthalpy and entropy. Third, attractive interactions form between the solute and the solvent. These exoergic interactions are called solubility interactions. The strengths of these interactions, and hence the strength of sorption, depend on the respective solubility properties of the solute and the solvent.

The solubility interactions relevant to the sorption of non-ionic analytes by sensor materials containing non-ionic organic functional groups are listed below, beginning with non-oriented interactions and ending with orientation-dependent interactions. (The list does not include the term 'van der Waals interactions' because of some ambiguity in its use; some authors use it with reference to dispersion interactions only, while others refer to dispersion, induction, and orientation interactions as van der Waals interactions.)

- a) induced-dipole/induced-dipole interactions, also called dispersion interactions.
- b) dipole/induced-dipole interactions, also called dipole induction interactions
- c) dipole/dipole interactions, also called dipole orientation interactions
- d) hydrogen bonding interactions

It might seem that a multiparametric approach to solubility is needlessly complicated, and that a single parameter such as the cohesive energy density of Hildebrand, δ_H^2 might suffice. The shortcoming of this single parameter is that vapors with obvious dissimilarities are sometimes ranked similarly; for example, polarizable, non-hydrogen bonding toluene has a similar parameter to dipolar, hydrogen bond basic ethyl acetate. As a result, it is now customary to break down overall δ_H^2 values into component parts which correspond to the interactions listed above.^{37,38}

$$\delta_T^2 = \delta_d^2 + \delta_o^2 + 2 \delta_{ind} \delta_d + 2 \delta_a \delta_b \quad (3)$$

In equation 3, subscripts d, ind, o, a, and b refer to dispersion, induction, orientation, acid, and base respectively, while subscript T refers to the total.

It is thus well established that a solute/solvent interaction must be broken down into its component interactions to fully understand solubility dependent phenomena. Furthermore, chemometric investigations using principle components analysis and factor analysis have shown conclusively that several factors (three to five) are required to interpret extensive data on the solubility of gaseous solutes into non-aqueous solvents.^{39,40}

THE PARTITION COEFFICIENT

Before quantifying individual solubility properties and interactions, it is important to establish a means of quantifying the total absorption to which these interactions contribute. This is easily achieved using the partition coefficient, K . This thermodynamic parameter measures the equilibrium distribution of solute molecules between the gas phase and the solvent phase, as illustrated in Figure 1. The partition coefficient is defined as the ratio of the concentration of the solute in the stationary phase (or sensor thin film coating material), C_s , to the concentration of the solute in the vapor phase, C_v :

$$K = C_s / C_v \quad (4)$$

It is related to the standard Gibb's free energy of solution of a gaseous solute, ΔG_s^0 , by:

$$\Delta G_s^0 = - R T \ln K \quad (5)$$

where the standard states are unit concentration in the gas phase and unit concentration in solution.

The partition coefficient is particularly useful when applied to piezoelectric sorption detectors because it can be directly related to the frequency shifts determined when vapors sorb into the coatings.⁴¹⁻⁴⁴ The equation derived for SAW delay lines is as follows:⁴⁴

$$\Delta f_v = \Delta f_s C_v K / \rho \quad (6)$$

This simple relationship relates the frequency shift caused by vapor sorption, Δf_v , to the partition coefficient and experimentally determined sensor characteristics. The variable ρ is the density of the coating material, as before. The variable Δf_s represents the frequency shift observed when the sorbent coating was applied to the bare SAW device, and provides a measure of the amount of material on the sensor.

The validity of the relationship in equation 6 has been experimentally confirmed by comparing partition coefficients calculated via equation 6 (SAW partition coefficients) for a variety of vapors on a fluoropolyol-coated SAW sensor with those determined by gas-liquid chromatography (GLC) using fluoropolyol as the stationary phase.⁴⁴ The structure of this material is shown in Figure 4. SAW partition coefficients and GLC partition coefficients ranked the vapors in the same order. The most strongly sorbed vapors were those with low saturation vapor pressures and functionalities capable of hydrogen bonding. Least strongly sorbed were vapors which interact principally by dispersion interactions.

The magnitudes of these partition coefficients are worth examining. Dimethyl methylphosphonate (DMMP) is a vapor commonly used to simulate more toxic organophosphorous compounds.^{14,15,44} The log of its partition coefficient on fluoropolyol, determined from SAW frequency shifts, was 6.5.⁴⁴ The gas phase DMMP concentration for this measurement was 20 mg/m³. The log K determined by GLC was 7.5; this measurement refers to the vapor at infinite dilution in the gas phase.⁴⁴ (Partition coefficients for this vapor on fluoropolyol decrease with increasing vapor concentration.) These numbers demonstrate that the concentration of DMMP in the coating material is on the order of one to ten million times more concentrated than the DMMP in the gas phase. Thus, absorption is very effective at collecting and concentrating analyte molecules on the sensor's surface.

Partition coefficients also help to define the inherent selectivity of a sensor coating material. Two common interferents in many environments are water, from ambient humidity, and hydrocarbons, from fuels. The log of the partition coefficient of isooctane on fluoropolyol determined by SAW measurements was 2.1.⁴⁴ Comparison of this value with that for DMMP indicates selectivity for DMMP over isooctane of greater than four orders of magnitude. By a similar analysis, selectivity for DMMP over water is over three orders of magnitude. These results show that substantial selectivity is possible using absorption and solubility interactions. This degree of selectivity may be sufficient to use a single sensor in well characterized, stable, analytical environments where the analyte is present in moderate or high concentrations. In more difficult field environments where organic vapors must be detected at trace concentrations, this degree of selectivity provides excellent information for analysis by pattern recognition techniques.

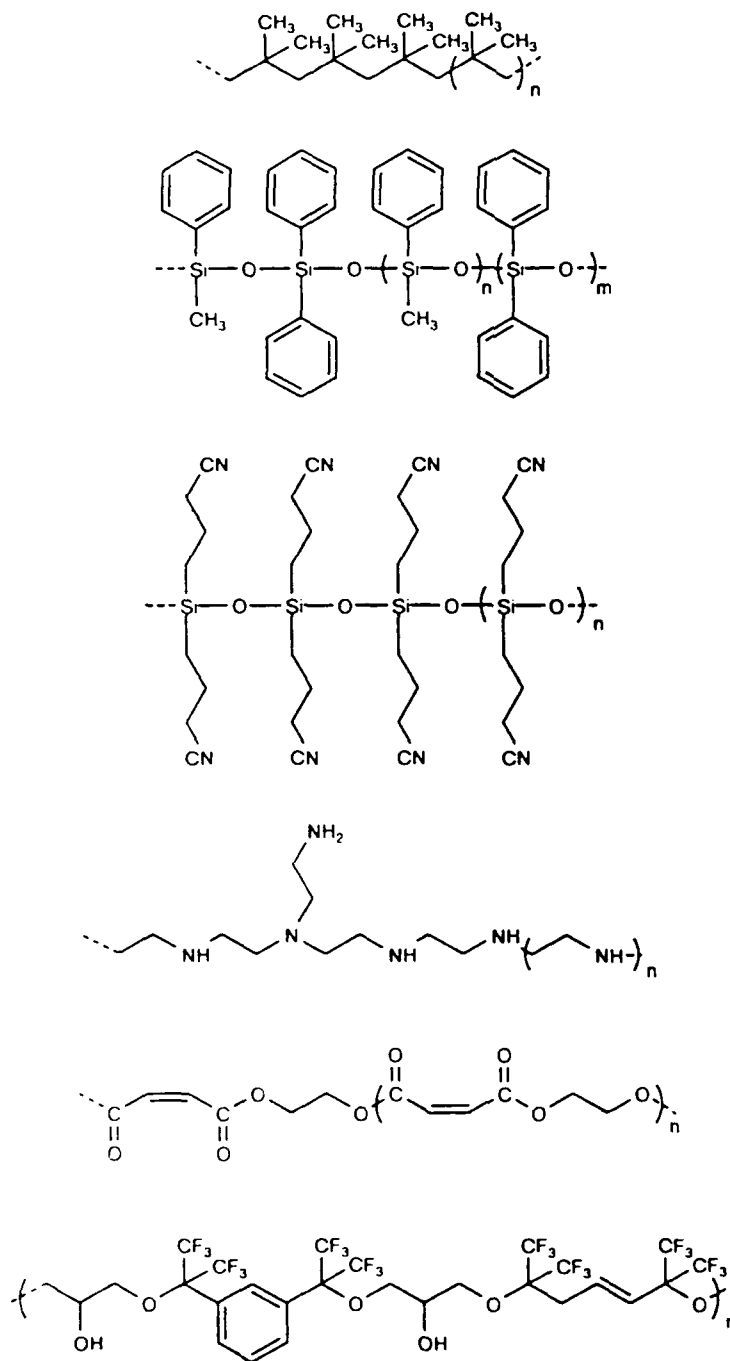


Figure 4. Selected chemical structures of sorbent polymers. Shown from top to bottom: poly(isobutylene), a phenylmethyl-diphenylsiloxane copolymer, polybis(cyanopropyl)siloxane, poly(ethylenimine), poly(ethylene maleate), and fluoropolyol. These structures emphasize, in the order shown, dispersion interactions, polarizability, dipolarity(minimizing basicity), basicity(minimizing dipolarity), basicity and dipolarity, and acidity, with qualifications noted in the text.

It should also be noted that partition coefficients are strongly temperature dependent. Sorption normally decreases with increasing temperature. The more strongly sorbed a vapor is, the greater the decrease as temperature rises.⁴⁴ As a result, piezoelectric sorption detectors become less sensitive and less selective as the temperature increases. This result also indicates that if partition coefficients measured by techniques such as GLC are to be used to evaluate a sensor coating material, the measurements should be made at the same (or nearly the same) temperature as the temperature at which the sensor operates (usually near room temperature). Partition coefficients measured at higher temperatures, as is more common in the GLC literature, underestimate both the sensitivity and selectivity with which vapors can be absorbed on sensors operating at room temperature.

SOLVATION PARAMETERS AND SOLUTE PROPERTIES

In the past, considerable attention has been given to parameters that describe the solubility properties of solvents. Kamlet and Taft⁴⁵ introduced a number of useful parameters obtained from the UV spectra of various indicator dyes dissolved in the solvents and referred to as solvatochromic parameters. These parameters for bulk liquid solvents are not always relevant to the properties of monomeric isolated (solute) molecules, especially in the case of compounds that form associated networks as pure bulk liquids.

