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**Classical Least Squares
Transformations of Sensor Array
Pattern Vectors into Vapor Descriptors**

**Simulation of Arrays of Polymer-Coated Surface
Acoustic Wave Sensors with Mass-Plus-Volume
Transduction Mechanisms**

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Summary

A new method of processing multivariate response data to extract chemical information has been developed. Sensor array response patterns are transformed into a vector containing values for solvation parameter descriptors of the detected vapor's properties. These results can be obtained by using a method similar to classical least squares, and equations have been derived for mass-transducing sensors or volume-transducing sensors. Polymer-coated acoustic wave devices are an example of mass-transducing sensors. However, some acoustic wave sensors, such as polymer-coated surface acoustic wave (SAW) devices give responses resulting from both mass-loading and decreases in modulus. The latter effect can be modeled as a volume effect. In this paper we derive solutions for obtaining descriptor values from arrays of mass-plus-volume-transducing sensors. Simulations were performed to investigate the effectiveness of these solutions and to compare them with solutions for purely mass-transducing sensor arrays. It is concluded that this new method of processing sensor array data can be applied to SAW sensor arrays even when the modulus changes contribute to the responses. The simulations show that good estimations of vapor descriptors can be obtained by using a closed form estimation approach that is similar to the closed form solution for purely mass-transducing sensor arrays, Estimations can be improved using a nonlinear least squares optimization method. The results also suggest ways to design SAW arrays to obtain the best results, either by minimizing the volume sensitivity or matching the volume sensitivities in the array.

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1.0 Introduction

Multivariate analytical data can be handled in a variety of ways. In the simplest case, the multivariate instrument provides sufficiently resolved data that the issue is reduced to a univariate calibration. For example, the peak height of a chromatographic peak that is fully resolved from other analytes and interferences provides detection and quantification. Similarly, in mass spectrometry, a peak with a unique mass-to-charge ratio is sought to detect a given species without interference from other species.

Alternatively, the entire response vector from a multivariate instrument can be processed as a multivariate pattern-recognition and/or calibration problem. This approach is especially appropriate for response systems that are not perfectly selective. Thus, spectra from multicomponent mixtures can be processed to quantify each species in the mixture. Classical least squares (CLS) approaches are well-known methods for this analytical task. They require that the spectra for the individual species be known in advance and that spectral intensities combine in a linear fashion.

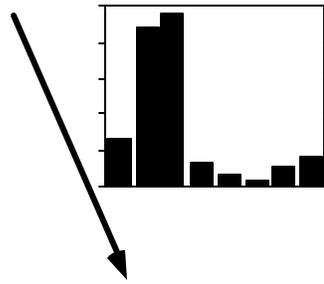
The patterns from sensor arrays represent another multivariate analysis problem that is addressed by processing the entire response vector. Pattern recognition is typically carried out using statistical pattern recognition or neural network methods.[1–3] These approaches generally require training, i.e., measuring the response patterns of known calibration samples that represent the classes of interest, i.e. analytes and potential interferences, and developing models to match future samples with calibration samples. When confronted with a compound that does not belong to a class in the training, an array instrument cannot be relied upon to classify that compound correctly.

Over the last few years, we have developed a new approach for extracting chemical information from multivariate sensor-array data.[4–8] The multivariate pattern vector is transformed into values of descriptors for the detected compound. In principle, this method can be used to obtain descriptors for an unknown compound that was not in the training, providing chemical information about that unknown for characterization, classification, and possibly identification.

Other multivariate techniques, such as infra-red spectra and mass spectra, provide data that can be interpreted to learn something about an analyte even if no training data or reference spectra are available. Sensor-array responses encode information about the interactions of analytes with the sensing films, and therefore the array data encode information about the analyte properties that participate in those interactions. We have developed methods to extract that information. Descriptors can be determined from the pattern vectors of detected single compounds by either inverse least squares (ILS) methods in which a model is determined by training for each descriptor or by a novel variant of classical least squares (CLS) methods to be described below in which the pattern vector is transformed into values for all the descriptors simultaneously.

