Acoustic Wave Microsensor Arrays for Vapor Sensing

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I. Introduction

The concept of using sensor arrays for chemical analysis gained widespread recognition in the 1980s and has continued vigorously in the 1990s. The advantages that sensor arrays offer over individual sensors are sensitivity to a wider range of analytes, improved selectivity, simultaneous multicomponent analysis, and the capability for analyte recognition rather than mere detection. By analogy with olfaction systems comprising multiple receptors and neuronal pattern recognition, sensor arrays for gas-phase detection are sometimes dubbed "electronic noses".

An analytical instrument with a sensor-array detector and multivariate data analysis can be applied to a host of different detection problems. In this regard, it is similar to other multivariate instruments such as spectrometers or multichannel analyzers. With a sensor array, however, rather than relying on the absorbance of incident radiation or some other inherent feature of a molecule, responses of each sensor (or channel) are related to the interactions between analyte molecules and sensing materials. Understanding those interactions and designing arrays to take advantage of them have been two of the central themes in sensor array development, especially in the field of acoustic wave sensor arrays. The role of fundamental interactions and their relationships to the chemical information encoded in sensor array responses were introduced in the first papers in this field and continue to be explored today.

Dr. Jay W. Grate leads an interdisciplinary research group in chemical microsensors and microfluidics in the Environmental Molecular Sciences Laboratory at the Pacific Northwest National Laboratory. His research integrates aspects of the chemical sciences, material sciences, and measurement sciences into new microanalytical principles, methods, and systems. Development of chemical sensor arrays has focused on the interactions of organic vapors with polymeric sensing materials, rational polymer design, acoustic wave sensors, and multivariate data analysis techniques.

By far, the greatest numbers of chemical sensor array studies have involved acoustic wave sensors and chemiresistor sensors of various types, with notable progress in optical chemical sensor arrays in recent years. (See, for examples, other articles in this special issue.) Acoustic wave sensor arrays for gas-phase chemical sensing will be the focus of this review, with two pimary goals: (1) to comprehensively cite papers on acoustic wave sensor arrays according to the criteria set out below and (2) to review original studies and recent progress in polymer-coated acoustic wave sensor arrays, with emphasis on issues such as interaction mechanisms, chemical diversity, coating selection approaches, array design, and multivariate data analysis.

II. Acoustic Wave Sensor Arrays

This section will cite and group original peer-reviewed research papers on acoustic wave sensor arrays that describe data collected from differently coated sensors and evaluation with multivariate data analysis techniques. Research papers are distinguished from reviews, topical articles, and conference proceedings papers, which are cited later in the review where appropriate. In general, however, conference papers are not considered. As a practical matter, this limits the number of papers to

Table 1. Research Papers Describing Acoustic Wave Sensor Arrays with Multivariate Data Analysis

subset	refs
arrays based on surface acoustic wave sensors	3−25
arrays based on thickness shear mode sensors	26−62
arrays for sensory applications	10, 30, 31, 33−35, 38−42, 46−52, 61
arrays in conference proceedings published in *Sensors and Actuators*	63−78

a manageable number while maintaining quality. As noted by Janata, proceedings papers are not subject to the same rigor of peer review as original research papers in archival journals and are often duplicative.[1]

The initial literature search was set up using boolean logic to include *sensor* and *array* and several terms for acoustic wave sensors (*acoustic wave or microbalance or piezoelectric or SAW or QCM or TSM or BAW*). Chemical Abstracts (file CAPLUS) was searched using STN International; sensor and array were linked in the same information unit in this search. A similar search was performed on INSPEC (the database for physics, electronics, and computing) using DIALOG, with no special linking between the sensor and array terms. The search in INSPEC was further limited to (*chemical or vapor or gas*). The INSPEC search yielded only a few relevant papers in addition to those found in Chemical Abstracts. However, it was useful in distinguishing between journal papers and conference papers published in *Sensors and Actuators*.

Some studies known to the author were not retrieved by these searches. The word array was not a keyword for some papers using sensors and pattern recognition. Additional searches in Chemical Abstracts expanding array to (*array or pattern or neural*) recovered a few additional relevant references. It was also noted that *quartz-resonator* is another designation for acoustic wave sensors based on TSM devices. Several additional references were found in searches incorporating this term.

Research papers in peer-reviewed journals on acoustic wave sensor arrays with multivariate data analysis are cited in the first three groups of Table 1. Several papers on acoustic wave sensor arrays published in *Sensors and Actuators* volumes covering conferences were recovered in the searches above, and these are listed in the last group of Table 1.[2] The peer-reviewed research papers are divided into two groups based on sensor type. Surface acoustic wave (SAW) devices form the first group, and thickness shear mode (TSM) devices, also known popularly as quartz crystal microbalance (QCM), form the second group. Papers from either of these categories that describe arrays for sensory applications are collected in a third grouping.

The distribution of research papers by year and journal are shown in Figure 1, using the citations in the first and second groups from Table 1. Journals with at least five papers are shown individually. Papers from all other journals are grouped in
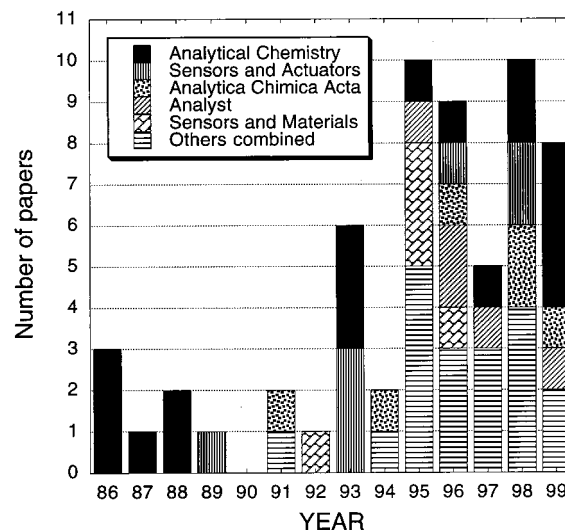

Figure 1. Plot showing the number of peer-reviewed research papers by year describing acoustic wave sensor arrays with multivariate data analysis at the time of the writing of this review. Journals with at least five papers are shown individually and the remaining papers are grouped in "others". Data for 1999 are not for the whole year.

"others". The rate of publication in the acoustic wave sensor array field increased substantially in the mid 1990s. It is evident that *Analytical Chemistry* played a leading role in the publication of acoustic wave sensor array papers beginning in 1986 and continuing today.

The research papers in peer-reviewed journals cited in Table 1 serve as the core set for this review and are the ones referred to whenever pointing back to Table 1. Additional original research papers and review articles not cited in Table 1 will be referenced as they relate to the subjects under discussion. This review will not attempt to cover acoustic wave sensors in particular applications or as electronic noses. However, given the well-defined chemical diversity achievable using acoustic wave sensors, as well as other desirable characteristics such as reversibility, reproducibility, high sensitivity, and tolerance for humid atmospheres, acoustic wave sensors represent a good technology for sensory applications. There are many papers on acoustic wave sensor arrays for odor sensing in Table 1.

After introducing some of the basic concepts related to the operation of acoustic wave sensors, the remainder of this review will address issues related to interaction mechanisms, chemical diversity, coating selection approaches, array design, and multivariate data analysis. These topics will be addressed with emphasis on polymer-coated acoustic wave sensors, which represent the class of sensors where relationships between structure, properties, chemical interactions, chemical diversity, and array performance have been most thoroughly investigated. These issues are relevant to the performance of arrays in many application areas and as "electronic noses". In addition, progress in the field of acoustic wave sensor arrays can inform investigations using other types of sensor arrays, either directly or by analogy.

III. Acoustic Wave Microsensors

A great variety of acoustic wave devices have been developed and demonstrated for chemical sensing applications in the gas and liquid phases. These include TSM devices, SAW devices, Leaky SAW devices, surface transverse wave (STW) devices, Love wave devices, shear-horizontal acoustic plate mode (SH-APM) devices, flexural plate wave (FPW) devices, thin film resonators, and thin rod flexural devices. The TSM device fabricated on quartz is also known by a variety of other names including QCM, bulk acoustic wave (BAW) device, piezoelectric crystal sensor, and quartz-resonator sensor. Except for the thin rod devices, all these consist of a piezoelectric substrate with thin film or interdigitated metal electrodes used to convert electrical energy to mechanical energy in the form of acoustic waves.

There have been many reviews on acoustic wave chemical sensors for gas- and liquid-phase sensing.[79-95] These sensors have also been the subject of at least two books.[96,97] Previous reviews by the present author with various coauthors have covered topics such as acoustic wave device types, operating instrumentation, and the physical mechanisms for their responses;[90-94] the applications of linear solvation energy relationships to chemical sensors and arrays;[95,98,99] glass transition behaviors;[92] and early studies in acoustic wave biosensors.[94] Many topics were covered in a book chapter on acoustic wave sensors with 280 references.[93] However, none of these articles have specifically addressed the literature on acoustic wave sensor arrays as defined in the previous section.

Thus far, array-based vapor sensing with acoustic wave devices has been confined primarily to the use of TSM and SAW devices, although work on arrays based on FPW devices is in progress.[100,101] TSM and SAW sensors are shown schematically in Figure 2.
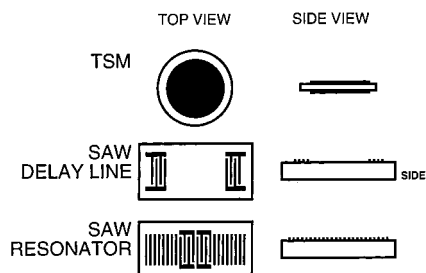
Figure 2. Schematic diagram of TSM, SAW delay line, and SAW resonator devices in top and side views.

TSM sensors typically consist of a quartz plate with thin film metal electrodes on each surface. The device generates transverse waves that travel unguided through the bulk of the crystal in a direction normal to the crystal surfaces. This produces surface particle displacements that are parallel (in-the-plane) to the surface. Transverse waves with surface-parallel particle displacements are often referred to as shear horizontal, or SH.

Interdigital transducers (IDTs) on SAW sensors are used to generate transverse waves guided by the surface of the device and travelling parallel to that surface. The IDTs on SAW devices can be fabricated

Table 2. A Scheme for Classifying Acoustic Wave Devices

wave-guiding mechanism	particle displacement direction of transverse component	
	surface normal[a]	surface parallel
bulk		TSM
surface	SAW	STW, Leaky SAW,[b] Love wave
plate	FPW	SH-APM

[a] A component of the transverse wave displacements is surface normal. [b] The surface parallel component is dominant in Leaky SAW devices only for certain ranges of crystal cuts.
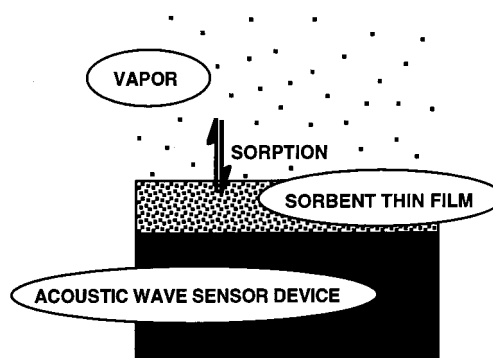
Figure 3. Schematic diagram of the sorption of vapor molecules from the gas phase into a sorbent thin film on a sensor device.

in delay line or resonator[102-104] configurations on a variety of piezoelectric substrates. ST-cut quartz is the typical substrate, and the waves generated are Rayleigh waves. These have one component of particle displacement that is normal to the surface, in contrast to the TSM device.