More recently, parameters that characterize solubility properties of monomeric solutes have been devised. We refer to them as solvation parameters in order to distinguish them from the above-mentioned solvent parameters. We will use scales of these solvation parameters to quantify solute(vapor) solubility properties, and to compare one vapor to another. In addition, these parameters are useful in linear solvation energy relationships(LSER), which we will use as a tool to quantify coating material solubility properties in the next section. As is customary, parameters for solutes are distinguished with a subscript 2, while parameters for solvents have a subscript 1. In the context of vapor sensors, the vapors are solutes which dissolve in the (solvent) sensor coating.

The solute parameters that are of interest in the present treatment of sorption are the hydrogen bond parameters α_2^H and β_2^H , the dispersion parameter $\log L^{16}$ (which also includes cavity effects), and parameters for dipolarity and polarizability π_2^* , R_2 , and δ_2 .

The hydrogen bond parameters are derived from thermodynamic measurements on hydrogen bond complexation, and are related to Gibbs free energy. The α_2^H parameter is a measure of hydrogen bond acid strength. This scale was derived using values of equilibrium constants for the complexation of acids by reference bases(such as pyridine) in an inert solvent(tetrachloromethane).^{46,47} Similarly, the β_2^H scale, which measures hydrogen bond base strength, was derived from values of equilibrium constants for the complexation of bases by reference acids(such as 4-fluorophenol) in tetrachloromethane.^{48,49} These measurements provide constants for 1:1 complexation. Some compounds, such as phenols and anilines, can act as bases via both their heteroatomic substituents and the aromatic ring. In such cases, 1:1 β_2^H values are replaced by larger effective β_2^H values for interactions with bulk liquid solvents.

Dispersion interactions are accounted for in the $\log L^{16}$ parameter. Like the hydrogen bond parameters, $\log L^{16}$ is a Gibbs free energy related quantity, being obtained from the gas-liquid partition coefficient (or Ostwald solubility coefficient) of the solute on hexadecane at 25°C.⁵⁰ (L is the symbol for the Ostwald solubility coefficient, which is defined identically to the partition coefficient as in equation 3.) Hence, this parameter is a combination of exoergic dispersion interactions leading to an increase in $\log L^{16}$, together with an endoergic cavity term in hexadecane leading to a decrease in $\log L^{16}$.

R_2 is a parameter for polarizability; it provides a quantitative measure of the ability of a solute to interact with a solvent through n and π electron pairs.⁵¹ It is calculated from molar refractions as we will explain in a later section on polarizable materials. The δ_2 parameter is an empirical approximation for polarizability used in the past, taken as 1.0 for aromatic compounds, 0.5 for polyhalogenated aliphatic compounds, and 0 for all other compounds.⁵² We mention it here only for historical clarity, since it is now replaced by R_2 .

Finally, the parameter π_2^* measures the ability of a compound to stabilize a neighboring charge or dipole.^{35,36,52,53} Hence, this parameter is important with regard to the dipole/dipole and dipole/induced dipole interactions. For non-protonic, aliphatic solutes with a single dominant dipole, π_2^* values are approximately proportional to molecular dipole moments. Dipole moments themselves can be used for the understanding of molecular properties, and we will use them below when discussing functional groups and materials, but they have not proven to be as useful as π_2^* in LSER correlations.⁵¹ π_2^* is the only solvation parameter that is in any way related to solvatochromic solvent parameters, in that π_2^* is taken as π_1^* for non-associated compounds. Additional π_2^* values have been estimated or obtained via $\pi_2^*/\text{dipole moment}$ correlations.

The chemical significance of these parameters is best understood by considering examples. Parameters for a variety of typical organic compounds are presented in Table I, and additional examples are given in the discussion below. Alkanes, being capable only of dispersion interactions, have zero values for δ_2 , R_2 , π_2^* , α_2^H and β_2^H . Some typical $\log L^{16}$ values for liquid alkanes are 2.16 for n-pentane, 2.67 for n-hexane, 2.91 for cyclohexane, and 4.69 for n-decane. Values of $\log L^{16}$ for alkanes increase with increase in their normal boiling points and, indeed, are almost linear with $\log P^0$ where P^0 is the vapor pressure at 25°C. Functionalized organic compounds which are liquids at room

Table I. Solvation Parameters for Solutes

Solute	Polarizability R_2	Polarity: * π_2	Acidity α_2^H	Basicity β_2^H	Dispersion $\log L^{16}$
n-hexane	0	0	0	0	2.67
toluene	.601	.55	0	.14	3.34
chloroform	.425	.58	.20	.02	2.48
triethylamine	.101	.15	0	.67	3.08
acetone	.179	.71	.04	.50	1.76
N,N-dimethylformamide	.367	.88	0	.66	3.17
ethanol	.246	.40	.33	.44	1.49
phenol	.805	.72	.60	.36 ^a	3.86

^a Effective value for β_2^H for the solute in a bulk solvent, see text.

temperature have $\log L^{16}$ values which range from 1 (e.g. methanol) or 2 (n-propanol) to values of 4 or 5 for less volatile liquids such as octanol, nitrobenzene, or dimethyl methylphosphonate. All other things being equal, the $\log L^{16}$ values for a homologous series will increase with increasing molecular weight (and decreasing volatility).

Aromatic or halogenated hydrocarbons have significant values of R_2 and π_2^* .

Values for R_2 are typically in the range of 0 to 1, with normal alkanes being zero by definition. Halogenation increases polarizability, resulting in R_2 values for dichloromethane and tetrachloromethane of 0.387 and 0.458 respectively. Aromatic content also results in significant polarizability; the R_2 values for benzene and phenol are 0.610 and 0.805 respectively.

Dipolarity and polarizability are common to many organic functional groups; hence a wide variety of compounds have significant π_2^* values. These values for organic liquids are normally in the range of 0 to 1, being 0 for cyclohexane (by definition), and 1.0 for very dipolar compounds like dimethyl sulfoxide and nitrobenzene. Intermediate values are found for compounds like ethanol (.40) and acetone (.71).

The hydrogen bond parameters α_2^H and β_2^H are also scaled so that alkanes are zero.

A great variety of hydrogen bond bases exist, and β_2^H values have been determined for approximately 500 such bases. The values of β_2^H for most compounds fall in between 0 and 1. Examples of bases include acetone (.50), primary aliphatic amines (.70), and dimethyl sulfoxide (.78).

Typical hydrogen bond acids are alcohols, phenols, and carboxylic acids, although NH bonds can also lead to hydrogen bond acidity when activated as in aniline.^{48,49} Hydrogen bond acidities can reach values as high as 0.86 (perfluoro-t-butanol) or 0.95 (trifluoroacetic acid), with values for more typical acids being in the range of 0.3 to 0.6. For example, the values for ethanol, phenol, and acetic acid are 0.33, 0.60, and 0.55 respectively.

It should be noted that hydrogen bond acidity and hydrogen bond basicity differ significantly from proton transfer acidity and basicity.⁴⁶⁻⁴⁹ Although correlations between these two phenomena can sometimes be made within chemical families, no general relationship exists. As an example, consider triphenylmethane: although this compound is a proton transfer acid, it is not a hydrogen bond acid at all. The proton transfer acidity is determined by the stability of the conjugate base, whereas the conjugate base is irrelevant to

the hydrogen bond acidity. All discussions of acidity or basicity in this paper refer to hydrogen bonding, unless otherwise noted.

The range of solutes for which all the six above mentioned solvation parameters are known is very wide, and includes examples of nearly all the monofunctionalities encountered in organic chemistry. At the moment, all six parameters are known for several hundred solutes. (These values can be found in the references cited above.) Further values, when needed, can usually be estimated. Since values of π_2^* , α_2^H , and β_2^H are very

nearly constant along any homologous series, it is reasonably easy to estimate values for the homologues. $\log L^{16}$ is almost linear with either carbon number or $\log P^0$ along an homologous series, and so, again, values can be estimated in this way. The δ_2 parameter is trivial, but R_2 needs either to be determined or to be estimated. This is usually not too difficult, because molar refractions are almost additive, at least to a first approximation.

With the development of these solvation parameters, it is a simple matter to determine the solubility properties of organic vapor analytes. The objective in sensor coating material design is then to develop materials which will interact strongly with the analyte properties.

LSER AND STATIONARY PHASE SOLUBILITY PROPERTIES

To fully understand the interactions occurring between an analyte and the sensor coating, it is also necessary to understand the solubility properties of the coating material (which we will refer to as the stationary phase or solvent). The simplest qualitative approach to estimating a stationary phase's solubility properties is to examine the functional groups in its structure. For example, referring to Table I, one would estimate that a phase containing ketones would be more dipolar but less basic than one containing aliphatic amines. This approach can be useful as a starting point, but it is not entirely satisfactory for structures with multiple functional groups or self-associating groups. Experimental sorption data can provide additional information which is relevant to sensor applications. The sorption characteristics of a diverse set of vapors on a particular phase provide insight into which vapor properties contribute to stronger sorption.⁴⁴

Nevertheless, it is desirable to have a more quantitative method which will evaluate each of the various individual types of solubility interactions (such as dispersion, acid-base, etc. as described previously). The method must also be applicable to the types of materials applied to sorption detectors, including non-volatile liquids, liquid polymers, and solid elastomeric polymers. We have used linear solvation energy relationships (LSER) to systematically evaluate sorption data, evaluate stationary phase solubility properties, and to sort out the relative strengths of multiple simultaneous interactions. Multiple linear regression analyses of measured partition coefficients against vapor solvation parameters lead to the following LSER equations to describe sorption:^{51,53-56}

$$\log K = c + d\delta_2 + s\pi_2^* + a\alpha_2^H + b\beta_2^H + l\log L^{16} \quad (7)$$

$$\log K = c + rR_2 + s\pi_2^* + a\alpha_2^H + b\beta_2^H + l\log L^{16} \quad (8)$$

These equations are useful because the individual terms can be identified with particular solute-solvent interactions. The various explanatory variables δ_2 , R_2 , π_2^* , α_2^H , β_2^H , and $\log L^{16}$ are the solute parameters described in the previous section.