Figure 1.1 illustrates this alternative concept for handling sensor-array data. In conventional pattern recognition, response vectors are compared to response vectors (or models of them) from the training. In the new approach, the response vector is converted to descriptor values. Though these methods have been derived for sensor arrays, the mathematics is not restricted to sensor arrays. The approach is suitable for any multivariate instrument wherein the response of each channel can be modeled by a suitable linear relationship, such that the new method transforms the multivariate response into values for the descriptors in the linear relationship.

sensor array patterns



descriptors

$$R_2 \quad p_2^H \quad S_{a_2}^H \quad S_{b_2}^H \quad \log L^{16}$$

Figure 1.1. Illustration of the Goal of Converting an Array Response Vector, Shown as a Bar Graph, into Descriptors of the Detected Vapor, Where the Descriptors Are the Solvation Parameters from a Linear Solvation Energy Relationship for Vapor Sorption

In this paper, we have set out the mathematics for obtaining descriptors from sensor-array data, where the individual sensors provide signals that are related to the amount of vapor sorbed by the selective coatings on each of the sensors' surfaces. We have specifically considered sensors where the analyte is absorbed into the thin polymer film with which it interacts by solubility interactions. The absorption aspect of such chemical sensors is shown in Figure 1.2. The amount of vapor sorbed may be expressed as a mass or a volume or a combination of the two. The mass-plus-volume transduction case is of particular interest because some polymer-coated surface acoustic wave (SAW) devices respond by this mechanism.[9] Modulus change contributes to the otherwise gravimetric response transduction of the increase in volume of the film on vapor sorption. There is no closed-form CLS solution for obtaining the vapor descriptors for the mass-plus-volume transduction case. However, such a solution does exist for a special case, an estimated solution can be derived for the more general case, and optimization methods can be used to improve values from the estimation approach. Simulations are performed to investigate the various approaches for the mass-plus-volume transduction case and to determine if SAW sensor array data can be processed by this method. It is found that descriptor values can be obtained from SAW sensor-array data by these approaches.

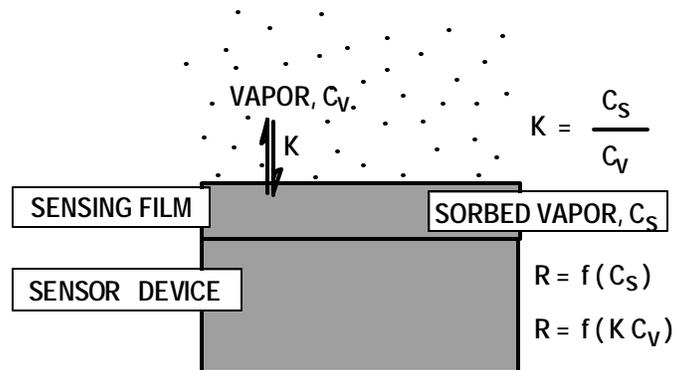


Figure 1.2. Schematic Illustration of the Absorption of Vapor Molecules from the Gas Phase into the Bulk of a Thin Film on a Chemical Sensor, Where the Equilibrium Distribution Is Given by K , the Partition Coefficient

2.0 Linear Solvation Energy Relationships

The chemometric methods to be described apply only if the channels of the multivariate instrument give responses that can be modeled with suitable linear relationships containing analyte descriptors. For sensor arrays, the sorption of a vapor into a polymer on a sensor channel can be modeled with Linear Solvation Energy Relationships (LSERs), and the descriptors are solvation parameters. LSERs are a form of linear free-energy relationship. This approach has been developed for acoustic-wave sensors where the responses are proportional to the mass of the vapor sorbed by a polymer thin film. It has been shown that the responses of such a sensor can be modeled with LSERs.[6,10–15] Thus, the array of polymer-coated sensors can be regarded as a multivariate sorption detector where the responses of each channel can be modeled with an LSER.[4]

The absorption of vapors into selective thin films, such as polymers, is governed by solubility interactions. The amount of vapor sorbed at equilibrium is given by the partition coefficient, K , which relates the concentration of the vapor in the sorbent film, C_s , to the concentration of the vapor in the gas phase, C_v (see Figure 1.2).

$$K = C_s / C_v \quad (2.1)$$

The LSER equation expresses $\log K$ as a linear combination of terms that represent particular solubility interactions.[11,14,16]

$$\log K = c + r R_2 + s \pi_2^H + a \Sigma\alpha_2^H + b \Sigma\beta_2^H + l \log L^{16} \quad (2.2)$$

In this relationship, R_2 , π_2^H , $\Sigma\alpha_2^H$, $\Sigma\beta_2^H$, and $\log L^{16}$ are solvation parameters that characterize the solubility properties of the vapor,[16] and which serve as descriptors of the vapor properties. The parameter 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 capability 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 298K (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 $\log L^{16}$.