A useful method for classifying the various acoustic wave devices is according to the waveguiding mechanism and the surface particle displacements of the transverse component of wave motion.[94] Table 2 presents such a scheme, with TSM sensors classified as generating bulk waves with surface parallel displacements, while the typical Rayleigh wave SAW device generates a surface wave with a surface normal component to the particle displacements. Surface wave devices with surface parallel displacements include the Leaky SAW, STW, and Love wave devices. The table also notes the FPW and SH-APM devices, where plate waves are guided by multiple surfaces of a finite solid. The various acoustic wave devices have been described and contrasted in detail previously.[90,93,94]

The key feature of these acoustic wave devices for purposes of gas-phase sensing is that measurable acoustic wave characteristics are altered upon sorption of an analyte onto the surface of the device or an applied layer (adsorption), or into the bulk of an applied thin film (absorption). Thus, the sensor response consists of a sorption step, involving phase transfer equilibria and kinetics, and a transduction step, leading to an analytical signal. The absorption of vapor molecules from the gas phase into a sorbent thin film on a sensor device is shown schematically in Figure 3. The rapid reversible response of a polymer-coated SAW device as a result of vapor absorption is shown in Figure 4.[105]
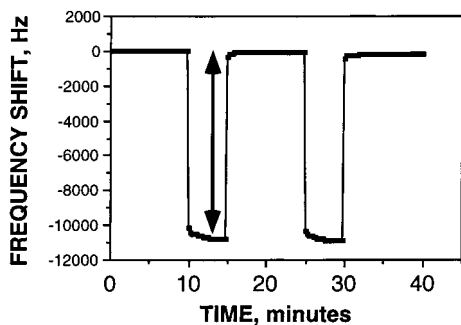
Figure 4. The response of a polymer-coated 158 MHz SAW device to two exposures to an organic vapor showing very fast response, reversibility, and reproducibility. The double headed arrow indicates the response, Δf_v. Figure adapted from ref 105.
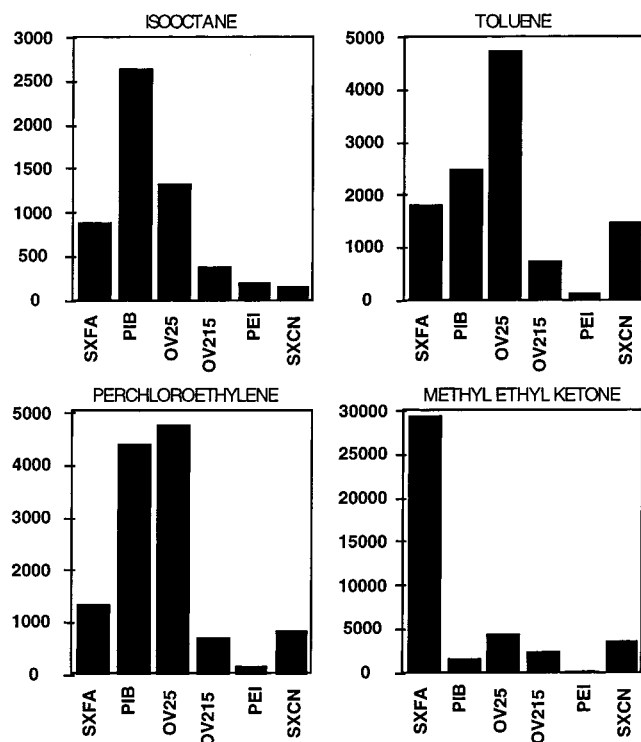

Figure 5. Bar graphs depicting different patterns to different vapors as detected by a six SAW sensor array. Polymers are depicted in Figure 8.

The critical feature with regard to array-based sensing is that the sorption of a vapor varies with the structure and properties of the applied chemical coating. Therefore, an array of several devices with different coatings can produce several responses of different magnitude upon exposure to a particular vapor, leading to a pattern. The same set of coated devices exposed to a different vapor produces another pattern. Patterns for an array of six SAW sensors in response to four different vapors are shown in Figure

5. Judicious selection of coatings leads to patterns for different vapors that can be distinguished from one another, providing a basis for selectivity and classification. Sensor materials, their use in arrays, and materials selection are discussed below.

The transduction mechanism by which the analyte interaction leads to a signal has been the subject of considerable past research. The signal measured is usually proportional to the wave velocity, and it is well-established that wave velocity decreases in response to added mass on the surface. In most studies changes in wave velocity are determined by changes in the frequency of an oscillator circuit; hence, the response is called a frequency shift. It is also possible to measure wave attenuation or to determine both wave velocity and attenuation simultaneously. Measurement methods have been described in the reviews noted above.

The sensitivity of the wave velocity to added mass formed the basis for the original acoustic wave vapor sensors[106] and was the prevailing paradigm for many years. Investigations of polymer-coated TSM and SAW devices, however, ultimately revealed that polymer viscoelastic properties can play a significant role in sensor responses under certain circumstances. Several approaches have been used in these investigations, including simultaneous measurements of velocity and attenuation, impedance analysis, independent measurements of vapor sorption or added mass, and comparisons of the responses of TSM and SAW devices.[107-115] A scheme summarizing current understanding is shown in Table 3.

A thin film on a TSM device whose entire thickness moves synchronously with the surface particle displacement is defined as acoustically thin; physically, this condition is met when the film is very thin compared to the acoustic wavelength and the modulus of the film material is not too low (see below).[90,91,93,113-115] In this case, the signal will be proportional to the added mass due to vapor sorption. On a SAW device with an acoustically thin film, the signal will include the mass-loading response and may also include a contribution due to modulus decreases in the film due to vapor sorption ("swelling-induced modulus change").[109,110] To a first approximation, the modulus reduction is related to the increase in free volume in the film. The modulus contribution due to vapor sorption is expected to be significant if the initial modulus of the polymer film at the device frequency is high, but may be negligible if the initial modulus is low. Since this modulus contribution to the response is in the same direction as the mass contribution, this serves to amplify the vapor response signal. It appears that the change in modulus is proportional to the vapor concentration,

Table 3. Mass and Modulus Sensitivities of Polymer-Coated TSM and SAW Vapor Sensors

	TSM	SAW
acoustically thin	mass sensor	mass and modulus sensing: modulus contribution due to swelling-induced modulus changes; modulus contribution depends on initial modulus of the material
acoustically thick	mass sensing modified by viscoelastic contributions associated with inertial lag and film resonance	mass sensing modified by viscoelastic contributions associated with inertial lag and film resonance

at least at low vapor concentrations. Linear vapor sorption isotherms then give linear sensor calibration curves even when the response mechanism includes a modulus contribution in addition to the mass contribution.

Changes in the film modulus and viscoelastic effects come into play on both TSM and SAW devices if the film does not move synchronously with the surface particle motions. Such films have been referred to as "acoustically thick", leading to "film resonance effects". Responses under these conditions have been elucidated by Martin and Frye.[113−115] In the film resonance regime, vapor responses can be greater or less than those due to mass-loading, and can even be in the opposite direction from the mass loading response. Film resonance effects are accompanied by significant signal attenuation; variable displacements across the thickness of the film necessarily lead to strain and energy dissipation. Film resonance effects depend on film thickness, material modulus, and device frequency. Film resonance effects can be avoided using well-chosen thin film materials at the thicknesses that are typically used for vapor sensing and are less likely to be encountered in detecting trace vapor concentrations. Film resonance effects are more likely to be seen using thicker films exposed to very high vapor concentrations.

Because acoustic wave devices can be sensitive to polymer modulus, polymer-coated devices can also be used to observe or assign glass transition phenomena,[92,116] and modulus changes associated with the cross-linking of a single molecular monolayer have been observed.[117] Probing polymer viscoelastic properties with acoustic wave devices, especially TSM devices, remains a subject of lively research.[118−125]

Detailed discussion of acoustic wave device transduction mechanisms, however, is not the main subject of this review. In most array studies, the key aspect of sensor responses are that they are reversible, reproducible, and contribute to recognizable patterns at concentrations of interest.

IV. Early Array Studies

The first investigations of acoustic wave sensor arrays were reported by a group at the University of Washington (UW) using TSM sensors[26−29] and a group at the Naval Research Laboratory (NRL) using SAW sensors, both series of papers beginning in 1986. These studies introduced a number of issues relevant to array design and chemical information content that remain important for arrays of all types today.

Kowalski and Carey at the UW published a series of four papers, beginning with basic studies on coating selection and finishing with an application study involving analysis of multiple vapors in a drying operation.[26−29] The first paper described the analysis of data from TSM sensors coated with 27 different polymers and stationary phases which were tested against 14 vapors. The authors used principal components analysis (PCA) to reduce the number of coatings to a set of seven. The goal of the approach was to select the coatings so that "they span the space
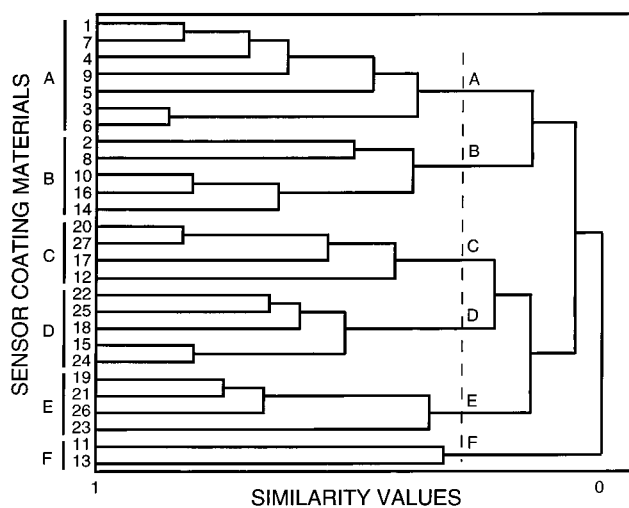

Figure 6. Dendrogram showing hierarchical cluster analysis results for 27 sorbent films tested on TSM devices. Six dissimilar groups of films are indicated with letters. Adapted from ref 26.

of all coatings using the fewest number of individual coatings while retaining analyte discrimination".[26] Sensitivity was not the first criterion for coating selection. It was found that seven principal components accounted for 95% of the variance in the data, and coatings with the best correspondence to each principal component were selected.