The coefficients d , r , s , a , b , and l evaluate the solvent properties which are complementary to those of the solute. (The constant c arises from the method of multiple linear regression.)

Thus, r measures the ability of the phase to interact with solute n and π electrons, and is an indication of polarizability. Usually r is slightly positive, but becomes negative if the phase contains a number of fluorine atoms.^{51,56} The s -coefficient measures the liquid phase dipolarity. The a -coefficient, being complementary to the solute hydrogen bond acidity, measures the liquid phase hydrogen bond basicity. Similarly, the b -coefficient, being complementary to the solute hydrogen bond basicity, measures the liquid phase hydrogen bond acidity. The l -coefficient is a combined measure of dispersion interactions that tend to increase l , and cavity effects that tend to decrease l . In practice, it is observed that the l -coefficient is a very good indicator of the ability of a GLC phase to separate adjacent members of an homologous series.⁵⁶

The only difference between equations 7 and 8 is in the treatment of polarizability. Equation 8 is the more recent equation, and is now preferred. The R_2 parameter is a more rational measure of polarizability than δ_2 , and regressions via equation 8 have been slightly better in terms of overall standard deviation and correlation coefficient than regressions via equation 7. The data required to characterize a phase by this method are the partition coefficients (at a single temperature) of about thirty solutes, chosen to provide a suitable range of all relevant parameters. In most laboratories, these will be most easily obtained from GLC retention times.

The use of equation 8 can be illustrated with results from fluoropolyol, a soft oligomeric liquid phase that we have examined in detail.⁴⁴ (Its structure is shown in Figure 4.) SAW sensors coated with this material are particularly sensitive to hydrogen bond bases, and we shall be able to reason why this is so. Twenty nine partition coefficients measured by GLC at 298°C gave the following regression equation with a correlation coefficient of 0.9902 and an overall standard deviation of 0.16.^{44,57}

$$\log K = -1.02 - 0.42 R_2 + 0.82 \pi_2^* + 1.85 \alpha_2^H + 4.90 \beta_2^H + 0.75 \log L^{16} \quad (9)$$

The very large b -coefficient of 4.90 shows that this phase interacts selectively with vapors that are hydrogen bond bases, and hence that the phase is a strong hydrogen bond acid.

We can go further than this. By evaluating the individual terms in equation 9 we can quantify the actual solute/solvent interactions for any given solute vapor. This is illustrated in Table II for the case of butanone as a typical hydrogen bond basic solute.

Table II. Evaluation of Multiple Simultaneous Interactions

Parameters	R_2	π_2^*	α_2^H	β_2^H	$\log L^{16}$
2-butanone	.166	.67	0	.48	2.29
Coefficients	r	s	a	b	l
fluoropolyol	-.42	.82	1.85	4.90	.754
Interaction terms	rR_2	$s\pi_2^*$	$a\alpha_2^H$	$b\beta_2^H$	$l\log L^{16}$
2-butanone/fluoropolyol	-.07	.55	0	2.35	1.73

$$3.39 \text{ (dispersion)} + .29 \text{ (dipole/induced-dipole)} - 1.95 \text{ (cavity)} = 1.73 \text{ (} l\log L^{16} \text{)}$$

The hydrogen bond term $b\beta_2^H$ contributes 2.35 log units to the overall log K value, as compared to a contribution of 0.55 log units from the $s\pi_2^*$ term, corresponding mainly to dipole/dipole interactions. Abraham and Fuchs⁵⁸ managed to dissect log L¹⁶ values into constituent terms due to dispersion interactions and cavity effects, plus a small dipole/induced dipole term. If we take, as a first approximation, the relative contributions on fluoropolyol to be the same as hexadecane, then we can assess the dispersive contribution as shown also in Table II. Interestingly, it turns out that even for the interaction between butanone and the very strong hydrogen bond acidic phase, dispersion interactions are larger than the hydrogen bond interaction.

It should be noted that these equations can be simplified for many materials that are not capable of all the solubility interactions considered. Hydrogen bond acidic phases, for example, are relatively uncommon, and in such cases the $b\beta_2^H$ term will not be significant.

In addition to characterizing stationary phases and unraveling multiple simultaneous interactions, equation 9 can be used to estimate partition coefficients and hence sensor responses(via equation 6). Any vapor whose solvation parameters are known can be evaluated in this way.

The LSER method has the advantages that the *constants generated* characterize the phase as a solvent and does so in terms of fundamental interactions with which chemists are familiar. The method can be applied to any liquid phase, so that polymers, GLC stationary phases, and laboratory solvents can all be characterized and compared by the same method. Thus, several common solvents as well as some N-substituted amide solvents have been so characterized,^{53,55} as have five Laffort and seventy-seven McReynolds GLC phases,^{51,56} and a few polymers.⁵⁴ Characterization of polymers used as sensor coatings is in progress and preliminary results have been reported.⁵⁹ In addition, several non-volatile bis-phenols have recently been prepared and characterized.⁶⁰

SENSOR COATING MATERIAL PROPERTIES

COATING MATERIAL PHYSICAL PROPERTIES

The essential physical properties of the coating are that it be non-volatile, so that it stays in place on the sensor, and that it allows facile diffusion of vapors to and from sites of selective interaction. In addition, the physical state of the material should not change under use nor should its physical properties lead to hysteresis effects. These requirements are satisfied by non-volatile liquids, and by amorphous oligomers or polymers.

Ideally, amorphous polymers should be elastomeric, i.e. above their glass transition temperature (T_g). In this state, constant thermal motion of the polymer chains allows rapid vapor diffusion.⁶¹ After a vapor has been sorbed and desorbed, the material is left in essentially the same state as it was prior to sorption. All other things being equal, sorption in elastomers is greater than in glassy materials,^{62,63} resulting in more sensitive sensors.

The "softness" of elastomeric materials has an additional advantage on piezoelectric sensors such as the SAW device which are sensitive to changes in material stiffness. The frequency shift (Δf_s) observed when the material is applied is not significantly affected by the materials elastic properties, as discussed above in conjunction with equation 2. This frequency shift is then a reasonable measure of the amount of material applied. Similarly, when vapor is sorbed, any further softening does not significantly influence the frequency shift (Δf_v). Thus soft materials allow a straightforward interpretation of sorption from sensor frequency shifts (e.g. according to equation 6).

Glassy polymers have a number of potential disadvantages on sensors. (Diffusion, sorption, and permeability in glassy polymers are covered in detail in references 61, 63, and 64.) Vapor diffusion is slower than in elastomers which can result in slower sensor response and recovery times. The diffusion process is frequently complex because increases in chain segmental motion and free volume can occur simultaneously with vapor transport, so that the diffusion rate increases as the vapor concentration in the polymer increases. During desorption the diffusion rate becomes slower as the vapor concentration decreases and the polymer stiffens, so that some vapor may be indefinitely retained. This could cause partial sensor irreversibility and creates possibilities for hysteresis. Further risk of hysteresis exists because sorption in glassy polymers can be influenced by adsorption in microvoids and microcracks. Such physical features may change before and after vapor sorption by mechanisms such as plasticization and flow, or by crazing. Finally,

the interpretation of vapor sorption from sensor frequency shifts may not be simple if changes in polymer stiffness during sorption contribute to the signal.

Partially crystalline polymers have some of the same potential disadvantages as glasses with the further consideration that crystalline domains act as excluded volumes to vapor sorption.^{61,64} Thus the crystalline domains do not contribute to sensor sensitivity since the vapor cannot reach sites of interaction. If the vapor interacts strongly enough to penetrate these domains and disrupt the crystallinity, the polymer may or may not recrystallize after desorption. (Polymer crystallization can be very slow.) This creates another potential mechanism for hysteresis.

In practice, some glassy polymers have yielded well-behaved SAW vapor sensors, while others have lead to poor reproducibility from sensor to sensor or from vapor exposure to vapor exposure, and some have shown poor recovery characteristics. Glassy polymers cannot be summarily ruled out, but the characteristics of sensors derived from them cannot be predicted as reliably as those based on elastomers. Film thickness and film morphology are likely to be important factors in the performance of glassy polymers on sensors. Thin films approaching the dimensions of random polymer coils or even molecular dimensions may not have the disadvantages that can result from the bulk properties of glassy polymers in thicker films.

Finally, the material must be compatible with the method by which it is to be applied to the transducer surface, and it must wet and adhere to that surface. We have observed, for example that certain substituted siloxanes will withdraw from the surfaces of glass-coated SAW devices, forming isolated beads instead of thin films. A variety of methods can be utilized to assure adhesion and improve film stability. The polymer, the surface, or both can be modified. Materials can be covalently attached to transducer surfaces, and/or cross-linked after application. Care must always be taken, however, that such modifications or processes not alter the desired chemical selectivity of the film, or impede vapor transport in and out of the film.

The chemical structure of the coating material determines its solubility properties, and hence the sensor sensitivity and selectivity. The greatest sensitivity to the target analyte can be achieved by including structural elements in the coating material which will maximize the solubility properties that will interact with the analyte vapor. All interactions that will enhance sensitivity to the vapor should be included, provided that they do not cause strong self-association of the material. Strong self-association, e.g. by the inclusion of both strong hydrogen bond donating and accepting groups in the same material, would require the breaking of solvent-solvent interactions before the vapor could interact to make new solute-solvent interactions.

The selectivity of a coating material will be greatest if it can be designed to interact with vapors by only a single type of solubility interaction. The coating solubility property associated with that interaction should be incorporated at the maximum strength. The logical approach to obtaining the greatest selectivity from an array of sensors is then to include individual coatings for each possible solubility interaction. These would be in addition to the sensor or sensors which maximize sensitivity to the target analyte(s). In this scheme, each sensor would provide unique information, and the array would probe all vapor properties which govern sorption.

In practice, using real materials, it is not possible to make a material which will interact only according to a single solubility property. All organic materials, for example, will undergo significant dispersion interactions. Materials which are basic are often also dipolar, and vice versa. Hydrogen bond acidic functional groups normally contain a basic atom as well. The strategy for selectivity must be to select a particular solubility property, incorporate it into a coating material at maximum strength, and to minimize all other solubility properties. In addition, unique combinations of solubility properties can be prepared in a single coating material. Using this type of analysis, the following categories are indicated as the "first-order" goals for sensor array coating development:

- a) maximize dispersion interactions
- b) maximize polarizability
- c) maximize dipolarity (minimize basicity)
- d) maximize basicity (minimize dipolarity)
- e) maximize both basicity and dipolarity
- f) maximize acidity (minimize basicity)

Each of these categories will be considered individually. They cover the full range of solubility interactions which normally occur between neutral organic molecules and functional groups. Using the principles discussed for these categories, the development of materials with other combinations of properties will be straightforward. As usual, the terms basicity and acidity in the discussion below always refer to hydrogen bond basicity and hydrogen bond acidity, respectively.