These parameters, except for R_2 , are related to free energies and were determined from experimental data on partitioning or complexation equilibria.[17–21] The R_2 parameter is different, since it is calculated from molar-refraction values for liquids and extended by a group contribution scheme.[22]

The LSER equation for a particular polymer is determined by regressing measured partition coefficients for a diverse set of vapors on the polymer against the solvation parameters of the test vapors, using the method of multiple linear regression.[23] The regression method yields the coefficients (s, r, a, b, and l) and the constant (c). In this treatment, we will refer to the polymer LSER coefficients as the polymer parameters. LSER coefficients for the polymers are generally obtained by regression of partition coefficients determined by gas chromatographic measurements, but they may also be determined from the responses of a mass-sensitive acoustic-wave device with a thin film of the polymer.[6,10,23]

In matrix algebra, a collection of LSER relationships can be expressed as

$$\mathbf{L} = \mathbf{V}_o \mathbf{P}_o + \mathbf{1c} \quad (2.3a)$$

Matrix \mathbf{L} , containing $\log K$ values, is related to matrix \mathbf{V}_o (number of vapors by five), containing the vapor solvation parameters, and matrix \mathbf{P}_o (5 by number of polymers), containing the polymer parameters. The constants of the LSER equations are given by the vector \mathbf{c} (1 by number of polymers), and $\mathbf{1}$ is a vector of ones (number of vapors by 1). The subscript of \mathbf{o} is arbitrarily chosen to distinguish the \mathbf{V} and \mathbf{P} matrices from those in the next equation.

If matrix \mathbf{V} is defined so that each vector contains the five vapor-solvation parameters and a vector of ones (number of vapors by six), and similarly \mathbf{P} is defined to contain the polymer parameters, including the constants (six by number of polymers), then the LSER relationship can be more simply expressed as

$$\mathbf{L} = \mathbf{VP} \quad (2.3b)$$

This latter convention in Equation 2.3b will be followed in the remainder of the paper (although the convention in Equation 2.3a has been followed in our original papers[4–7] on this method). The contents of the \mathbf{V} and \mathbf{P} matrices used in this paper are summarized in Table 2.1.

Table 2.1. Contents of the Matrices Containing the Vapor Descriptors and Polymer Parameters of the LSER Relationship

\mathbf{V}_o	R_2	π_2^H	$\Sigma\alpha_H$ 2	$\Sigma\beta_2^H$	$\log L^{16}$		
\mathbf{V}	R_2	π_2^H	$\Sigma\alpha_H$ 2	$\Sigma\beta_2^H$	$\log L^{16}$	1	
\mathbf{V}_a	R_2	π_2^H	$\Sigma\alpha_H$ 2	$\Sigma\beta_2^H$	$\log L^{16}$	1	Log \mathbf{C}
\mathbf{V}_b	R_2	π_2^H	$\Sigma\alpha_H$ 2	$\Sigma\beta_2^H$	$\log L^{16}$	1	Log $\mathbf{Y C}$
\mathbf{V}_c	R_2	π_2^H	$\Sigma\alpha_H$ 2	$\Sigma\beta_2^H$	$\log L^{16}$	1	Log $(\mathbf{I} + m \mathbf{Y}) \mathbf{C}$
\mathbf{P}_o	r	s	a	b	l^a		
\mathbf{P}	r	s	a	b	l^a	c	
\mathbf{P}_a	r	s	a	b	l^a	c	1
(a) This is the letter “l,” which is the LSER coefficient associated with $\log L^{16}$, not the number 1.							

The solvation parameters in the \mathbf{V} matrices are the descriptors to be determined from sensor-array response patterns. The solvation parameters are known for some 2000 compounds and can be estimated

for many more.[16,24] Values of these descriptors serve to characterize and classify unknown vapors, and comparisons with the descriptors for known compounds can potentially be used for identification.