These authors also applied a varimax rotation procedure to the principal components to obtain a set of orthogonal vectors that were chemically more descriptive and grouped stationary phases of similar structure. It was noted that each varimax rotated vector must represent a linear combination of fundamental interactions (such as van der Waals interactions, polarity, and Lewis acidity), and that these interactions "can be thought of as being vectors in feature space". The data set was also analyzed using hierarchical cluster analysis, and the results were displayed in a dendrogram that grouped coatings according to how similar their response patterns were across the data set. This dendrogram is shown in Figure 6. In general, the groupings found by this approach could be correlated with the coatings corresponding to particular varimax rotated eigenvectors.

The multivariate analyses used in this study were unsupervised learning techniques that explored how the array data were spread and clustered in feature space. It was recognized that the results of such analyses are dependent on the coatings and analytes in the data set. It is noteworthy that this first paper on acoustic wave sensor arrays with multivariate data analysis[26] directly addressed coating selection and discussed the relationship of various chemical interactions and chemical structures to chemical selectivity and array design. This data set was later reanalyzed with similar results using correspondence analysis, another unsupervised learning technique, which is applied to matrixes where the responses measure an interaction between the rows and columns;[32] the rows and columns are vapors and sensor coatings in this case.

In the next paper in the UW series, quantitative measures of performance were examined as they apply to individual acoustic wave sensors and to sensor arrays.[27] Measures such as sensitivity, selectivity, and limit of determination were defined for sensor arrays using the concept of the "net analyte signal" introduced by Lorber, and discussed in further detail in subsequent papers.[126–128] The net analyte signal is that portion of a response pattern that is unique to the analyte in the particular mixture. Sensitivity is then the net analyte signal divided by the concentration, and selectivity is the net analyte signal divided by the pure analyte signal, for example.

These figures of merit were used to compare sensor arrays designed to maximize chemical information and diversity using the PCA approach with sensor arrays selected solely on the basis of the sensitivites of individual sensors to the test analytes. In addition, the authors compared the case where a seven-sensor array is used to analyze a seven-vapor mixture with the overdetermined case where the seven-sensor array analyzes a three-component mixture. Results were much better for the overdetermined case. In addition, the PCA-selected array provided superior sensitivity and selectivity, and, on average, superior limits of detection. Thus, the diverse array provided better sensitivity than an array selected solely on the basis of individual sensor sensitivities. "The independent nature of the sensors is adding much needed stability for quantitative analysis".[27]

These authors also introduced simulation to the acoustic wave sensor array field, using simulated response vectors with 3% relative noise added. This noise model was based on the experimental observation that the sensors exhibited noise that was proportional to the magnitude of the response.

In the third paper in the UW series, multiple linear regression (MLR) and partial least squares (PLS) methods were compared in the analysis of two- or three-component mixtures with a nine-sensor array.[28] The nine coatings were selected from a set of 31 using the PCA method. MLR and PLS are two inverse least squares (ILS) methods.[129] PLS is much better suited to handling arrays where partial collinearity exists and performed better in all tests. In PLS, orthogonal latent variables are derived from the array responses, and those latent variables describing the greatest portion of the covariance are selected for quantitative analysis. Thus, two-component mixtures were analyzed using only two latent variables from the nine-sensor array. In this method, other latent variables that describe less of the covariance are discarded. Inclusion of these latent variables can actually degrade performance because they model noise rather than response. In this way, discarding latent variables filters noise from the array data. Therefore, PLS is advantageous because it is resistant to collinearity and reduces noise. While this eliminates the need for totally selective sensors, it "does not imply that selectivity and sensitivity are unnecessary attributes of an array device".[28] It was also noted that the coefficients in the latent variables are related to the importance of particular sensors in the array, but

this potential approach to coating selection was not explored.

The fourth paper in the UW series described a multicomponent analysis application.[29] The sensor array in the exhaust line of a solvent drying operation was used to profile the evaporation of each solvent and monitor the drying progress. A principal component regression (PCR) method was used for quantification. Like PLS, this ILS method is tolerant of collinearities in the sensor data. PLS was not used because of an issue with calibration samples.

The first investigations of SAW sensor arrays with pattern recognition analysis were published by the NRL group (Wohltjen, Ballantine, Rose-Pehrsson, and Grate) in 1986 and 1988,[3,4] with an additional paper in 1993 describing a self-contained SAW array system with automated sampling and preconcentration.[5] In the first of these papers, 12 coatings on 112 MHz SAW delay lines were tested against 11 vapors.[3] The dataset was investigated with unsupervised learning techniques such as PCA and cluster analysis (dendrograms). Potential relationships between vapor properties and vapor/coating interactions were considered in terms of solvatochromic parameters for the vapors and the chemical structures of the coatings. (It should be noted that the solvatochromic parameters were for the compounds as liquids and should not be confused with free energy related solvation parameters for the compounds as monomeric vapors, to be described below.) It was observed that cluster analysis sorted the vapors into groups consistent with vapor solubility properties. The non-hydrogen-bonding vapors were well separated from hydrogen-bonding vapors, for example.

A smaller array was selected from the original 12 coatings on the basis of considerations of collinearities among the coatings, as determined by MLR; PCA, which showed that 10 coatings accounted for 95% of the variance; and the use of supervised learning techniques to select sensors that were successful in discriminating between two classes of vapors in the data set. In this study, the goal was to discriminate between one class of vapors representing hazards and another class of vapors representing a wide range of potential interferences. Feature selection and classification routines identified a set of four coatings yielding 100% correct classification, and a discriminant function was optimized. Weight vectors for the coatings indicated which were most important in obtaining the desired classification results. It can be seen in the paper that the three most important coatings in the classification arrived at by supervised learning were also the three most dissimilar materials, as indicated by unsupervised cluster analysis. The fourth coating in the set optimized for the specific classification problem could be selected from the remaining cluster in the dendrogram.

In the second SAW sensor array paper, 10 coatings on 158 MHz SAW delay lines were tested against nine vapors and various binary mixtures, including mixtures with water (albeit at low water concentrations).[4] Some of these coatings and all of the vapors were common to those in the first paper. Therefore,

the new response data for the four coatings selected in the first study could be used as a "prediction set" to test whether the discriminant developed in the first data set could accurately classify vapors using data from the second study—data that were not in the training set. It was found that all the single organic vapors were correctly classified. This type of prediction set, using new SAW sensors (even at a different SAW frequency) tested at a different time, represents a rather stringent test for evaluating the usefulness of a pattern recognition algorithm, since it requires reproducibility in both fabrication and response characteristics.

The vapor mixture data were examined to see if the response to a mixture could be modeled as a linear combination of the responses to each vapor individually. In general, this was found to be the case, although exceptions were noted. Vapor mixtures were not all correctly classified using the discriminant previously developed for single vapors, but new training yielded an eight-sensor set that correctly classified all the vapors and mixtures. (The data set from this study was later reanalyzed and used in simulations.[6])

In the final paper in this series, a smart sensor system consisting of a four-SAW sensor array with automated sample preconcentration was described.[5] This was the first example of an acoustic wave sensor array system with on-board preconcentration, and it was found that preconcentration aided in the selectivity of the overall analysis.

The original studies by the UW group and the NRL group illustrate a number of features of sensor array development. Many different coatings were evaluated against many different vapors, and the coatings were selected for small arrays by a variety of methods, including unsupervised and supervised learning techniques. Unsupervised methods were used to examine data spread, orthogonality, and clustering in feature space, while supervised learning techniques were used to optimize the sensor array relative to specific detection problems. In these studies the sensor arrays selected to collect as much chemical information as possible (i.e., most of the variance) or with the most diverse coatings were also best for quantification and classification purposes. The idea that the inclusion of noise in the multivariate analysis should be minimized was introduced in the use of PLS. Overall, the studies indicate that sensors should be selected for the array to obtain as much chemical diversity and information as possible. The approaches used also sought to minimize the numbers of sensors.

V. Rationalizing Sensor Responses in Terms of Vapor/Sorbent Interactions

While the early array studies were effective in demonstrating the power of sensor arrays for selective vapor detection, it was clear that there was a need to better understand the factors that govern sorption of vapors into the sorbent phases on the sensors. These factors govern the selectivities of each sensor and the range of chemical information to be obtained from an array of sensors. Papers from both the UW and NRL groups suggested that the relevant factors would be related to fundamental interactions such as van der Waals interactions, polarity, and hydrogen bonding between the vapor molecules and the sorbent phase. Consequently, efforts were begun to model the sorption of vapors, as indicated by the partition coefficient, K, in terms of parameters related to those interactions.

The partition coefficient quantifies the equilibrium distribution of vapor from the gas phase into a sorbent phase and thus indicates the effect (sorption) of all the interactions between the vapor and the sorbent. The partition coefficient gives the ratio of the concentration of the vapor in the sorbent phase, C_s, to the concentration of the vapor in the gas phase, C_v.

$$K = C_s/C_v \qquad (1)$$

The relevance of this parameter to vapor detection using coated acoustic wave sensors was noted in both TSM sensor studies[130−132] and SAW sensor studies.[133,134] The response of an acoustic wave sensor to the mass of vapor absorbed is related to the partition coefficient, as shown in eq 2.[90,91,134]

$$\Delta f_v = n\Delta f_s C_v K/\rho \qquad (2)$$

The sensor's response to the mass of vapor absorbed, a frequency shift denoted by Δf_v, is dependent on the frequency shift due to the deposition of the film material onto the bare sensor (a measure of the amount of polymer on the sensor surface), Δf_s, the vapor concentration, the partition coefficient, and the density of the sorbent phase, ρ. The multiplier n is equal to 1 for mass-loading responses. If swelling-induced modulus changes increase the responses, then n will be equal to that amplifying factor.

It was proposed in 1988 that the interactions contributing to sorption and the value of the partition coefficient could be modeled with linear solvation energy relationships (LSERs),[134] and this approach was described in detail in 1991.[95] The methodology is based on a set of solvation parameters describing the solubility properties of monomeric compounds. These parameters can be correlated with solubility-dependent phenomena, such as the partition coefficient, by regressing the measured partition coefficients of a series of diverse compounds against the solvation parameters of those compounds by the method of MLR. The resulting LSER equation takes the form of eq 3 for the absorption of vapors.[95,98,135]

$$\log K = c + rR_2 + s\pi_2^H + a\Sigma\alpha_2^H + b\Sigma\beta_2^H + l\log L^{16} \qquad (3)$$

The log of the partition coefficient is expressed as a linear combination of terms related to particular fundamental interactions and solubility properties. The solvation parameters R_2, π_2^H, $\Sigma\alpha_2^H$, $\Sigma\beta_2^H$, and $\log L^{16}$ characterize the solubility properties of the vapor,[135] where R_2 is a calculated excess molar refraction parameter that provides a quantitative indication of polarizable n and p electrons; π_2^H measures the ability of a molecule to stabilize a neighboring charge or dipole; $\Sigma\alpha_2^H$ and $\Sigma\beta_2^H$ measure effective

hydrogen-bond acidity and basicity, respectively; and log L^{16} is the liquid/gas partition coefficient of the solute on hexadecane at 298 K (determined by gas–liquid chromatography). The log L^{16} parameter is a combined measure of exoergic dispersion interactions that increase log L^{16} and the endoergic cost of creating a cavity in hexadecane leading to a decrease in log L^{16}.