Dispersion interactions.

Dispersion interactions, also known as induced-dipole induced-dipole interactions and as London forces, are exemplified by aliphatic hydrocarbons in the condensed phase. Thus, the interactions between molecules of n-pentane (b.p. 35-36°C) in the liquid phase are entirely dispersion interactions. Although one might think that interactions between induced dipoles would be weak, the sum of such interactions in the liquid phase is actually quite significant. Such interactions account for why a small molecule such as n-pentane is a liquid at room temperature, and why hexadecane boils at 287°C and solidifies at 18°C. The significance of dispersion interactions is also illustrated in the calculations in Table II.

Materials for sensor coatings which interact by dispersion interactions are readily available. Poly(isobutylene) (see Figure 4) is a good example of a material we have used which is elastomeric and entirely aliphatic.¹⁵ Ethylene-propylene rubber is another candidate for this category. Unsaturated elastomeric aliphatic polymers such as poly(isoprene) and poly(butadiene) have similar sorption properties, but are subject to degradation by ozone⁶⁶ and would thus have limited lifetimes as sensor coatings.

Because the log L¹⁶ parameter includes both a dispersion interaction and a cavity effect, some care has to be taken when discussing the variation of the l-coefficient with change in the liquid phase. Amongst nonaqueous solvents, cavity effects are generally rather similar,⁶⁷ with a tendency to increase as the solvent cohesive energy density increases. Increase in cavity effects would lead to a decrease in the l-coefficient. Thus at 25°C l varies from 1.00 (hexadecane) through 0.90 (ethyl acetate) to around 0.80 for liquids such as methanol, NN-dimethylformamide, and acetonitrile.^{53,55} The effect of the l-coefficient is to influence the solubility of gaseous homologues; the larger the value of l, the more difference there will be in the gas-liquid partition coefficient.⁵⁶ Hence, it is advantageous to include some material with a large l value in any sensor array. It seems rather unlikely, however, that materials can be synthesized with a much larger tendency to undergo general dispersion interactions than simple alkanes (hexadecane) or simple polymers such as poly(isobutylene).

Our observation in SAW sensor research has been that hydrocarbon vapors are more strongly sorbed into elastomeric hydrocarbon polymers than into more functionalized polymers. This result is consistent with the cavity effect arguments above. For example, in a recent study involving ten coatings on SAW sensors, poly(isobutylene) produced the most sensitive sensor for isooctane.¹⁵ The second most sensitive sensor for isooctane was coated with a functionalized material derived from a poly(isoprene). Including a sensor which provides information about hydrocarbons is potentially important in arrays for some applications, because hydrocarbon fuels are common in so many field environments.

Polarizability.

Polarizability refers to the formation of a dipole in a non-dipolar molecule or structural unit when it is exposed to an electric field. The focus in this section is on materials which are more polarizable than the aliphatic materials discussed in the previous section on dispersion interactions. Polarizable materials will have greater interactions with dipolar vapors via dipole/induced-dipole interactions. Greater interactions with polarizable vapors are also expected. Note that the term polarizable refers to the ease with which a dipole is induced, whereas dipolar refers to the existence of a permanent dipole. These are distinguished from the term "polar", which is often used loosely (especially in chromatography) to include both these properties, and sometimes basicity. Thus, some would call benzene more polar than cyclohexane because it is more polarizable, though neither molecule is actually dipolar.

Although the concept of polarizability is well-established, it is not too easy to quantify. Molar refraction is often used as a measure of polarizability, but is not of much use in the present context. In Table III are given values of a molar refraction, MR_x defined as: ⁵¹

$$MR_x = 10 \left[\frac{(n^2-1)}{(n^2+2)} \right] V_x \quad (10)$$

where n is the refractive index at 20°C and V_x is the McGowan's characteristic volume in $(\text{cm}^3 \text{ mol}^{-1})/100$. Because of the volume term in molar refraction, the latter always increases with increasing size (compare values for the alkanes in Table III). The refractive index function itself is a rather better indication of the presence of polarizable electrons or a molecule; thus values of the refractive index are always larger for aromatic or halogenated

Table III. Some Criteria of Polarizability

Compound	$(n^2-1)/(n^2+2)$	MR _x	R ₂
methane	.168	0.421	0
n-butane	.205	1.378	0
n-hexadecane	.261	6.160	0
diethyl ether	.219	1.586	.04
ethyl acetate	.227	1.696	.11
ethanol	.221	0.992	.25
N,N-dimethylformamide	.259	1.673	.37
methanethiol	.253	1.044	.40
perfluoro-octane	.170	2.646	-1.23
tetrachloromethane	.274	2.025	.46
tetrabromomethane	.353	3.350	1.19
benzene	.295	2.112	.61
anisole	.303	2.776	.71
1,3-dibromobenzene	.345	3.673	1.17

aliphatic compounds than for other aliphatics. Quite recently, an "excess" molar refraction, i.e. the molar refraction in excess of the molar refraction of an alkane of the same characteristic volume, has been defined as R_2 .⁵¹

$$R_2 = MR_X - MR_X \text{ for an alkane of the same } V_X \quad (11)$$

By subtracting the molar refraction for an alkane of the same characteristic volume, the dispersive component of molar refraction (already accounted for in $\log L^{16}$ in LSER correlations) is removed. Values for R_2 are listed in Table III. These provide a quantitative indication of polarizable n and π electrons. (It can be seen from the R_2 values in Table III that the empirical δ parameter is actually just a coarse approximation to R_2 , and so we need deal with the δ parameter no further.)

As noted previously, the presence of aromatic groups or heavy halogen atoms in a compound promote polarizability. Significantly, introduction of fluorine substituents lowers the excess molar refraction below alkane values. This lack of polarizability is why fluorinated compounds are often more volatile than their non-fluorinated counterparts, and why fluorinated organic vapors can be difficult to sorb.

Stationary phase materials which fit the requirements of this category are the phenylsilicones which are used as GLC stationary phases. Polyphenylmethylsiloxane, containing 50% phenyl substitution is available as OV17, and 75% phenyl substitution is available as OV25 (see Figure 4). Methyl- and phenyl siloxanes have been examined in detail, and it was confirmed that polarizability increases with phenyl substitution.⁶⁸ Substitution exceeding 75% by mole is undesirable, however, because the polymers become solids as the phenyl substituents introduce rigidity into the polymer chain.

The use of siloxanes in this category may appear to violate the premise of emphasizing a single interaction with the exclusion of all other interactions because the presence of oxygen atoms in the chain will confer some basicity. However, these oxygens are only weakly basic, being comparable to the weak basicity of aromatic groups. Thus, the solute hydrogen bond basicity of hexamethylsiloxane, $\beta_2^H = 0.16$, is about the same of that of benzene, $\beta_2^H = 0.14$. As an alternative to the silicones, we note that some apiezon greases are more polarizable than simple hydrocarbons.

Dipolarity (Minimize Basicity).

The incorporation of dipolar groups into a material increases the sorption of dipolar vapors by oriented dipole-dipole interactions. Sorption of polarizable vapors will also be increased by dipole-induced-dipole interactions. Dipolarity is greatest in heteroatomic functional groups, but these are also basic. Consequently, a method is required to determine which types of functional groups maximize dipolarity with the least basicity. We will examine dipole moments as a measure of dipolarity, and solute β_2^H values as a measure of basicity. Examples are listed in Table IV.

The first entry, 1,1,1-trifluoroethane, illustrates the use of halogens to achieve dipolarity without basicity. Trifluoropropyl-substituted silicones used as GC stationary phases use this property. Nevertheless, the dipole is not particularly strong. Stronger dipoles are seen in molecules with cyano, amide, sulfoxide, amine-N-oxide, and phosphoryl groups. Most of these are also strongly basic and cannot be considered in this category. Carbonyl groups in ketones and esters are also dipolar, but less so than the others.

This analysis leaves cyano groups as the most desirable dipolar functionality. Fortunately, commercial materials containing cyano groups are readily available. Silar 10C, for example, is a GC stationary phase consisting of a polymeric siloxane with 100% cyanopropyl substitution (see Figure 4). It is one of the most dipolar GC stationary phases available, and is a logical candidate for this category of materials. Tris(cyanoethoxy)propane is another well known GLC stationary phase which is highly dipolar.

It should be emphasized, however, that the analysis above has used the properties of monomeric molecules to predict properties of solvent stationary phases. While this is a reasonable first step, it is best followed by experimental measurements on actual solvents. Thus, the parameters discussed above show that a nitrile is more dipolar than an ester when they are monomers. That the same trend is observed when these functional groups are present in solvents was confirmed by an LSER comparison of acetonitrile and ethyl acetate (using data obtained at 298°C.)⁵³ Further characterization of dipolar stationary phases (at appropriate temperatures) for sensor applications would be worthwhile.

Of the three types of interactions examined thus far, the two strongest are the dispersion interactions and dipole-dipole interactions. Dispersion interactions contribute significantly to sorption, especially if the vapor has a low saturation vapor pressure. Dipole-dipole interactions can be significant when both the vapor and the sorbent material are dipolar. Dipole-induced-dipole interactions are relatively less important.⁶⁹

Table IV. Dipolarity and Hydrogen Bond Basicity

Compound	Dipole moment ^a (Debye)	β_2^H	Functional Group
1,1,1-trifluoroethane	2.32	0	CF ₃ CH ₃
acetonitrile	3.92	.44	RCN
triethylamine	.66	.67	R ₃ N
diethylamine	.92	.70	R ₂ NH ($\alpha_2^H = 0$)
diethyl ether	1.15	.45	ROR
ethyl acetate	1.78	.45	R(C=O)OR
acetone	2.88	.50	R ₂ C=O
N,N-dimethylacetamide	3.81	.73	R(C=O)NR ₂
dimethylsulfoxide	3.96	.78	R ₂ S=O
pyridine-N-oxide	4.2 ^b	.81	(R)N-O
triphenylphosphine oxide	4.3 ^b	.92	R ₃ P=O

^agas phase values unless otherwise noted.
^bliquid phase value.