3.0 Classical Least Squares Approach

The conventional CLS approach used in absorbance spectroscopy[25] models the response-matrix \mathbf{R} (samples by channels) containing the responses of the spectrometer, as

$$\mathbf{R} = \mathbf{C}\mathbf{S} \quad (3.1)$$

where \mathbf{C} is a matrix of concentrations (samples by analytes), and \mathbf{S} is a matrix of pure component spectra (analytes by channels). If \mathbf{S} is known, the concentrations \mathbf{C} can be determined from \mathbf{R} .

$$\mathbf{C} = \mathbf{R}\mathbf{S}^T(\mathbf{S}\mathbf{S}^T)^{-1} \quad (3.2)$$

The superscript T denotes the transpose of a matrix.

We have developed a variant of CLS that can be used to obtain descriptors from multivariate instruments where the responses follow the general form of the following equation.[16,24]

$$\mathbf{R} = \mathbf{S}_V \mathbf{C} 10^{(\mathbf{V}^* \mathbf{P}^*)} \mathbf{S}_P \quad (3.3)$$

The matrix \mathbf{R} (analytes by channels) contains the responses of the multivariate instrument to tests against compounds presented as single-component samples. The matrix \mathbf{S}_V is a diagonal matrix containing analyte-specific parameters that influence the response independent of the specific interactions of the analyte with each channel. Specific interactions of the analyte with detector channel properties are modeled in the general linear relationship $\mathbf{V}^* \mathbf{P}^*$ (not necessarily an LSER), where \mathbf{V}^* contains analyte descriptors, and \mathbf{P}^* contains parameters specific to the properties of detector channels. (The * superscript is an arbitrary choice to denote this general case and distinguish it from specific cases below where the \mathbf{V} and \mathbf{P} matrices refer to vapor descriptors and polymer parameters, respectively.) The matrix \mathbf{S}_P contains channel-specific sensitivity parameters that are independent of the analyte interactions. The matrix \mathbf{C} contains the analyte concentrations as usual. Thus, this response function contains vapor-specific parameters, followed by the interaction model, and completed with the channel-specific terms after the exponential.

A solution containing the descriptors in \mathbf{V}^* can be found by augmentation of \mathbf{V}^* and \mathbf{P}^* and solving for the augmented \mathbf{V}^* , designated \mathbf{V}^*_a .

$$\{\log(\mathbf{R}\mathbf{S}_P^{-1})\} \mathbf{P}^*_a{}^T (\mathbf{P}^*_a{} \mathbf{P}^*_a{}^T)^{-1} = \mathbf{V}^*_a \quad (3.4)$$

The solution, \mathbf{V}^*_a , contains the analyte descriptors in \mathbf{V}^* as well as the log of the product of analyte-specific sensitivity factor times the analyte concentration, $\mathbf{S}_V \mathbf{C}$.

Specific cases for sensor arrays described below provide examples of this general response model and its solution.

4.0 Arrays of Mass-Transducing Sensors

The gravimetric response of a polymer-coated acoustic wave sensor to the absorption of a vapor into the sensing layer is related to the partition coefficient as shown in Equation 2.2.[26–32]

$$R = \Delta f_v = n \Delta f_s C_v K / \rho_s \quad (4.1)$$

The sensor's response, R , to the mass of vapor absorbed, a frequency shift denoted by Δf_v , is related to the amount of sorbent polymer on the sensor as indicated by Δf_s , the frequency shift due to the deposition of the film material onto the bare sensor. It further depends on the concentration of the vapor in the film as given by the product of the vapor concentration in the gas phase and the partition coefficient, $C_v K$. The density of the sorbent phase is given by ρ_s . The product of the frequency shift due to application of the polymer, Δf_s , and the inverse of the polymer density, ρ_s , represents a sensitivity factor. (It is a factor in the proportionality of the response to the vapor concentration.)

If the observed response is entirely due to mass-loading, then $n = 1$. Purely gravimetric sensing is observed if the acoustic wave sensor is a thickness shear mode (TSM) device with an acoustically thin film[33–35] or a surface acoustic wave (SAW) device with an acoustically thin film of a polymer with a low initial modulus.[34–36]

If the polymer-coated SAW device has a response related to both the mass of the vapor sorbed and a decrease in the polymer modulus, then n will be a number greater than one.[9,34,35,37] This case will be considered separately below as a mass-plus-volume transducing sensor.