The coefficients (*s*, *r*, *a*, *b*, and *l*) are related to the properties of the sorbent polymer that are complementary to the vapor properties and hence characterize the solubility properties of the sorbent material. The *a* and *b* coefficients, being complementary to the vapor hydrogen-bond acidity and basicity, represent the sorbent phase hydrogen-bond basicity and acidity, repectively. The *s* coefficient is related to the sorbent phase dipolarity/polarizability. The *l* coefficient is related to dispersion interactions that tend to increase the *l* coefficient and cavity effects that tend to decrease the *l* coefficient. Larger values of the *l* coefficient indicate that differences between the partition coefficients for a series of homologous vapors will be larger (compared to a material with a smaller value of the *l* coefficient). The *r* coefficient refers to the ability of the phase to interact with solute n and π electron pairs and provides an indication of polarizability. The constant *c* arises from the method of multiple linear regression used to obtain eq 3.

The use of MLR with a particular set of vapor descriptors in the form of the solvation parameters is a biased technique in that it assumes all the variance is accounted for by the interactions associated with those particular descriptors. However, LSERs have been successful in correlating a vast amount of solubility-dependent phenomena, often to the precision of the available data.[135–137] Thus, the case has been made that a set of descriptors of the type given in eq 3 are appropriate for solubility dependent phenomena and that many processes in chemistry and nature are related to solubility dependent phenomena.[136] On the other hand, it is not expected that LSERs will effectively correlate data that are significantly influenced by factors other than solubility interactions.

In the areas of gas-phase sorption and sensor development, partition coefficients and the LSER method have been applied to the characterization of the solubility of gaseous solutes in polymers,[138] partitioning into gas–liquid chromatographic stationary phases,[139–142] adsorption on solid sorbents,[143] characterization of sorbent phases for sensors,[134,140,144,145] estimation of polymer-coated sensor responses,[108] elucidation of sensor transduction mechanisms,[107,109,110,134] investigation of responses of fullerene-coated sensors,[146] and comparisons with cavitand-based sensing materials.[147] It has been further demonstrated that acoustic wave sensor response data can be correlated with solvation parameters to create LSER equations related to sorption, as it is observed using SAW devices coated with sorbent phases.[7]

The terms in the LSER equation can be calculated for particular vapor/polymer pairs in order to deter- mine which interactions are most important in contributing to the partition coefficient and the free energy of the sorption process. When dipolar or hydrogen-bonding interactions can be set up between a vapor and a polymer, they can play a significant role in determining the value of the partition coefficient and the sensitivity of a sensor. However, it is also the case that all vapors interact with all sorbent polymers to varying degrees by the dispersion interaction. Indeed, dispersion interactions are a significant driving force for the sorption of organic vapors by polymers. Consequently, it is established that polymer-coated acoustic wave sensors will never be more than semiselective, and there will always be some collinearity between various polymer-coated sensors in an array.

The form of the LSER equations and their success in correlating vapor sorption by polymers implies that the inherent dimensionality of sorption data is limited to ca. 5 or less. In other words, for the sorption of neutral vapors by amorphous materials, nature provides a limited number of interactions for distinguishing those vapors from one another. However, a number of considerations apply to this conclusion. The constant term not associated with any particular solvation parameter can be variable and significant. The fundamental interactions may not be completely orthogonal; therefore, there could be less than five orthogonal axes in multivariate sorption data. Finally, a sensor response involving sorption may be influenced by other factors that increase the chemical information and thus the number of independent axes in the data. If modulus contributions are vapor dependent (*n* not equal to a constant for a given polymer), this could increase the dimensionality of acoustic wave sensor array data. If the sorption of vapors by a sensing materials is influenced by size or shape, this would also increase the dimensionality of sensor array data. Similarly, inclusion of kinetic data in addition to equilibrium data would add variance and dimensionality not indicated by the LSER formalism.

Nevertheless, the formalism associated with the LSER methodology, providing understanding based on the systematic consideration of vapor sorption in terms of particular interactions, suggests an approach for achieving chemical diversity in an array based on sorbent polymers. This will be described in a subsequent section.

VI. Sensing Materials

A great variety of materials have been employed as layers on the surfaces of acoustic wave devices to modify the sensitivity and selectivity for chemical analytes. Because these devices are indiscriminate in their sensitivity to sorbed mass, an acoustic wave sensor will give responses to most vapors at some concentration, with or without a coating. Without a coating, surface adsorption yields a response. Surface coatings generally enhance the sorption of analytes at the surface. As a result, it is trivial to apply materials to acoustic wave devices and get sensor responses. Materials applied range from conventional chromatographic stationary phases and polymers to

such unusual materials as soot extracts,[148] as well as structured materials such as bullfrog olfactory receptor proteins, dendrimers, and cavitands (see below). There have been several reviews on mechanisms for chemical selectivity or chemically selective layers for various applications.[79−82,84,86,95,149−151]

The key issue with regard to layers for individual sensors is the extent to which the applied material enhances the sensitivity and selectivity of the sensor, while affording reversibility and reproducibility. In the context of arrays, each material must be responsive, reversible, and reproducible, and the set of materials should maximize the collection of relevant chemical information for detecting and discriminating analytes. Each material will ideally provide useful information that is not already supplied by other materials in the array; in other words, different materials will not simply be redundant. At the same time, it must be realized that real materials will not provide responses that are orthogonal to one another. The remainder of this section will survey the types materials used as sensing layers on acoustic wave devices and indicate their use in arrays. Selection of sets of materials for arrays will be described in subsequent sections.

A great variety of amorphous sorbent phases deposited by solvent casting have been investigated and incorporated into arrays. These include gas chromatographic stationary phases and polymers, for example. This was the approach used in the original piezoelectric sorption detector based on TSM devices[106] and in the original acoustic wave sensor array studies for UW and NRL described above. Sorbent materials must be nonvolatile to remain on the sensor as a thin film, and they will ideally allow rapid vapor diffusion throughout the film. Desirable characteristics offered by these materials include rapid response, reversibility, easy processing into adherent thin films on sensor surfaces, and variable selectivity based on chemical structure. Chemical structure influences properties, which then influence sensitivity and selectivity.

In general, research in polymeric sorbent materials has focused on chemical selectivity and diversity, synthesis of materials that are not commercially available, performance and stability as thin films, selections of sets of polymers for arrays, and use of polymer-coated arrays in detection applications.

A glass transition temperature below the operating temperature of the sensor provides consistently rapid diffusion in amorphous polymer films. In experiments with thin films on SAW devices monitored in an oscillator circuit, slow diffusion in glassy polystyrene has been contrasted with rapid diffusion in and through polysiloxane films,[152] which have very low glass transition temperatures. The responses in Figure 4 illustrate rapid response time on a SAW sensor with a poly(vinyl tetradecanal) films, a polymer prepared and used on the basis of its glass transition temperature being below room temperature.[104,105] The response is essentially complete within the 12-s interval between data points. In experiments on SAW devices using an in-phase and quadrature measurement technique for extremely rapid data

collection, Frye has shown response times of less than 200 ms with rubbery polyisobutylene films on a 100 MHz SAW device.[153] Because siloxane linkages in polymers have very high mobility, if not excessively hindered, providing polymers with low glass transition temperatures, several authors have noted and used substituted polysiloxanes as sensor phases.[14,24,43,95]

Because strongly hydrogen bond acidic polymers with low glass transition temperatures for chemical sensing are not commercially available, a number of synthetic efforts have focused on this polymer type.[22,134,144,145,154−157] Recently, Grate and Kaganove prepared a carbosiloxane material for sensing purposes where inorganic oligodimethylsiloxane segments were alternated with organic segments in the chain of the polymer.[155] In this approach, the organic segments offer chemical interactions to modify the selectivity of the material while the siloxane segments are used to obtain desirable physical properties such as the glass transition temperature. Bisphenol-containing polymers (referred to as BSP polymers) were prepared by this technique. This synthesis technique can potentially be used to prepare a great variety of sorbent polymers with tunable chemical and physical properties, with the option of cross-linking the materials via olefinic end groups.[155,158] The bond-forming reaction for these polymerizations is the hydrosilylation reaction, whose use in generating polymers of many architectures and functionalities has been reviewed.[158]

Recently Rapp and co-workers described an approach for cross-linking a great variety of substituted siloxane polymers for use on SAW sensors in an array.[14] Free radical reactions to cross-link the polymers were initated with ultraviolet light and 2,2-diethoxyacetophenone as the photoinitiator. It was found that cross-linking offered sensors with superior stability compared to un-cross-linked polysiloxanes.

McGill and co-workers have described a new vacuum method for deposition of polymer thin films on surfaces based on matrix-assisted pulsed laser evaporation.[159] In this approach, chemically synthesized polymers that might normally be deposited by solvent casting methods can be lifted into the gas phase by gentle methods and deposited on surfaces.

Layers deposited from the gas phase by plasma polymerization have been described in a number of sensing studies[36,37,160,161] and at least two array papers with multivariate data analysis.[36,37] In addition, Ricco and co-workers have described the use of plasma-polymerized and plasma-grafted materials in arrays with pattern recognition.[162] The reactive conditions involved in plasma polymerization generate gas-phase precursors that are incorporated into the growing surface film. A great variety of starting materials can be used, including molecular precursors such as chlorotrifluoroethylene, hexamethyldisiloxanes, and amino acids, as well as sputtered polymers. Because of the reactive nature of the process, it can be difficult to predict the physical and chemical properties of the resulting layers. For example, layers derived from hexamethyldisiloxanes have been reported to be hydrophilic,[163] in contrast

to the hydrophobic precurser and the hydrophobic character of conventional poly(dimethylsiloxane) polymers. Consequently, these layers are potentially challenging for the design of arrays where each layer has well-understood properties contributing to the overall information gathering capability of the array. Nevertheless, they can be successful in the empirical approach.[36,37]

Electrochemical deposition of conducting polymers has been described in one of the array papers in Table 1.[48] Eight films of polypyrrole and its derivatives were evaluated in an odor-sensing application.