Hydrogen Bond Basicity (Minimize Dipolarity)

A wide variety of functional groups can provide basicity, but most of them are also dipolar, as seen in the analysis in the previous section. Reasonably strong basicity with very little dipolarity can be obtained from aliphatic amines, as seen in Table IV. These groups have β_2^H values of ca. 0.7. Tertiary amines are the most straightforward candidates because they contain no -NH groups that might donate hydrogen bonds and cause self-association of the sorbent material. However, the NH groups in primary and secondary aliphatic amines actually have negligible acidity. Their α_2^H values are zero, and these amines are suitable for this category. The same cannot be said for aromatic amines, whose NH groups are weak acids. For example, the α_2^H value for aniline is 0.26.

Secondary amine functionality is available in poly(ethylenimine), which has a repeat unit of $-(CH_2CH_2NH)-$ (see Figure 4). This soft organic polymer has been used as a coating on SAW devices, yielding sensors with sensitivity to hydrogen bond acids such as water.¹⁵ The linear form of poly(ethylenimine) has a T_g of -20°C and a T_m of 60°C .⁷⁰ Thus, it can be partially crystalline. Nevertheless, the usual preparation of this material from ethylenimine yields a branched material, and this is much less likely to contain crystalline domains.

An interesting class of materials to consider for the basicity category is the polyphosphazenes. These materials contain nitrogens in the backbone and sometimes have low T_g values. Amine-substituted polyphosphazenes are likely to be particularly basic, and could be useful on sensors if they can be obtained as non-crystalline elastomers.

Hydrogen Bond Basicity and Dipolarity

As noted above and illustrated in Table IV, the functional groups providing the greatest strength in both basicity and dipolarity are amides, sulfoxides, amine-N-oxides, and phosphoryl groups. (The phosphoryl group, $P=O$, is found in, for example, organic phosphates, phosphonates, and phosphine oxides.) Amides, if used for materials in this category, should be derived from secondary amines, so that there are no NH groups. The hydrogen bond acid strength of these groups are similar to that of aliphatic alcohols ($\alpha_2^H = 0.38$ for N-methylacetamide, compared to 0.33 for ethanol), so the presence of $RNHCOR'$ functionality in a polymer would give rise to significant self-association.

Esters are also dipolar and basic, but less so than the groups above. If the properties of esters are desirable for a particular sensing application, then those same properties can be obtained at greater strength with some of the other functional groups above. Nevertheless, esters suitable for application on sensors are so readily available that they must be discussed here. Many esters are available as GLC stationary phases, and many polyesters are elastomeric and can be bought or easily made.⁷¹ An example is shown in Figure 4.

Amides are probably the next most readily available functional group, but most polyamides (nylons, for example) are glassy or crystalline or both. We have used polyvinylpyrrolidone on SAW sensors, but it is a glass with $T_g = 180^\circ\text{C}$,⁷⁰ and sensors derived from this material were not highly reproducible.^{14,15} Conceivably, elastomers with amide groups could be synthesized.

Additional functional groups that might be incorporated in an elastomer are the sulfone, amine-N-oxide or phosphoryl groups. In this regard, we note that viscous, fluid polysiloxanes with pyridine-N-oxide groups have been reported.⁷²

Hydrogen Bond Acidity

When we examined basicity, we compared solute β_2^H values for various functional groups, even though we were actually going to use these groups in the stationary phase solvent. Solute β_2^H values revealed the basic properties inherent to the monomeric functional groups. These properties do not change substantially in the solvent phase when the solvent is non associated. Scales of solute β_2^H values and solvent β_1 values rank aprotic bases in approximately the same way.

Hydrogen bond acids, however, associate via hydrogen bonding in the solvent phase, which influences how they will interact with solutes. Association occurs because functional groups that can donate hydrogen bonds will normally also contain an atom capable of accepting a hydrogen bond. A classic example is acetic acid, which is a strong hydrogen acid as a monomer. However, it readily self-associates to form a strongly bound dimer.

We will continue to examine solute parameters to understand the properties inherent to particular functional groups. Those groups with the strongest acidity and the least basicity will provide the sensitivity and selectivity required for sensor coating materials. Minimizing basicity will reduce self-association. Solute α_2^H and β_2^H values for representative acids are given in Table V.

The principle functional group for hydrogen bond acidity is the OH group in aliphatic alcohols and phenols. In certain cases, NH groups can also be acidic. Carboxylic acids will not be considered here because of their tendency to dimerize. The acidity of hydroxyl groups can be substantially increased by electron withdrawing halogen substituents, with the bonus that basicity is decreased at the same time. Thus, hexafluoroisopropanol is an excellent hydrogen bond acid with negligible base strength. Fluoroalcohols, phenols, and substituted phenols are indicated as candidates for acidic sensor coating materials.

Materials which fit this category are not readily available. Thus, among the 77 stationary phases characterized by McReynolds, and more recently characterized by LSER methods, none were strong acids.⁵⁶ In the sensors field, the strongly acidic material with which we have the greatest experience is an oligomer we refer to as fluoropolyol (Figure 4).^{14,15,44} This material can be synthesized by methods in the literature.⁷³ The hexafluoroisopropanol group has also been incorporated into polymers, although these were not elastomers.⁷⁴⁻⁷⁶ Recently, an alternative strongly acidic phase has been developed which is readily prepared. It is a non-volatile phenolic liquid containing the hexafluorobisphenol-A structural unit. Characterization by GLC and LSER indicates that it is a stronger acid than fluoropolyol.⁶⁰

Although they are not as readily available as other materials, strongly hydrogen bond acidic stationary phases are very important because of the great variety of organic bases that one might want to detect. Sensors coated with materials in this category have excellent sensitivity to strongly basic vapors such as organophosphorus compounds.^{14,15,44}

Table V. Comparisons of Hydrogen Bond Acids

Compound	α_2	β_2
water	.35 ^a	.38
ethanol	.33	.44
2,2,2-trifluoroethanol	.57	.18
hexafluoroisopropanol	.77	.03
phenol	.60	.36 ^b
3-fluorophenol	.68	.24 ^b
3,5-di(trifluoromethyl)phenol	.82	-
acetic acid	.55	.43
trichloroacetic acid	.95	-
tetrachloropyrrole	.72	-
chloroform	.20	.02
bromomalononitrile	.49	-

^aValue for 1:1 hydrogen bonding. The effective α_2 value for water in a bulk solvent is 0.65.

^bEffective values for β_2 for the solutes in bulk solvents, see text.

COATING SELECTION STRATEGIES FOR ARRAY DETECTORS

In selecting coatings for a sensor array, it is important to remember that pattern recognition techniques are information processing methods.⁷⁷⁻⁸¹ Like all such methods, they rely on the quality and quantity of the information being provided. When pattern recognition methods are applied to vapor detection using sensor arrays, the information is encoded in the numerical responses of the individual sensors. A randomly chosen set of coatings for a sensor array is unlikely to provide optimal information. (Indeed, closely correlated sensors can produce instabilities in some numerical analyses.) A set of sensors in which each sensor probes a different solubility interaction will provide more information than a set in which most of the sensors probe the same type of interaction.

The discussion of sorption and solubility presented above provides detailed information for developing sensors that maximize particular interactions. Given an understanding of these interactions, and the coating material properties which contribute to them, it is possible to intelligently choose a set of coated sensors in which each sensor provides unique information. The most general type of array would be one with approximately six coatings according to the categories outlined above. The set of coatings in Figure 4 illustrates the types of materials that might be chosen for such an array. This is not an optimal set: the materials pictured are restricted to those which have been previously reported on SAW sensors, or are well-known GLC stationary phases. There is substantial room for innovation to produce materials that better maximize the particular interaction(s) that each pictured material represents. The polyester is a case in point, as previously noted. In selecting materials for this set, it is advantageous to have materials whose solubility properties have been characterized, for example by the LSER methods discussed.

An array of this type could be adapted to a wide range of applications. The sensors included probe the full range of solubility interactions discussed above, and there is a sensor whose selectivity has been maximized for each particular interaction. When this array is applied in a detector for a particular analyte, it may already contain a good sensor for that analyte. After a collection of a suitable data set, a pattern recognition algorithm could be developed so that this analyte can be correctly recognized.

Optimization of an array for any particular application will depend on what could be referred to as the boundary conditions of the analytical problem. The first such condition is the analyte to be detected. This could be a particular compound or class of compounds. Questions associated with this condition are: How fast must it be detected? Must it be detected reversibly? And what sensitivity is required? If it must be detected at very low concentration levels, then it may be desirable to develop a sensor which maximizes

sensitivity to that analyte. Indeed, it is always desirable to have a sensor with the best achievable sensitivity and selectivity for the target analyte, whether the sensor is to be used alone or in an array. This sensor would then be included in the above array and a pattern recognition algorithm developed.

The second boundary condition will be the definition of the analytical environment, especially with regard to the presence of other compounds which could cause sensor signals. The general array developed above may already be sufficient to discriminate against such compounds. However, if a potential interference is of particular concern, then a sensor selective for it may be developed and included. Alternatively, if the analytical environment is well characterized, and unlikely to change, then it may be possible to reduce the number of sensors in the array and still have satisfactory discrimination. For example, it may not be necessary to have both a basic and a basic/dipolar material, or both a polarizable and a dipolar material. It will all depend on what types of molecules must be distinguished from one another, and at what concentrations.

The rigorous (and ideal) approach to selecting coating materials for difficult applications begins with a large set of carefully selected materials. This set would include materials in all the categories discussed above, plus material(s) optimized for the target analyte(s), and possibly materials optimized for potential interferences of particular concern. It might also include materials that represent combinations of interactions which were not explicitly discussed above. For example, one might include a material which is both highly polarizable and dipolar.