The responses of a set of gravimetric acoustic wave sensors in matrix algebra is given by

$$\mathbf{R} = \mathbf{C} 10^{(\mathbf{VP})} \mathbf{D}^{-1} \mathbf{F} \quad (4.2)$$

Matrix \mathbf{R} (vapors by polymers) contains the response values as frequency shifts for polymer-coated sensors in response to vapor samples. In this relationship, \mathbf{C} (number of vapors by number of vapors) is a diagonal matrix of the concentrations of the vapors, and \mathbf{F} (number of sensors by number of sensors, or number of polymers by number of polymers) is a diagonal matrix of the Δf_s values of the sensors. Similarly, \mathbf{D} (number of polymers by number of polymers) is a diagonal matrix of the sorbent polymer densities. The superscript of -1 denotes the inverse of the matrix.

It is possible to solve for the vapor descriptors in \mathbf{V} given the responses, \mathbf{R} , the polymer parameters, \mathbf{P} , and the sensitivity factors, $\mathbf{D}^{-1} \mathbf{F}$, but the solution requires knowledge of \mathbf{C} .[4] Since the concentration of an unknown vapor is not normally known, it is more useful to rearrange the response model so that one solves for the log of the concentration simultaneously with determining the descriptor values. Augmentation of the \mathbf{V} matrix (to \mathbf{V}_a) to contain the log of the vapor concentration in addition to the descriptors for each vapor and augmentation of the \mathbf{P} matrix (to \mathbf{P}_a) with a vector of ones (see Table 2.1) allows rearrangement of the response model.

$$\mathbf{R} = 10^{(\mathbf{V}_a \mathbf{P}_a)} \mathbf{D}^{-1} \mathbf{F} \quad (4.3)$$

Solutions for obtaining descriptors from array pattern vectors are then given as follows.[4]

$$\{\log (\mathbf{R} \mathbf{D} \mathbf{F}^{-1})\} \mathbf{P}_a^T (\mathbf{P}_a \mathbf{P}_a^T)^{-1} = \mathbf{V}_a \quad (4.4a)$$

$$\{\log (\mathbf{r} \mathbf{D} \mathbf{F}^{-1})\} \mathbf{P}_a^T (\mathbf{P}_a \mathbf{P}_a^T)^{-1} = \mathbf{v}_a \quad (4.4b)$$

This solution in Equation 4.4a is shown for an entire matrix of responses, \mathbf{R} , where \mathbf{V}_a gives the values of the descriptors $R_2, \pi_2^H, \Sigma \alpha_2^H, \Sigma \beta_2^H$, and $\log L^{16}$, as well as the log of the concentration. Alternatively, if the solution is expressed for a *single* sample as in Equation 4.4b, the vector of descriptors within \mathbf{v}_a is obtained from a single response vector, \mathbf{r} .

Note that the response function in Equation 4.2 is similar to that in the more general Equation 3.3, where \mathbf{S}_p is $\mathbf{D}^{-1} \mathbf{F}$, and there are no analyte-specific sensitivity factors (\mathbf{S}_v). The solution in Equation 4.4 is similar to the general solution in Equation 3.4.

5.0 Arrays of Volume-Transducing Sensors

If the sensors in an array respond to the amount of vapor sorbed by the sensing film, where the amount that determines the signal is a volume rather than a mass, the response function can be expressed as

$$R = v_v C_v K S \quad (5.1)$$

This function relates the response, R , to the vapor-specific volume, v_v , and the vapor concentration in the film, $C_s = C_v K$. These are related to the volume fraction of vapor in the polymer/vapor solution, $\phi_v = v_v C_v K$. [5] The sensitivity is given by S .

This response function can apply to chemiresistor sensors coated with composite films of carbon black in a polymer matrix [2,38–44] where vapor sorption causes an increase in the volume of the film. The signal is a change in resistance, and detailed studies have shown [44] that sensor-resistance changes are related to the extent of volume increase regardless of the identity of the vapor producing the volume increase. Hence, they respond to the amount of vapor as a volume.