Many papers have described the use of lipids as sensing layers. These have been applied by solvent casting and Langmuir−Blodgett deposition, and in some cases they have been blended with polymers. The initial emphasis on these materials was drawn from the importance of lipids in biological olfaction systems.[31,33,102] Many of the references in Table 1 use lipid layers as all or part of the array, especially in sensory applications.[10,31,33,34,41,46,51,57,61,102] The typical lipid provides both hydrophobic sorption sites as well as basic, dipolar, and/or ionic headgroups where polar interactions can occur. Some arrays with lipid coatings have also included polymers and other amorphous sorbents as coatings on some of the sensors. A detailed study of the response stability of coated TSM sensors demonstrated very good results for eight of the lipids tested.[57]

Self-assembled monolayers (SAMs) of many types have been investigated as sensing layers. These have included conventional alkyl SAMs, carboxylate-terminated SAMs, and metal ion complex terminated SAMs.[162,164−170] (SAMs used to anchor cavitands and SAMs of dendrimers have also been investigated; see below). In general, SAMs influence the adsorption of vapors on the surface, and cannot provide the same sorptive capacity as a thin film providing bulk absorption. However, these layers have exhibited many interesting properties, including for example, responses in the opposite direction as mass loading,[164] apparent sorption of vapor multilayers or clusters,[166] and vapor sorption dependencies on the SAM adsorption time and gold surface morphology.[165] In some cases, SAMs have been investigated by simultaneous infrared spectrosopic investigations and acoustic wave sensing.[166,167,171] None of the research papers in peer-reviewed journals cited in Table 1 employ SAMs as the basis for chemical sensing arrays, but they have been discussed for array sensing in topical accounts.[162,168]

Dendrimers represent another type of material for sensing that has been applied as SAMs and as multilayers.[168,172,173] Dendrimers are a type of branching macromolecule which will reversibly sorb vapors by solubility interactions. As monolayers they offer greater sorptive capacity than typical SAMs.[168] The surface of the dendrimer can be prepared with different solubility properties from the bulk (i.e., exo vs endo receptors). However, an acoustic wave sensor will detect vapors sorbed at both sites, so modifying dendrimer surfaces does not necessarily alter the sorption and detection of vapors by the core. In this regard, dendrimers having cores and surfaces with

different properties may be less selective than sorbent materials that represent one or the other of those properties, but not both. So far, the majority of dendrimer work on acoustic wave sensors has employed macromolecules with amido or amino linkages as the bond-forming functionalities in the core. Since these functional groups are all hydrophilic, these layers may be expected to be sensitive to humidity. No research papers employing dendrimer arrays were found for inclusion in Table 1, but the suitability of such materials for use in arrays has been noted in a topical account.[168]

Fullerene molecules have been incorporated into a sensing film by an assembly process that produced multilayers linked in a network fashion.[174] This deposition approach ensured a very stable film with no loss of fullerene due to evaporation. A subsequent study showed that this film had similar sorption characteristics to fullerene powder, except for the influence of amino groups used in the film assembly process.[146,175] In addition, the sorption selectivity was similar to that of nonpolar amorphous polymers, albeit while offering somewhat less sensitivity as a SAW coating.

A number of approaches have been investigated in an attempt to get more selectivity than can be achieved by sorption into amorphous phases. Selectivity based on size and shape would offer significant advantages in chemical detection. Arrays with and without liquid crystal phases were compared in order to assess the ability of the anisotropic liquid crystal materials to contribute to isomeric discrimination based on shape.[8] Inclusion of the liquid crystal materials in the array improved discrimination between various aromatic vapors and their structural isomers. Dickert has described the use of cyclodextrins and calix-resorcinarenes in an array format for recognizing isomers.[60] Even xylene isomers could be distinguished. Ide, Nakamoto, and Moriizumi demonstrated the basis for distinguishing optical isomers using cyclodextrin molecules in 1995.[176] Bodenhofer et al. have described the successful discrimination of optical isomers using polysiloxane stationary phases with chiral amide side chains on TSM sensors.[56]

In addition to the successful use of cavitand molecules in an array-format described by Dickert, there have been many other investigations of cavitands on TSM or SAW devices. (Cavitands include molecules such as cyclodextrins, calixarenes, and resorcinarenes.) Cavitand-coated sensors have been exposed to gas-phase vapors and responses have been observed.[177−189] However, cavitand-coated sensors do not respond solely to molecules with an ideal fit in the cavity. Reponses are observed to a great variety of small molecules, and selectivity patterns are often similar to more common amorphous polymers.[147] These correlations and molecular modeling indicate that solubility interactions—specifically the capacity of the vapor to gain van der Waal interactions on transfer from the monomeric state in the gas phase to the condensed phase of the sensing film—provide the primary driving force for absorption into the film. Sorbed molecules may occupy both intra- and intercavity sites. However, the presence of a preor-
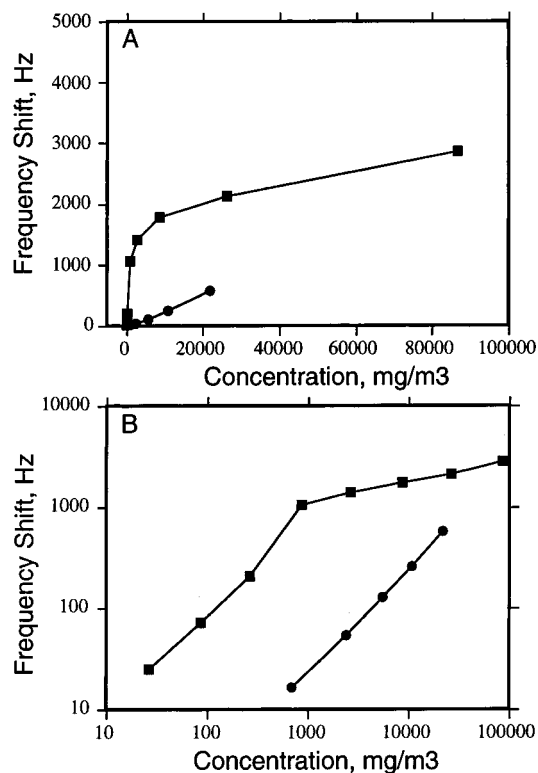
Figure 7. Calibration curves for the response of a TSM device coated with a clathrate forming metal complex, (4-methylpyridine)$_4$(SCN)$_2$Ni (solid squares). Calibration curves for poly(isobutylene), an amorphous polymer, are shown for comparison (solid circles).[190] Responses to toluene are shown in linear and log−log scales. Figure adapted from ref 190.

ganized cavity does offer a significant advantage in terms of sensitivity compared to amorphous polymers. The formation of a cavity to accommodate a dissolved vapor molecule in a polymer entails an energetic cost that need not be paid in order to sorb a molecule in a preorganized cavity. Therefore, cavitand-coated sensors can offer higher sensitivity than polymers, especially if applied to the sensor in multilayers. Issues with regard to the use of cavitands on acoustic wave sensors have been discussed in more detail in a previous review.[93]

Materials that crystallize in phases with channels or cavities containing solvent molecules, i.e., clathrates, can also be used as sensing materials with the advantage of preorganized cavities if the structure is maintained after the solvent molecules evaporate. Finklea, for example, has described sensing films on TSM devices based on clathrate-forming (4-methylpyridine)$_4$(SCN)$_2$Ni complexes.[190,191] These sensors were ca. 100 times more sensitive to small organic vapors at low concentration than poly(isobutylene)-coated TSM devices. This result is illustrated with calibration curves in Figure 7. The nonlinear calibration curve showing "saturation" behavior implies the existence of a fixed number of favorable binding sites. Use of clathrate formers for sensitive vapor detection on TSM devices was first reported by Ehlen et al. in a brief report.[192]

Recently Wu reported results of odor sensing using bullfrog olfactory receptor proteins. Receptor-protein-

coated crystals were more sensitive to caproic acid than either denatured receptor protein or bovine serum albumin used as controls.[61]

One of the array studies reported in Table 1 used metalloporphyrins as the sensing material on TSM devices.[47] The sensitivity and selectivity among vapors with donor atoms (N, O, and or S) varied with the metal substitution. This array was successful in following changes in the headspace composition from fish as the storage time increased.

Reactive layers for acoustic wave sensors have been described by Zellers et al.[193−197] A variety of metal complexes were investigated for their ability to selectively react with and retain olefin vapors. Though not reversible, they can be regenerated. These have not been reported in sensor arrays.

VII. Array Design and Material Selection

Given the very large number of potential sorbent phases for sensors and sensor arrays, some methods are required for selection and classification. As noted above, all the materials in the array must provide sensitivity, rapid reversible responses, and reproducibility. Screening for stability and reproducibility as thin films on sensors represents a prerequisite to selection for a sensor array. Effects of environmental factors such as temperature and humidity have also been noted.[12,75,107,198]

Many approaches exist for selecting sets of materials for a sensor array, and these will be considered here in three categories. Materials may be selected on the basis of diversity in structures and properties, unsupervised learning methods that explore experimental or simulated sensor array data, and methods that evaluate the success of various arrays in performing classification or quantification tasks. Each of these approaches is described below. Frequently, multiple approaches are used in any given study where a subset of candidate coatings is selected for the final array. Several of the papers in Table 1 explicitly describe such downselection of materials for arrays.[3,4,9,11,12,14,19,22,24,26,32,33,35,39,40,42,48,50,58]

A. Diversity in Structure and Properties

Chemical diversity in sensor arrays can be readily achieved by selecting sets of materials having chemical structures that provide a variety of properties and interactions. One approach to obtaining such diversity is to begin by testing a great variety of materials. For example, the early studies described above tested over 10 materials on SAW devices and 27 stationary phases on TSM devices. One study cited in Table 1 described screening tests of 68 materials,[39,50] while another described screening 38 materials.[33] Although this approach may provide sufficient diversity for successful chemical analysis, it does not in itself assure maximum diversity. For example, as stated above, there are no hydrogen bond acidic polymers among commercial gas chromatographic stationary phases. Therefore, selecting from among 100 such phases will not provide an array with the diversity known to be achievable.