Once the materials are chosen and sensors are prepared, it is necessary to collect a "training set", the data set of sensor responses from which the pattern recognition algorithm will be developed. The design of a good training set is not trivial. Once again, the operative principle is that the quality of the algorithm developed will depend on the quality of the information in the training set. The data set should be properly balanced to include both vapors to be classified as hazards, and vapors which should be ignored. An unbalanced data set can lead to random or chance classification results.^{82,83} The set should include the target analyte(s), expected potential interferences, and expected mixtures. If the analytical environment is well characterized and unlikely to change, then the data set can be precisely designed. If unknown potential interferences could be encountered, as in a field environment, then the data set should include a wide variety of vapors representing all the types of vapor properties that might be encountered. An understanding of vapor solubility properties, as discussed in the section on solvation parameters above, can be useful in selecting such a set of vapors.

After the training set is collected, statistical pattern recognition techniques can be used to narrow down the number of coatings to be used in the array. The correlation matrix will reveal sensors that are providing redundant information. Dendrograms are useful for grouping coatings according to their similarity to one another, thus revealing which coatings are most dissimilar. Principle components analysis can be used to determine which coatings best span the feature space(see below) defined by all the coatings tested. These techniques provide information which is useful in choosing dissimilar coatings for the array.¹⁴⁻¹⁷ Supervised learning techniques are also useful in selecting the final set of coatings for which an algorithm can be developed to correctly classify the target analyte(s).^{14,15} The latter techniques are not completely automated. A knowledgeable scientist directs the process, analyzes intermediate results, and makes decisions along the way. Finally, the algorithm is refined and completed.

Clearly, the rigorous approach requires a lot of resources. This is why it is important to have a rational scientific understanding of coating materials and sensor arrays in order to streamline the process. A random approach would clearly be wasteful, and may not produce satisfactory results.

When vapor mixtures are involved, it is important to distinguish between two types of problems that can be solved. One is the recognition of the target analyte, usually a hazardous vapor, in the environment.^{14,15} In this case, it is only important to correctly identify the presence of the hazard, regardless of whether it is present singly or in a mixture. It is not important to identify all components in the mixture. If the array detector is to be used to recognize more than one hazard, then a separate algorithm (referred to as a discriminant in pattern recognition terms) is developed for each one. A second type of problem to which sensor arrays and pattern recognition can be applied is multicomponent analysis, i.e. the simultaneous identification of all the components in a mixture.^{17,19,24}

In considering the use of sensor arrays and pattern recognition for the detection and correct classification of hazardous vapors, it is important to understand that these techniques do not operate by checking the observed pattern against a library of vapor signatures. Thus, it is not necessary to have a signature of a potentially interfering vapor stored in memory in order to discriminate against it. Pattern recognition techniques plot out the pattern of responses to a vapor challenge as a point in n-dimensional hyperspace(called feature space), where n is the number of sensors, and each of the n-axes represents the response of the sensor associated with that axis.⁷⁷ Any vapor which is dissimilar to the target analyte (according to the criteria by which the sensors respond to vapors) will be plotted in a different region of feature space than the target analyte. Thus, dissimilar vapors can be successfully discriminated against even if they have not been tested in the training

set. In addition, this method does not require that the calibration curves for all vapors be linear in order to obtain correct classification and discrimination. These are some of the reasons why these techniques can be very valuable in a field environment where unknown potential interferences could occur. These features of pattern recognition techniques also illustrate why it is important to choose sensor coating materials carefully; a diverse set of sensors with strong, selective, and uncorrelated responses will more effectively spread different vapors out in feature space, facilitating discrimination. In addition, it turns out that having independent sensors also adds stability to quantitative analysis.¹⁷

The discussion in this paper has been to use a single sensor technology in the array, namely piezoelectric sorption detectors. This simplifies the hardware required in the packaged detector. However, one might argue that using different sensor technologies is more likely to produce sensors which each provide distinctly different information. This is a valid approach. There is a counter argument, however, which must be considered. If the additional sensor technologies provide information about species which never interact with the sensors for the target analyte, then that information may be superfluous. The analyst should carefully decide on what information is needed, and choose sensors and sensor technologies accordingly. If the sensor for the target analyte is a sorption detector, then the primary concern with regard to interferences is other vapors that may sorb into the sensor coating material. Hence, using other sorption detectors to obtain information about such vapors is logical.

CONCLUDING REMARKS

THIRD ORDER STRATEGIES TO ENHANCE SELECTIVITY

The development of selective coating materials represents the first order approach to selectivity using chemical sensors. Because some species must be detected at trace concentrations when other vapors may be present in the background at much higher concentrations, sensor arrays in combination with pattern recognition are useful as a second order approach to enhancing selectivity, and for gathering more information about the analytical environment. A number of third order approaches can be used with such a sensor system to further enhance selectivity. These focus on how the sample is treated before it reaches the sensor(s). Examples of such strategies include the chemical conversion of analytes to other compounds prior to detection, pre-concentration or selective pre-concentration of analytes prior to detection, chromatographic separation of analytes prior to detection, and the use of selectively permeable membranes or tubing prior to detection. (Of course, these methods can also be used in conjunction with single sensors, in which case they would be second order strategies.)

An excellent example of these strategies has been reported by Kindlund et al. for the selective detection of ppm concentrations of halogenated hydrocarbons in humid air using a silicone oil coated QCM.⁸⁴ These authors used a pre-concentrating stage to collect their gas sample. Thermal desorption resulted in a concentrated vapor pulse in which the water and hydrocarbons were partially separated because of differences in their heats of absorption. By placing a length of teflon coated nylon tubing between the preconcentration stage and the QCM, the pulses due to hydrocarbons and water could be separated. (The teflon was coated on the inside of the tubing; water was retained longer than the hydrocarbons.) Alternatively, the authors found that by using a length of water permeable perfluorinated polymer tubing, the water pulse could be essentially eliminated.

Grate et al. have used a pre-concentrator in combination with a SAW sensor array.^{59,85,86} The main intent was to increase the sensitivity of the detector for detection of organophosphorous compounds at trace levels. Using a small Tenax-packed tube thermally desorbed with a resistive coil, 0.1 mg/m³ concentrations of DMMP in air of various humidities could be easily detected within two minutes. Some improvement in selectivity was also anticipated since water and volatile organics are less effectively retained by the Tenax than the less volatile DMMP. It was found that the water was (apparently) desorbed from the Tenax more rapidly than DMMP, such that two separate pulses reached the sensor array. (The preconcentrator was connected to the sensor array via a short piece

of Teflon tubing; no effort was made to influence this separation by choice of tubing material or length.) The water was detected as a sharp peak almost immediately after thermal desorption was begun. A poly(ethylenimine) coated sensor gave a large signal for this water pulse. The fluoropolyol-coated sensor intended primarily for organophosphorous vapors also detected this water pulse with a much smaller response. The subsequent DMMP pulse was detected by the fluoropolyol-coated sensor as a broader, more intense peak after the water peak. Thus, water was eliminated as a factor in detecting the DMMP at trace concentrations.

OTHER INTERACTIONS AND MATERIALS FOR SELECTIVE SORPTION

The focus of this article has been on materials and interactions that can be used to selectively detect organic vapors, with an emphasis on reversible detection via solubility interactions. Complexation of analytes by hydrogen bonding has been considered in detail. A strategy for sensor array design follows quite logically from this treatment. Before concluding, it is worthwhile to point out other interactions and materials which can be used on piezoelectric chemical sensors. Although some of these interactions may be less reversible or less sensitive than those above, or are used primarily in detecting inorganic gases, they are included here to illustrate alternative mechanisms for selectivity.

In addition to hydrogen bonding, other complexation mechanisms which can be useful include coordination to metal ions, Lewis acid Lewis base interactions, and charge transfer interactions. The potential use of coordination interactions has been discussed by Nieuwenhuizen, et al.^{11,12} Zellers, et al. have reported SAW sensors which detect select olefins by coordination to Pt complexes.⁸⁷ These sensors were not reversible, but they could be readily regenerated. Charge transfer interactions have been utilized by many groups to detect NO₂ using phthalocyanines.⁸⁸ The NO₂ is a strong oxidant and accepts an electron from the phthalocyanine. Halogens can be detected similarly. Lewis acid Lewis base interactions have been utilized in the detection of SO₂, which is a Lewis acid, using basic amines.⁴ NO₂ was a significant interference, which is logical since it is also a Lewis acid.

A special case of complexation of potential use in sensors involves cage or inclusion compounds. Materials such as cyclodextrins⁸⁹ and calixarenes⁹⁰ will complex hydrophobic compounds of appropriate size within their hydrophobic cavities. The cavity provides a site where solubility interactions occur in a particular steric arrangement. An example involving a sorption process is a recent report describing the separation of enantiomers using a GLC stationary phase which contained a chiral cyclodextrin mixed with a silicone oil.⁹¹ Modified cyclodextrins have also been applied to QCM devices for the detection of benzene.⁹² (Toluene was the most significant interference of those tested.)

Oligomers and polymers, as presented above, are a logical choice for the sorption of organic vapors, and can also be useful in detecting inorganic gases and vapors. Although only pure materials were discussed, blends of materials could be used to achieve the desired properties. For example, polyvinylpyrrolidone(PVP) produces sensors which respond to water,^{14,15} but it is a glassy material. PVP can be plasticized using poly(ethylene glycol)(PEG),^{70,93} and such a blend would likely make a useful moisture sensor. This approach utilizes a blend to modify the physical properties of a polymer

which has desirable chemical properties. Since PEG is also hydrophilic, its inclusion in the blend does not substantially compromise the chemical properties of the PVP. (However, terminal OH groups on the PEG will associate with amide groups of the PVP.)

Conversely, a polymer with the correct physical properties and innocuous chemical properties can be blended with a material which has the correct chemical properties, as was done with the cyclodextrins in silicone oil noted above.

Ion-containing polymers can also be considered. Such polymers could interact with analytes by ion/dipole interactions and/or ion/induced-dipole interactions. In addition, many oxygen containing anions such as sulfonate or phosphate are particularly strong hydrogen bond acceptors (hence the hydrophilicity of Nafion).

Porous adsorbent solids represent another alternative. Bare SAW sensors are sufficiently sensitive to detect adsorption of molecules on their surface.⁹⁴ This does not make a very sensitive or selective chemical sensor, and so coating materials are virtually always used to enhance sensitivity and selectivity. Application of a porous solid layer increases the surface area, and hence the sensitivity. In one case, ZnO served as both the piezoelectric material and the chemically selective material.⁹⁵ More recently, zeolites have been immobilized on SAW surfaces, and selectivity for small molecules is reported.⁹⁶ Since bulk absorption into organic materials tends to increase with the molecular size of the solute due to increased dispersion interactions, a sensor which is selective for small molecules could clearly provide unique information when included in an array.