Table 4. Interactions, Structures and Materials[a] that Embody Chemical Diversity According to the LSER Approach

interactions and properties	chemical structures, examples, and comments
dispersion interactions	Aliphatic hydrocarbon polymers or substituents. Fluorination will decrease dispersion interactions. Poly(isobutylene) (PIB) and poly(dimethylsiloxane) (PDMS) are useful examples. These are characterized by large l coefficients and are useful for sorbing aliphatic hydrocarbons or for distinguishing between members of a homologous series.
polarizability	Aromatic groups increase polarizability relative to aliphatic groups. Phenyl-containing materials are useful, such as phenyl-substituted poly(siloxanes). Phenyl-substituted materials such as OV-25 (75% phenyl−25% methylpolysiloxane) are very good for sensitivity to chlorinated hydrocarbons and, in combination with aliphatic materials, help to distinguish between various low polarity vapors such as aliphatic hydrocarbons, aromatic hydrocarbons, and chlorinated hydrocarbons.
dipolarity (minimize basicity)	Fluoroalkyl-substituted materials provide modest dipolarity without basicity. Fluoropropyl-substituted poly(siloxanes) such as OV-202 and OV-215 are candidate materials. However, the overall value of these weak sorbent materials in arrays may not be great and will be application dependent.
dipolarity allowing basicity	Nitrile groups are highly dipolar groups with only moderate basicity compared to many other highly dipolar functional groups. Polysiloxanes with cyanopropyl (Silar 10C or SXCN) and cyanoalkyl (OV-275) groups are useful, and poly(ethylene maleate) (PEM) has also been found to have similar properties. These help to distinguish vapors with high dipolarity.
basicity minimizing dipolarity	Aliphatic amines can provide basicity while minimizing dipolarity. In principle, poly-(ethylenimine) (PEI) has secondary and tertiary amines, but typical commercial samples actually also have quaternary amines serving as ionic centers that interact with vapors with dipoles. This polymer has been poorly behaved in various sensor studies. Aminopropyl-substituted poly(siloxanes) are also candidates. Basicity favors interation with hydroxyl-containing vapors such as organic acids and alcohols, and materials such as PEI are strong sorbents for water.
basicity and dipolarity	Many functional groups are both very dipolar and very basic, including amides, urethanes, and sulfoxides. Like other basic materials, these sorb acids, alcohols, and water. Poly(vinyl-pyrolidone) (PVP) for example, is a strong sorbent for water.
hydrogen bond acidity	Fluorinated alcohols and phenols maximize hydrogen bond acidity and minimize basicity, while not having the basicity and self-association of carboxylic acids. Several materials have been synthesized to provide these properties including fluoropolyol (FPOL), a hexafluoro-2-propanol-substituted polysiloxane (SXFA), and fluorinated bisphenol materials (BSP3 and BSP6) (see the text). These materials are useful in detection of basic vapors including organophosphorus compounds.

[a] The structural units of some of these polymers and their abbreviations are given in Figure 8.

A rational approach to obtaining a set of polymers that span all of "coating space" is suggested by the systematic consideration of vapor sorption set out in the LSER approach.[95] The materials in the array should ideally probe all of the available interactions and solubility properties that can be used to distinguish one vapor from another. Thus, the chemical structures and functional groups of the polymers in the array should be varied so that each polymer will emphasize some interaction more than the others. The stronger each such interaction can be set up, the greater will be the spread of the vapors in feature space. Understanding how chemical structures and functionalities lead to particular solubility properties can be used to select materials representing all of the desired properties.

This approach was set out in detail previously, and it was proposed that an array could be designed to gather the maximum chemical information by including materials with the properties indicated in Table 4.[95] The groupings in this table recognize that some properties often occur in combination, such as basicity and dipolarity, when considering real functional groups and materials. This table also briefly indicates the chemical structures that provide these properties and comments on polymeric materials for use as sensor phases. Given the large number of candidate materials available for sensing, there exist many combinations of materials that could span the coating space defined in Table 4.

While structure determines properties and thus can be used to obtain diverse properties, it is also possible to measure those properties and select accordingly. The values of the LSER coefficients provide information about the solubility properties of polymers and, hence, guidance in the selection of polymer to emphasize particular properties and interactions. Fourteen sorbent materials selected to span coating space on the basis of their structures were characterized at 298 K using the LSER method. Structural units for 12 of these polymers are shown in Figure 8. (Two of the original 14 materials were eliminated from consideration due to poor physical properties.) Six polymers were selected for a potential array, and their LSER coefficients are given in Table 5. The table also gives the range of each LSER coefficient over the 12 candidate polymers. This set follows the structure/property scheme in Table 4 and maximizes the range in values of each LSER coefficient with the exception of the r coefficient. All the materials except OV-202 and OV-25 represent an extreme in some property represented by the LSER coefficients. A similar selection could have been made on the basis of structure/property understanding alone, but the LSER approach provides a nice systematic confirmation that such an approach does in fact lead to diversity in properties.

If one begins coating selection based on sorbent properties, a final selection would have to consider whether each of the materials provides reproducible
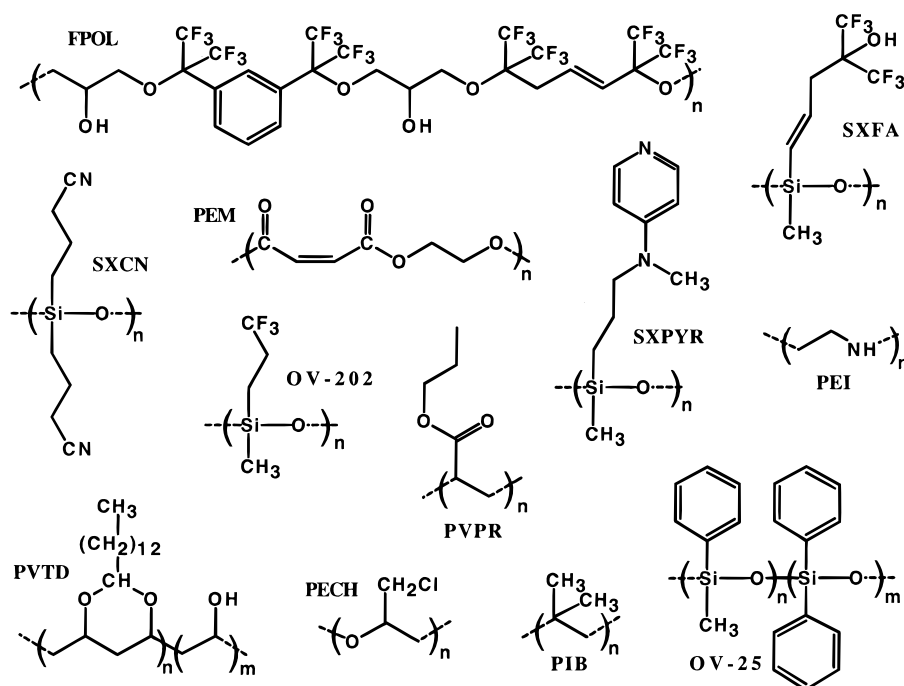
Figure 8. Structural repeat units for 12 polymers characterized by the LSER method. Abbreviations in this figure are used throughout the article. Silar 10C and OV-215 are gas chromatographic stationary phases with the same structures as SXCN and OV-202 in this figure.

Table 5. LSER Coefficients for Selected Polymers

polymer[a]	polarizability (r)	dipolarity/polarizability (s)	basicity (a)	acidity (b)	dispersion/cavity (l)
PIB	−0.077	0.366	0.180	0.000	1.016
OV-25	0.177	1.287	0.556	0.440	0.885
OV-202	−0.480	1.298	0.441	0.705	0.807
PEM	−1.032	2.754	4.226	0.000	0.865
PEI	0.495	1.516	7.018	0.000	0.770
SXFA	−0.417	0.602	0.698	4.250	0.718
Range[b]					
min	−1.03	0.37	0.18	0.00	0.72
max	0.67	2.75	7.02	4.25	1.02

[a] Repeat units for these polymers are shown in Figure 8. [b] Range out of 12 of 14 polymers; two were eliminated due to unsuitable physical properties.

behavior on sensors under dry and humid conditions. The principles of chemical diversity can be used to ensure that a large set of candidate coatings represents a truly diverse set before downselection based on performance as thin films on sensors. A diverse array, once established, could be used in a great variety of applications with training for each application.

Several of the papers in Table 1 have recognized and/or utilized these principles in selecting sets of polymers and stationary phases to obtain chemical diversity in acoustic wave sensor arrays. In some cases these principles help to set up candidate coatings from which further downselection is made. In others they help to set up the array to be tested. Diverse arrays in recent years based primarily on structural and solubility property considerations have been published by Grate, Rapp, Hierlemann, Slater, and Zellers.[11,21,22,43,58] The principles have been recognized throughout Zellers polymer-coated array studies,[7−9,12,17] with LSER models explicitly addressed in one paper[7] and a six-polymer diverse array selected for another.[21]

B. Spread and Clustering of Array Data in Feature Space

Unsupervised learning techniques refer generally to the idea of looking at array data without imposing a desired classification result. In general they look at the variance in the data (typically by PCA) and the clustering of the data (typically by dendrograms) in feature space, using PCA and dendrograms, repectively. In addition, it has been useful to examine measures of the distance between vapor clusters to the scatter in each such cluster (i.e., the ratio of variation within group to variation between different groups). The results obtained by any of these methods may depend on the normalization and scaling procedures used to preprocess the data, as well as the selection of samples included in the analysis, and hence are subject to some interpretation.

PCA was described in connection with the early array studies and continues to be a useful technique in acoustic wave sensor array studies. Approximately 20 of the papers in Table 1 use PCA to examine the spread of vapors in feature space and a number have used PCA as part of a coating selection process.
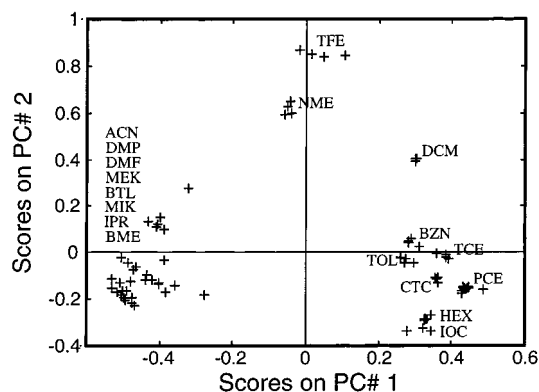
Figure 9. PCA plot for the detection of 18 organic vapors by a diverse set of 11 sorbent polymers.[22] The first principal component discriminates hydrogen bond basic vapors on the left from aliphatic, aromatic, and chlorinated hydrocarbons on the right.[22] Adapted from ref 22.

Table 6. Principal Components Analysis for a Small Diverse Array[a]

PC	variance (%)	PIB	PECH	FPOL	PDPP	OV-25	OV-275
				contribution to each PC[b] (%)			
1	52.9	17.1	0.0	29.9	23.7	25.3	4.0
2	33.6	20.7	43.8	0.2	10.0	7.2	18.0
3	11.5	4.3	13.4	5.6	.08	2.7	73.3
4	1.1	6.9	15.0	10.1	60.5	5.7	1.9
5	0.8	10.6	24.8	4.7	4.1	55.1	0.8

[a] Results from ref 24. [b] Abbreviations correspond to those in Figure 8 and Table 4, except for poly(diphenoxyphosphazene), PDPP.

Figure 9 shows a principal components plot derived from a diverse polymer-coated sensor array. The first principal component discriminates hydrogen bond basic vapors on the left from aliphatic, aromatic, and chlorinated hydrocarbons on the right, a result that can be attributed to the inclusion of strongly hydrogen bond acidic polymers in the array.[22]

Slater and co-workers recently described extensive PCA studies in conjunction with a set of 17 materials deliberately selected or synthesized to provide a chemically diverse coating set.[58] In addition to criteria such as repeatability and stability, these authors used PCA to select coatings for particular sets of vapors, as well as for the design of a general purpose array. Percentage cumulative contributions for particular materials as determined from the first two principal components were used to assess the value of including particular sensors in an array. Results depend on the particular vapors included in a sample set.