Finally, the implications of absorption vs. interfacial adsorption need to be addressed. Although initially controversial, such effects have now been investigated extensively in GLC.⁹⁷ Interfacial adsorption can occur at the gas/liquid interface, the liquid/solid interface, and if some of the solid is not covered by the liquid, the gas/solid interface. Interfacial adsorption at the gas/liquid interface always occurs as part of a sorption process. Thus in the absorption of a vapor into an absorbent polymer, molecules are first adsorbed from the gas phase to the polymer/gas interface, and go on to dissolve in the bulk of the polymer (be absorbed). At equilibrium, the amount absorbed normally greatly exceeds the amount left adsorbed, and the amount adsorbed can be ignored. The cases where interfacial adsorption are most likely to become significant are the sorption of non-polar vapors on thin films of polar phases, or possibly the sorption of polar vapors on thin films of non-polar phases. It should be noted that these trends are the opposite of those seen in bulk absorption. Should sensor technologies lead to the use of thinner and thinner films of the selective material, the ratio of surface area to bulk will increase. The importance of interfacial adsorption will increase, and there is a potential for reduction in selectivity.

APPLICATIONS TO OTHER SENSORS AND TECHNOLOGIES

The phenomenon of sorption is inherent to the great majority of chemical sensors for gases and vapors. Indeed, if a chemical sensor is defined as consisting of a physical transducer and a chemically selective layer,⁹⁸ then sorption of the analyte by the selective layer is the first step in obtaining a signal. Although this definition is not intended to be exclusive, it is a useful one since it illustrates the design approach normally used to create a chemical sensor. Piezoelectric sorption detectors epitomize this definition. A firm understanding of sorption processes provides detailed guidance in the design and choice of selective layers for sensors and arrays.

The same principles can be applied to vapor sensor design using a variety of other physical transducers, or to the interpretation of their behavior. The generation of a signal can be analyzed in terms of two conceptual steps, the first of which is sorption. In the second (conceptual) step, the sorbed vapor influences some physical property of the film material which results in a change in the signal from the transducer. Piezoelectric sorption detectors respond to changes in mass.

The suspended gate CHEMFET, a vapor sensor investigated by Janata et al., is amenable to this type of two step analysis.^{99,100} In order to be detected, a vapor must be sorbed and cause a change in work function. Using electropolymerized polypyrrole as the chemically selective layer, these authors prepared sensors which responded well to hydrogen bonding vapors such as water or alcohols, but were insensitive to hydrocarbons. Since polypyrrole is an excellent hydrogen bond base, hydrogen bond acids such as those detected are certain to be effectively sorbed, thus satisfying the first requirement. The sensors' responses indicate that the second requirement is also met. The direction of the responses provide evidence that the electrons in the layer are held more tightly when alcohol is sorbed, or that hydrogen bonding is occurring, or both. The slope of the response as a function of gas phase alcohol concentration indicates that either a bulk effect is occurring, or that the adsorption isotherm is logarithmic in the experimental concentration range.²⁷ This analysis illustrates how considerations of sorption mechanisms and solubility interactions are fundamental to the understanding of sensor responses, even when the transduction mechanism does not directly measure the mass of the sorbed vapor.

In a deliberate effort to tailor selectivity via the sorption characteristics of the chemically selective layer, Grate et al. have prepared chemiresistors for organophosphorous detection where the selective layer consists of a blend of fluoropolyol and phthalocyanines.¹⁰¹ The fluoropolyol serves to promote organophosphorous sorption, while the phthalocyanines carry the current which is altered by vapor sorption. An

examination of selectivity patterns showed that the primary determinant of selectivity was the strength of sorption into fluoropolyol.

Finally, we wish to point out that sorption and solubility interactions are important in a variety of technologies in addition to sensors, including chromatographic separations, extractions, permselective membranes, development of impermeable barriers, and paints and coatings. Moreover, the non-covalent interactions (so-called long range forces) which we have discussed are central to many areas of chemistry and biochemistry, especially in the field of molecular recognition. The methods we have presented serve to elucidate the roles of these fundamental interactions, and to simplify otherwise complicated relationships. Our systematic application of solubility concepts to sensor coating materials allows selectivity in chemical sensors to be rationalized and understood in terms of the same concepts which are applied in a variety of other scientific disciplines.

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LITERATURE CITED

1. King, W.H. *Anal. Chem.* 1964, 36, 1735-1739.
2. Alder, J.F.; McCallum, J.J. *Analyst (London)* 1983, 108, 1169-1189.
3. McCallum, J.J. *Analyst (London)* 1989, 114, 1173-1189.
4. Guilbault, G.G.; Jordan, J.M. *CRC Critical Reviews in Analytical Chemistry*, 1988, 19(1), 1-28.
5. Mierzwinski, A.; Witkiewicz, Z. *Environmental Pollution*, 1989, 57, 181-198.
6. Wohltjen, H.; Dessy, R.E. *Anal. Chem.* 1979, 51, 1458-1475.
7. Wohltjen, H. *Sens. Actuators* 1984, 5, 307-325.
8. Ballantine, D.S., Jr.; Wohltjen, H. *Anal. Chem.* 1989, 61, 704A-617A.
9. Bastians, G.J. *Chemical Sensors*, Edmonds, T.E. Ed.; Blackie: Glasgow and London, 1988, 295-319.
10. Venema, A.; Nieuwkoop, E.; Vellekoop, M.J.; Nieuwenhuizen, M.S.; Barendsz, A.W. *Sens. Actuators* 1986, 10, 47-64.
11. Nieuwenhuizen, M.S.; Barendsz, A.W. *Sens. Actuators* 1987, 11, 45-62.
12. Nieuwenhuizen, M.S.; Venema, A. *Sensors and Materials* 1989, 5, 261-300.
13. D'Amico, A.; Verona, E. *Sens. Actuators* 1989, 17, 55-66.
14. Ballantine, D.S., Jr.; Rose, S.L.; Grate, J.W.; Wohltjen, H. *Anal. Chem.* 1986, 58, 3058-3066.
15. Rose-Pehrsson, S.L.; Grate, J.W.; Ballantine, D.S., Jr.; Jurs, P.C. *Anal. Chem.* 1988, 60, 2801-2811.

16. Carey, W.P.; Beebe, K.R.; Kowalski, B.R.; Illman, D.L.; Hirschfeld, T. *Anal. Chem.* **1986**, *58*, 149-153.
17. Carey, W.P.; Kowalski, B.R., *Anal. Chem.* **1986**, *58*, 3077-3084.
18. Carey, W.P.; Beebe, K.R.; Sanchez, E.; Geladi, P.; Kowalski, B.R.; *Sens. Actuators* **1986**, *9*, 223-234.
19. Carey, W.P.; Beebe, K.R.; Kowalski, B.R. *Anal. Chem.* **1987**, *59*, 1529-1534.
20. Stetter, J.; Jurs, J.P.; Rose, S.L. *Anal. Chem.* **1986**, *58*, 860-866.
21. Abe, H.; Yoshimura, T.; Kanaya, S.; Takahashi, Y.; Mmiyashita, Y.; Sasaki, S. *Anal. Chim. Acta* **1987**, *194*, 1-9.
22. Abe, H.; Kanaya, S.; Takahashi, Y.; Sasaki, S. *Anal. Chim. Acta* **1988**, *215*, 155-168.
23. Ema, K.; Yokoyama, M.; Nakamoto, T.; Moriizumi, T. *Sens. Actuators* **1989**, *18*, 2912-296.
24. Otto, M.; Thomas, J.D.R. *Anal. Chem.* **1985**, *57*, 2647-2651.
25. Muller, R.; Lang, E. *Sens. Actuators* **1986**, *9*, 39-48.
26. Janata, J. *Sens. Actuators* **1987**, *12*, 121-128.
27. Janata, J. *Principles of Chemical Sensors*, Plenum Press: New York, **1989**.
28. Chuang, C.T.; White, R.M.; Bernstein, J.J., *IEEE Electron. Device Lett* **1982**, *EDL-3*, 145-148.
29. White, R.M.; Wicher, P.J.; Wenzel, S.W.; Zellers, E.T. *IEEE Trans. Ultrason., Ferroelectrics, Freq. Contr.* **1987**, *UFFC-34*, 162-171.
30. Wenzel, S.W.; White, R.M. *IEEE Trans. Electron Devices* **1988**, *35*, 735-743.

31. Wenzel, S.W.; White, R.M. *Appl. Phys. Lett.* 1989, 54, 1976-1978.
32. Ricco, A.J.; Martin, S.J. *Appl. Phys. Lett.* 1987, 50, 1474-1476.
33. Martin, S.J.; Ricco, A.J.; Niemczyk, T.M.; Frye, G.C. *Sens. Actuators* 1989, 20, 253-268.
34. Ullevig, D.M.; Evans, J.F.; Albrecht, M.G. *Anal. Chem.* 1982, 54, 2341-2343.
35. Kamlet, M.J.; Doherty, R.M.; Abboud, J.-L.M.; Abraham, M.H.; Taft, R.W. *CHEMTECH* 1986, 16, 566-576.
36. Abraham, M.H.; Doherty, R.M.; Kamlet, M.J.; Taft, R.W. *Chem. Br.* 1986, 22, 551-554.
37. Hansen, C.M. *J. Paint Technol.* 1967, 39, 104.
38. Schoenmakers, P.J. *Optimization of Chromatographic Selectivity*; Elsevier: New York, 1986.
39. Wold, S.; Andersson, K. *J. Chromatogr.* 1973, 80, 43.
40. Chastrette, M. *J. Chromatogr. Sci.* 1976, 14, 357.
41. Janghorbani, M.; Freund, H. *Anal. Chem.* 1973, 45, 325-332.
42. Edmunds, T.E.; West, T.S. *Anal. Chim. Acta* 1980, 117, 147-157.
43. McCallum, J.J.; Fielden, P.R.; Volkan, M.; Alder, J.F. *Anal. Chim. Acta* 1984, 162, 75-83.
44. Grate, J.W.; Snow, A.; Ballantine, D.S., Jr.; Wohltjen, H.; Abraham, M.H.; McGill, R.A.; Sasson, P. *Anal. Chem.* 1988, 60, 869-875.