Zellers and co-workers recently used PCA as part of an investigation into vapor recognition with small arrays of polymer-coated SAW sensors.[24] They found that 98% of the variance in a data set of six polymers by 16 vapors was captured by the first three principal components, and the percent contribution of each polymer to each principal component was reported. These results are shown in Table 6. Polymers providing the largest cumulative fractional contributions to the first three principal components were also identified. It should be emphasized that selection on the basis of PCA does not guarantee optimal discrimination of particular vapors in the test set,
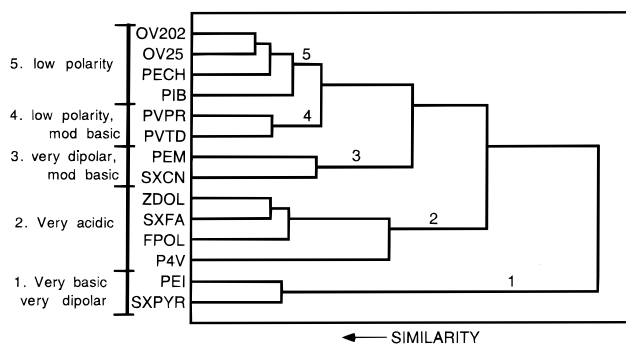

Figure 10. Dendrogram showing cluster analysis of sorbent polymers according to their LSER coefficients.[145] The coating abbreviations correspond to materials in Figure 8, except for P4V and ZDOL, which are not shown. Adapted from ref 145 with permission from the Royal Society of Chemistry.

since PCA measures variance, not discrimination.

There have been several studies that have used dendrograms to display the results of cluster analysis and select sets of materials for arrays.[3,4,9,22,26,39,48] The dendrogram in Figure 6 is an example. The dendrogram shows similarities and differences among the sorbent materials relative to the vapor molecules included in the data set. Cao and co-workers used a dendrogram to help reduce a set of 35 materials preselected from an initial 68 coatings down to a final set of 12.[39] In addition, dendrograms have been used to show clustering of polymeric sorbents on the basis of LSER coefficients, as shown in Figure 10.[145] (Because the scaling of LSER coefficients relative to free energies is different for different interactions, this method tends to emphasize differences in hydrogen-bonding interactions.) Grate and co-workers considered dendrograms and calculated distances between clusters in feature space as the number and diversity of polymers was varied.[22] A diverse 11-polymer set, a seven-polymer set lacking hydrogen bond acidic polymers, a set of four mostly low polarity polymer, and a diverse set of four polymers were compared. To obtain a consistent measure of separation in these studies, the sensor data were pattern normalized to put all the data on a hypersphere of radius one, and distances between points or clusters were expressed in degrees. It was demonstrated that the maximum dendrogram distance was greatest using a diverse polymer set and least using a polymer set consisting of primarily low polarity polymers. In addition, it was shown that this result was a consequence of polymer diversity rather than number. However, chemical diversity was not critical for some particular vapor pairs, e.g. for separating two low polarity vapors.

Another method of evaluating data in feature space considers the spread of data within clusters compared to the distances between different clusters. Nakamoto and co-workers described this type of approach in coating selection using Wilks' λ and partial λ values in a stepwise regression method.[33] Wilks' λ serves as a pattern separation index expressing the degree of pattern separation among many groups. Partial λ values indicate the contributions of particular sensors. An initial set of 38 materials was decreased to 26 by eliminating 12 poorly responsive materials.

Then the remaining 26 were reduced to a selection of eight based on the stepwise regression method utilizing statistics associated with partial λ values for the remaining sensors. Wilks' λ was also reported to be used in coating downselection by Cao and co-workers[42] and has been mentioned by Slater and co-workers.[45] This method is expected to select for coatings that minimize variation within group and hence prefers coatings with linear calibration curves; nonlinear calibration curves will increase variation within a group.

C. Performance in Analytical Tasks

Arrays can also be selected and optimized on the basis of their success relative to one or more metrics (objective functions). Typically these metrics would be based on success in classifying or quantifying compounds, singly or in mixtures. This does not necessarily select a complete, diverse array. Rather it will select for coatings that are most significant in distinguishing and/or quantifying the vapors under consideration. Chemical diversity that is not necessary for the particular task under investigation will not necessarily be included in the array.

Simulations have proven to be a very efficient way to explore the effectiveness of various coating combinations and to perform tests whose design or sheer numbers would be difficult to accomplish experimentally. Thus, by applying a model for noise and other variations expected to occur to the calibration data for a candidate set of coatings against a set of vapors, it is possible to search among all possible coating combinations and evaluate each set against the performance metric. The influence of changes in the noise model can be examined. In addition, the method can be applied to different detection problems, such as mixtures of increasing complexity. These approaches evaluate whether an array will successfully discriminate vapors of concern, provide a general approach for selecting optimal coatings sets for particular applications, and provide quantitative statistical predictions of array performance.[9]

Simulation techniques to investigate array performance have been reported in several peer-reviewed research papers by the Zellers group at the University of Michigan (UM).[6,8,9,12,17,21] These authors introduced disjoint principal components regression (DPCR) to the acoustic wave array field in 1993 and extended it to the classification and quantification of both individual vapors and mixture components (EDPCR).[6] In this approach, principal component models for each single vapor are developed from calibration data. No pattern normalization is performed so that concentration information is retained in the models. Typically one principal component is used for each vapor. To classify a sample, its pattern vector is compared with the principal component models for known vapors and it is assigned accordingly. Samples representing binary mixtures (or potential binary mixtures) are evaluated for their fit to a plane defined by the principal component vectors for two single vapors. Constraints on vapor concentrations or mixture complexity aid in classification/quantification. The technique relies implicitly on linear calibration

curves for individual components and linear additivity to the components in mixture responses; these assumptions are used in simulating mixture data from single compound responses. Both assumptions appear to be valid in general for polymer-coated sensors. In simulations using EDPCR, models for random and systematic variations in sensor are developed, and these error models are applied assuming a Gaussian error distribution. "The population of error-enhanced synthetic responses is sampled iteratively, and each sample is treated [as] an unknown that is then assigned an identity and concentration by comparison with the EDPCR models".[24]

Zellers and co-workers have applied simulations in investigating liquid crystal coated sensors for isomeric discrimination, optimization of arrays for low polarity compounds, assessing temperature and humidity effects, determining limits of recognition, and investigating recognition as a function of number of sensors in an array and the complexity of mixtures.[8,9,12,17,24] The first optimization study used EDPCR in simulations to select four sensor arrays providing the least error in identifying single or binary mixture data from exposures to hexane, isooctane, benzene, xylene, chloroform, and trichloroethylene. This vapor set permits tests investigating within-class and between-class discrimination among aliphatic, aromatic, and chlorinated hydrocarbon vapors. Sixteen candidate coatings were screened for stability and reproducibility. Simulations considered all four-coating combinations from a 10 coating set in the analysis of single and binary mixtures from the six-vapor test set. Many coating combinations provided high identification rates with no statistical difference among the top 15 coating sets. Experimental results in this study confirmed the additivity assumption for mixtures and provided excellent agreement between predicted and experimental array results. In addition, arrays were optimized for specific binary and ternary mixtures.

Very recently, Zellers and co-workers used EDPCR simulations to comprehensively examine the effects of sensor number and polymer selection in the array when recognizing vapors singly and in mixtures of increasing complexity.[24] The study began with a set of six polymers with diversity in structure and properties in accordance with the principles described earlier in this review. These polymer-coated sensors were tested against 16 vapors in experiments where vapor samples were collected on a preconcentrator and desorbed to the sensors; frequency shifts reported were the response peaks referenced to predesorption baselines. Using these calibration data, rates of recognition with imposed error models were assessed for all two-, three-, four-, five-, and six-sensor arrays from the base set of six polymers. Single vapors were recognized with excellent recognition rates using optimal arrays having as few as three sensors. Optimal arrays with at least four polymers gave recognition rates greater than or equal to 97% for all 16 individual vapors at concentrations from 5 to 25 times the limit of detection. One optimal three-sensor array performed similarly.

Simulations of mixture analyses were performed on subsets of the 16 vapors. The authors noted that any mixture analysis should address recognition and discrimination of all possible combinations of a given subset of vapors to have practical utility. High recognition rates were obtained for binary mixtures considered easy to moderately easy using arrays of two or more sensors. Difficult binary mixtures provided substantially lower recognition rates regardless of array size. In other words, if two or three optimally selected coatings were not sufficient to discriminate the vapors, additional coatings were of little or no help. Similarly, three-vapor mixtures considered easy were readily recognized using arrays with three or more sensors, but difficult three-vapor mixtures were only poorly recognized by three-sensor arrays, and additional sensors did not improve recognition rates. Easy four-vapor mixtures could be analyzed, but mixtures of five or six vapors could not be analyzed effectively.

These simulations explored single and multicomponent recognition problems in a thorough way beginning with a diverse set of polymers, by selecting optimal polymer sets for specific recognition problems. The detailed error model incorporated variation due to factors such as sample delivery, calibration error, baseline noise, drift, and sensitivity fluctuations, lending credibility to the results. Single vapor recognition is not a difficult problem; a wide range of vapors can be recognized with arrays of only three sensors. Mixture recognition is more difficult. In all cases, recognition was reduced at lower concentrations. For tractable binary and ternary mixtures, recognition rates did not improve with array size once the optimal two or three sensors were selected. Thus, the inclusion of additional dissimilar polymers to the optimally selected small array did not improve recognition. Mixtures beyond four components were not tractable. In general, the optimally selected polymer sets mixed a nonpolar polymer coating (polyisobutylene) with much more polar hydrogen bonding coatings comprising OV-275 as a very dipolar basic polymer or fluoropolyol as a very hydrogen bond acidic polymer, or both. The use of simulations permitted a study of considerable scope and the examination of questions that are quite difficult to address experimentally.

Array optimization has also been discussed with regard to the visual emperical regions of influence (VERI) pattern recognition method, developed at Sandia,[199] and applied to the selection of polymers for determination of mixtures of water and carbon dioxide.[19] From three polyimides and poly(n-vinyl pyrrolidone), a two-sensor array based on poly(n-vinyl pyrrolidone) and one of the polyimides was selected. Array optimizations based on the VERI method have also been discussed in two topical accounts.[162,199] As in other simulations, combinations of candidate materials are exhaustively searched for those providing the best recognition accuracy, and the effects of applied noise models or changes in sensitivity are also investigated. Polymer-coated arrays were considered in one of these accounts.[199] Thirteen polymer candidates were used in computations showing accuracy versus polymer number in the array. In this approach, degradations in sensitivity were much more deleterious to large arrays than small arrays, with five to six polymers indicated as being optimal for achieving and maintaining discrimination among the individual vapors and binary mixtures considered.