45. Kamlet, M.J.; Abboud, J.M.; Abraham, M.H.; Taft, R.W. *J. Org. Chem.* 1983, 48, 2877
46. Abraham, M.H.; Duce, P.P.; Grellier, P.L.; Prior, D.V.; Morris, J.J.; Taylor, P.J. *Tetrahedron Letters* 1988, 29, 1587.
47. Abraham, M.H.; Grellier, P.L.; Prior, D.V.; Duce, P.P.; Morris, J.J.; Taylor, P.J. *J. Chem. Soc., Perkin Trans. 2* 1989, 699.
48. Abraham, M.H.; Grellier, P.L.; Prior, D.V.; Morris, J.J.; Taylor, P.J.; Lawrence, C.; Berthelot, M. *Tetrahedron Letters* 1989, 30, 2571.
49. Abraham, M.H.; Grellier, P.L.; Prior, D.V.; Morris, J.J.; Taylor, P.J. *J. Chem. Soc., Perkin Trans. 2* 1990 in press.
50. Abraham, M.H.; Grellier, P.L.; McGill, R.A.; *J. Chem. Soc., Perkin Trans. 1* 1987, 767-803.
51. Abraham, M.H.; Whiting, G.S.; Doherty, R.M.; Shuely, W.J. *J. Chem. Soc., Perkin Trans. 2*, submitted.
52. Kamlet, M.H.; Doherty, R.M.; Abraham, M.H.; Taft, R.W. *Quant. Struct. -Act. Relat.* 1988, 7, 71.
53. Abraham, M.H.; Grellier, P.L.; Hamerton, I.; McGill, R.A.; Prior, D.V.; Whiting, G.S. *Faraday Discuss. Chem. Soc.* 1988, 85, 107.
54. Abraham, M.H.; Grellier, P.L.; McGill, R.A.; Doherty, R.M.; Kamlet, M.H.; Hall, T.M.; Taft, R.W.; Carr, P.W.; Koros, W.J. *Polymer* 1987, 28, 1363-1369.
55. Abraham, M.H.; Whiting, G.S.; Doherty, R.M.; Shuely, W.J. *J. Chem. Soc., Perkin Trans. 2*, submitted.
56. Abraham, M.H.; Whiting, G.S.; Doherty, R.M.; Shuely, W.J. *J. Chromatogr.* to be submitted.

57. This is a preliminary equation, Abraham, M.H.; Grate, J.W., et al.
58. Abraham, M.H.; Fuchs, R. *J. Chem. Soc., Perkin Trans. 2* 1988, 523.
59. Grate, J.W., presented at the 198th National Meeting of the American Chemical Society, Miami Beach, FL, 10-15 September 1989.
60. Abraham, M.H.; Hamerton, I.; Rose, J.B.; Grate, J.W., in preparation.
61. Rodgers, C.E. In *Polymer Permeability*; Comyn, J., Ed.; Elsevier: New York, 1985; pp 29-34.
62. Guillet, J.E. *Advan. Anal. Chem. Instrument.* 1973, 11, 187-235.
63. Jacques, C.H.M.; Hobfenberg, H.B.; *Polym. Eng. Sci.* 1974, 14, 441-448.
64. Hobfenberg, H.B.; Stanuet, V. in *The Physics of Glassy Polymers*; Hayward, R.N., Ed.; Applied Science Publishers Ltd: London, 1973; pp 504-546.
65. Grate, J.W. *Proceedings of the Third Meeting of the Joint Services Technical Working Group for Chemical and Biological (CB) Mini-Microsensors*; Silvestri, A., Katzoff, L., Eds.; U.S. Army Chemical Research, Development and Engineering Center, Aberdeen Proving Ground, MD, 1988; pp 29-32.
66. Fog, H.M.; Reitz, B. *Anal. Chem.* 1985, 57, 2634.
67. See the scaled partical theory calculations of Abraham, M.H.; Nasehzadeh, A. *J. Chem. Soc., Faraday Trans. 1* 1981 77, 321-340.
68. Brady, J.E.; Bjorkman, D.; Herter, C.D.; Carr, P.W. *Anal Chem.* 1984, 56, 278-283.
69. Adamson, A.W. *A Textbook of Physical Chemistry*, Academic Press: New York, 1973; pp 323-328.
70. Blonsky, P.M.; Clancy, S.; Hardy, L.C.; Harris, C.S.; Spindler, R.; Tonge, J.S.; Shriver, D.F. *CHEMTECH* 1987, 758-762

71. Snow, A.W.; Ballantine, D.S., Jr.; Whitney, T.; Barger, W.R., Jr.; Klusty, M.; Wohltjen, H.; Grate, J.; Chaput, D. *Proceedings of the 1986 U.S. Army Chemical Research, Development and Engineering Center Scientific Conference on Chemical Defense Research*, CRDEC-SP-87008; Rausa, M.D., Ed.; U.S. Army, 1987, pp 695-703.
72. Zeldin, M.; Fife, W. K.; Tian, C.; Xu, J. in *Inorganic and Organometallic Polymers: Macromolecules Containing Silicon, Phosphorus and Other Inorganic Elements*, Zeldin, M.; Wynne, K.J.; Allcock, J.R., Eds.; ACS Symposium Series 360; The American Chemical Society: Washington, D.C. 1988, pp 199-208.
73. Field, D.E. *J. Paint Technol.* 1976, 48, 43.
74. Sprague, L.G.; Snow, A.W.; Soulen, R.L.; Lint, J.; Wohltjen, H.; Ballantine, D.S., Jr.; Grate, J.W. *Proceedings of the 1987 U.S. Army Chemical Research, Development and Engineering Center Scientific Conference on Chemical Defense Research*, CRDEC-SP-88C13; Rausa, M.D., Ed.; U.S. Army, 1988, 2, pp 1241-1251.
75. Chang, Y.; Noriyan, J.; Lloyd, D. R.; Barlow, J. W. *Polym. Eng. Sci.* 1987, 27, 693.
76. Barlow, J. W.; Cassidy, P. E.; Lloyd, D. R.; You, C. J.; Chang, Y.; Wong, P. C.; Noriyan, J. *Polym. Eng. Sci.* 1987, 27, 703.
77. Tou, J. T.; Gonzalez, R. C. *Pattern Recognition Principles*, Addison-Wesley: Reading, MA, 1974.
78. Williams, W. T.; Lance, G. N. *Statistical Methods for Digital Computers*, Enslein, K.; Ralston, A.; Wilif, R., Ed.; Wiley-Interscience: New York, 1975.
79. Stuper, A. J.; Brugger, W. E.; Jurs, P. C. *Computer Assisted Studies of Chemical Structure and Biological Function*, Wiley-Interscience: New York, 1979.
80. Massart, D. L.; Kaufman, L. *The Interpretation of Analytical Chemical Data by the Use of Cluster Analysis*, Wiley: New York, 1983.

81. Ramos, L. S.; Beebe, K. R.; Carey, W.P.; Sanchez, E.; Erickson, B. C.; Wilson, B. E.; Wangen, L. E.; Kowalski, B. R. *Anal. Chem.* **1986**, *58*, 294R-315R.
82. Stouch, T. R.; Jurs, P. C. *J. Chem. Inf. Comput. Sci.* **1985**, *25*, 45.
83. Stouch, T. R.; Jurs, P. C. *J. Chem. Inf. Comput. Sci.* **1985**, *25*, 92.
84. Kindlund, A.; Sundgren, H.; Lundstrom, I. *Sens. Actuators* **1984**, *6*, 1-17.
85. Grate, J.W.; Klusty, M.K.; Rose-Pehrsson, S.L.; Wohltjen, H. presented at the 199th National Meeting of the American Chemical Society, Boston, MA, April 22-27, 1990.
86. Grate et al., paper in preparation
87. Zellers, E. T.; White, R. M.; Rappaport, S. M.; Wenzell, S. W. Proc. 4th Int. Conf. on Solid-State Sensors and Actuators - Transducers '87, Tokyo, 1987, pp 459-461.
88. Snow, A. W.; Barger, W. R. In *Phthalocyanines Principles and Applications*, Lever, A. B. P.; Leznoff, C. C., Eds., in press.
89. Stoddart, R.; Zarycki, R. *Cyclodextrins*; Royal Society of Chemistry: London, **1989**.
90. Gutsche, C.D. *Calixarenes*; Royal Society of Chemistry: London, **1989**.
91. Shurig, V.; Novotny, H.P.; Schmalzing, D. *Angew.Chem. Int. Ed. Engl.* **1989**, *28*, 736-737.
92. Lai, C. S.-I.; Moody, G.J.; Thomas, J. D. R.; Mulligan, D. C.; Stoddart, J. F.; Zarzycki, R. *J. Chem. Soc., Perkin Trans. II* **1988**, 319-324.
93. Spindler, R.; Shriver, D. F. *Macromolecules* **1986**, *19*, 347-350.
94. Martin, S. J.; Ricco, A. J.; Ginley, D. S.; Zipperian, T. E. *IEEE Trans. Ultrason., Ferroelectrics, Freq. Contr.* **1987**, *UFFC-34*, 142-147.

95. Martin, S. J.; Schweizer, K. S.; Ricco, A. J.; Zipperian, T. E. Proc. 3rd Int. Conf. on Solid-State Sensors and Actuators - Transducers '85, Philadelphia, PA, 1985, IEEE Cat. No. CH2127-9/85/0000/0066, pp 71-71.
96. Bein, T.; Brown, K.; Frye, G. C.; Brinker, C. J *J. Am. Chem. Soc.* 1989, 111, 7640-7641.
97. Locke, D.C. in *Advances in Chromatography*; Giddings, J.C.; Grushka, E.; Cazes, J.; Brown, P.R. Eds.; Vol. 14, 1976, pp. 167-173.
98. Janata, J.; Bezegh, A. *Anal. Chem.* 1988, 60, 62R-74R.
99. Josowicz, M.; Janata, J. *Anal. Chem.* 1986, 58, 514-517.
100. Josowicz, M.; Janata, J.; Ashley, K.; Pons, S. *Anal. Chem.* 1987, 59, 253-258.
101. Grate, J. W.; Klusty, M.; Barger, W. R.; Snow, A. W. submitted for publication.