VIII. Multivariate Data Analysis

The research papers on acoustic wave sensor arrays in Table 1 utilize either statistical or neural network techniques for classification and quantification purposes. Both techniques are powerful approaches for handling array data that have been used throughout the sensor array field and in other analytical fields. Statistical techniques were used in the earliest TSM and SAW array studies described above, with neural networks being applied in this field later.[10,30,31,34] In a few cases, statistical and neural network techniques are compared, including a very recent paper.[25] In general, neural networks can create more complex boundaries around groups in the data and may perform better for data requiring such complexity (e.g., sensors providing nonliinear calibration curves). Sensors providing "well-behaved" responses may be more efficiently processed using statistical techniques and models for known sensor response behavior can be incorporated. The VERI technique, like neural networks, is capable of creating complex boundaries around class groups.

The problem of classifying a vapor presented to the array in the absence of simultaneous interferences is a fairly simple one. This result can be visualized by considering data that are pattern normalized to put all points on a hypersphere of unit radius. If the calibration curves over the concentration ranges of interest are linear, all the data for a particular single vapor at various concentrations plot as a point (with some uncertainty) on the hypersphere surface. Different compounds plot at different points and are thus distinguished. Tens to hundreds of different vapors could be distinguished in this way if presented to the array one at a time at suitable concentrations. Classifying single vapors and distinguishing them from one another can generally be achieved whether the array is chemically diverse or not, and without optimization.

Mixture analysis is considerably more challenging than single vapor analysis, and it is desirable to maximize the pattern separation to improve classification and precision. The concept of improving pattern separation can be visualized in the example above as increasing the distance between points on the hypersphere. Mixture data, assuming linear additivity, will plot on an arc connecting the points for the two individual compounds in a binary mixture. Better pattern separation leads to a "longer arc" between the individual vapors in this construct. It also leads to larger net analyte signals for the component compounds and, hence, better sensitivity and selectivity. Pattern separation is maximized through coating selection, investigation, and optimization methods, as described above.

For any particular application, it is not necessary to maximize the overall pattern separation among many vapors. Optimal selection of a small set of coatings may be sufficient for separating compounds of interest while disregarding separations among various other compounds so long as they do not interfere. On the other hand, increasing the overall distances among many vapor points would require a diverse array.

It is important to note that the conventional concept of limit of detection is somewhat changed in dealing with recognition using multivariate data. The limit of interest is really the concentration at which a compound can be detected, correctly classified (recognized), and quantified with meaningful precision even in the presence of other compounds. Thus, Kowalski et al. used limit of determination rather than limit of detection in describing determination of one compound in the presence of other components using the net analyte signal approach.[27] The limit of determination for a given analyte is dependent on the concentrations of all components and the orthogonality of the patterns between them.

Zellers et al. recently proposed that a limit of recognition be added to the parameters used to describe sensor array performance. These authors used the EDPCR method in simulations with added error models as described above to examine the recognition of individual vapors compared to 15 other vapors in the data set. Response vectors modified by error were assigned to vapors and incorrect assignments were noted. Error rates were assessed in simulations at lower and lower concentrations. The limit of recognition was defined as "the concentration below which the [recognition] error rate is greater than 5%". These authors defined a limit of detection as "the concentration producing detectable signals in all four sensors in the array". Limits of recognition were often at significantly higher concentrations than these limits of detection, meaning that the response patterns become confused before the responses are nondetectable. In some cases, however, the limit of recognition was less than the limit of detection defined in this way, indicating that not all sensors were required for recognition.

Both the limit of determination and the limit of recognition are dependent on the error model used. Selected error models are combined with the net analyte signal or used in statistical simulations incorporating calibration data in order to determine the respective limits. The two approaches can be regarded as complementary methods to investigate array performance.

Another significant problem in array analysis is the presence and detection of a compound that was not included in the training (calibration) set. Depending on the analysis method being used, such a compound will be reported as not recognized, recognized with uncertainty, or misclassified as something that was in the training. Target factor analysis tests whether a sample contains only the compounds in the training. Marth and co-workers have described such a technique using properties of random matrixes.[20]

They tested their approach on simulated and real data.

If a compound is detected that was not in the training, it would be useful to be able to characterize and classify it in some way. Although compounds not included in array training can be discriminated against, the current paradigm in sensor arrays is that only compounds in training can be recognized and classified. Grate, Wise, and Abraham have recently proposed that an unknown compound could be characterized in terms of its solvation parameters.[23] Using synthetic data, these authors showed that the array response vector in combination with LSER coefficients for the polymers on the array could be used to calculate the vapor solvation parameters. The mathematics are similar to classical least-squares methods and were developed so that characterization could be done even if the vapor concentration is not known; in fact, the concentration of the unknown could be estimated simultaneously with the determination of solvation parameters. Once so determined, the solvation parameters of the unknown vapor can be used to classify it in terms of properties or probable compound class. By matching the parameters with a database of parameters for known compounds, a number of possible candidates for the unknown can be identified. Alternatively, inverse least-squares methods can be used to determine models for individual solvation parameters based on training data; this approach does not require knowledge of the polymer LSER coefficients. Of course, this approach assumes that acoustic wave sensor responses can be adequately modeled with LSER equations. Practical considerations with regard to the real behavior or acoustic wave sensors and the selection of acoustic wave sensor type were discussed.

It has been implicitly assumed thus far that the responses for multivariate data analysis are the steady-state responses of the sensors representing equilibrium between the gas and sorbent phases. Additional information for discriminating vapors may be available if kinetic information on vapor diffusion into the sensing film is included. These data would effectively increase the dimensionality of the sensor data. Kinetic information has been used in conjunction with arrays based on plasma-polymerized layers and various organic compounds or polymers.[36-38] Time constants and "kinetic signatures" from array data were used in recognition and classification, with improved results compared to equilibrium responses alone. Effective utilization of kinetic information requires uniform thin films consistently applied, the ability to consistently vary the sample concentration rapidly from one concentration (typically zero) to another, and a signal measurement technique that can record meaningful data faster than the diffusion transient. This may entail using films where diffusion is slower than those typically selected for fastest response times.

Selectivity can also be influenced by the sampling method. Thermally desorbed preconcentrators were introduced to acoustic wave sensors by Kindlund[200] and to acoustic wave arrays by Grate and co-workers.[5] Preconcentrators have also been reported in

array systems by Zellers and Frye.[13,16,24] Preconcentrators influence selectivity through trapping efficiencies. In addition, different effective thermal desorption rates or partial chromatographic separation can lead to temporal separation in the delivery of vapors to the array. This effect was noted by Grate and co-workers, who observed that different compounds were released from a Tenax-packed preconcentrator at different rates as the temperature was increased, resulting in peak responses from sensors at different times for different compounds. Temporal separation or partial separation provides additional information for multivariate analysis. This type of data was recently examined by Shaffer et al. using statistical multiway methods.[15] The temporal separation offers a vector of data in addition to the array response vector. In general, second-order analysis offers the advantage of analyte quantification even in the presence of unknown interferences.[201]

IX. Sensor Array Systems

Sensor arrays are ultimately intended for use in some detection application, and this implies the creation of a complete analytical system utilizing the array as the detection element. The system engineered around the array can improve the stability, selectivity, and sensitivity of the measurement.[93] Controlled isothermal operation of the array reduces baseline drift and improves the reproducibility of measurements because vapor sorption is exponentially temperature dependent. Alternation of samples with zero gas provides a method to reduce the impact of baseline drift. Sample modification (such as humidity adjustment) and preconcentration can improve both selectivity and sensitivity. A number of papers have described SAW sensor arrays as the detectors of complete analytical instruments in a "box".[5,11,13,16,21]

X. Discussion

The field of acoustic wave sensors can serve as a case study in the development of vapor sensor array technologies. The early studies in this field treated the array as an instrument to be understood and optimized. This stands in contrast to array utilization as a black box investigated for its empirical ability to discriminate among vapors using neural networks or chemometrics to process the multivariate data. Improvements in acoustic wave sensor arrays and their applications to various analytical and sensory problems were conducted in parallel with more fundamental studies into vapor/polymer interactions, sensor transduction mechanisms, and sensor materials development.

A theme in this field since its inception has been the selection among candidate sensor coatings to obtain the maximum chemical information for vapor discrimination while the number of coatings is minimized. This theme was raised in the first paper by Carey and Kowalski,[26] was followed by elucidation of fundamental interaction mechanisms,[95,98] and has most recently been examined in a comprehensive

study by Zellers.[24] Selection of sensor coatings to obtain a small effective set is not simply a practical matter to simplify instrumentation. It also has analytical and physical significance. It is common in multivariate analysis that the measurement space defined by the number of channels or measurement variables of the multivariate instrument is much larger than the space in which the samples actually reside. As stated by Beebe, Pell, and Seasholtz, "In many chemical examples, the inherent dimensionality is relatively small compared to the number of measurement variables. It is limited by the number of physical phenomena that were changing during the data collection".[129] The number of real dimensions in a sensor array data set is limited by the number of interactions and processes that nature and the analytical instrument provide for discrimination.

Equilibrium array responses based on reversible absorption in amorphous polymers can serve as a baseline for chemical diversity and performance. In this case, the physically meaningful dimensions in the data are defined by the number of available interactions and their orthogonality. Dimensionality and discrimination can then be further enhanced by the use of materials that provide size or shape selectivity, the use of kinetic information from the sensor response, and/or selective or semiselective sampling approaches. Examples of all these approaches exist in the acoustic wave sensor array literature. The rigorous test for whether any of these other mechanisms are improving discrimination is to evaluate them in a sensor array format with multivariate data analysis. In general, it is also desirable to compare performance of an array with and without the additional selectivity mechanism included, although this is not necessary when evaluating chiral recognition.

To date, sorbent polymers represent the class of sensing materials on acoustic wave devices for which the principles of selectivity and array design are elucidated and understood in the most comprehensive manner. While other materials are worth considering, each must be evaluated in terms of what new interactions or selectivity mechanisms they might add to the chemical information provided by the sorbent polymers. Polymers also offer advantages in terms of synthesis and processing into thin films on sensor devices. For these and other reasons, sorbent polymers have been and will continue to be widely used as chemical sensor phases. Sorbent polymers also serve as the basis for a number of electronic nose approaches, including polymer-coated acoustic wave sensor arrays, arrays of chemiresistors with carbon particles dispersed in sorbent polymer matrixes,[202,203] and sorbent polymers with dyes incorporated for optical array-based chemical sensing.[204−208]

Given the fact that the sorption of vapors by polymers can be modeled in terms of fundamental interactions, the potential exists for polymer-coated acoustic wave sensor arrays to go beyond vapor recognition on the basis of empirical training. The principles are in place so that such an array could become an "interaction spectrometer".

XI. Acknowledgments

XII. References

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