In matrix algebra, the responses can be expressed according to

$$\mathbf{R} = \mathbf{Y} \mathbf{C} \mathbf{10}^{(\mathbf{VP})} \mathbf{S} \quad (5.2)$$

The matrix \mathbf{Y} is a diagonal matrix (number of vapors by number of vapors) containing the specific volumes of the vapors, and \mathbf{S} is the sensitivity matrix. To solve for vapor descriptors without knowledge of the concentration or vapor-specific volumes, one can again augment matrices. We define matrix \mathbf{V}_b as matrix \mathbf{V} augmented to contain the log of the product of the vapor concentration times the vapor-specific volume. The \mathbf{P} matrix must be augmented with a vector of ones as usual (giving \mathbf{P}_a). Then the response function and solutions are as follows. [5]

$$\mathbf{R} = \mathbf{10}^{(\mathbf{V}_b \mathbf{P}_a)} \mathbf{S} \quad (5.3)$$

$$\{\log(\mathbf{R} \mathbf{S}^{-1})\} \mathbf{P}_a^T (\mathbf{P}_a \mathbf{P}_a^T)^{-1} = \mathbf{V}_b \quad (5.4a)$$

$$\{\log(\mathbf{r} \mathbf{S}^{-1})\} \mathbf{P}_a^T (\mathbf{P}_a \mathbf{P}_a^T)^{-1} = \mathbf{v}_b \quad (5.4b)$$

Thus, an array of sorption-based sensors with signals proportional to volume increases represent a multivariate sensor system where it is possible, in principle, to solve for the descriptors of sorbed vapors. The value of the log of the product of the vapor concentration times the vapor-specific volume is also obtained, but it is of little value for classification.

Note that the response function in Equation 5.2 is similar to that in the more general Equation 3.3, where \mathbf{Y} contains the analyte-specific sensitivity factors (\mathbf{S}_v), and \mathbf{S} corresponds to \mathbf{S}_p . Then the solution in Equation 5.3 is similar to the general solution in Equation 3.4.

6.0 Mass-Plus-Volume-Transducing Sensors

If the individual sensors in the array respond to both the mass and volume of the vapor sorbed in the sensing film, then these are mass-plus-volume-transducing sensors. This case is significantly more complicated than mass- or volume-transducing sensors alone, but solutions, estimation, and optimization approaches can be found.

For this case, the response functions for mass- and volume-transducing cases can be added.

$$\mathbf{R} = \mathbf{C} 10^{(\text{VP})} \mathbf{D}^{-1} \mathbf{F} + \mathbf{Y} \mathbf{C} 10^{(\text{VP})} \mathbf{S} \quad (6.1a)$$

$$\mathbf{R} = 10^{(\text{Va Pa})} \mathbf{D}^{-1} \mathbf{F} + \mathbf{Y} 10^{(\text{Va Pa})} \mathbf{S} \quad (6.1b)$$

This case is of interest because polymer-coated SAW devices[3,31,32] can be examples of mass-plus-volume-transducing sensors. In addition to detecting the mass of a sorbed vapor, the SAW sensor response may be amplified by a response to the decrease in polymer modulus as the sorbed vapor plasticizes the film. The plasticizing effect is related to increases in polymer free volume, and hence the modulus response can be modeled as a volume response (i.e., a swelling-induced modulus change). Polymer modulus changes are proportional to increases in polymer free volume[9,36,37,45,46] brought about by vapor sorption. (We are assuming acoustically thin films for this analysis.)

The response model for a SAW sensor incorporating a modulus amplification can be expressed as[9]

$$\Delta f_v = (\Delta f_s C_v K / \rho_s) + f_L (v_v C_v K) (\Delta f_s A_{\text{SAW}} / \alpha) \quad (6.2)$$

which simplifies to

$$\Delta f_v = (\Delta f_s C_v K / \rho_s) + v_v C_v K S_{\text{sw}} \quad (6.3)$$

when the sensitivity factors for the modulus response are grouped into S_{sw} , where the “sw” subscript refers to the swelling-induced modulus change, i.e., the volume sensitivity.

A closed-form solution can be obtained for the special case of Equation 6.1 where the volume sensitivity is a multiple, m , of the overall mass sensitivity, i.e., $\mathbf{S} = \mathbf{D}^{-1} \mathbf{F} m$. In this case, the response model is

$$\mathbf{R} = \mathbf{C} 10^{(\text{VP})} \mathbf{D}^{-1} \mathbf{F} + \mathbf{Y} \mathbf{C} 10^{(\text{VP})} \mathbf{D}^{-1} \mathbf{F} m \quad (6.4)$$

which can be rearranged to look like

$$\mathbf{R} = (\mathbf{I} + m \mathbf{Y}) \mathbf{C} 10^{(\text{VP})} \mathbf{D}^{-1} \mathbf{F} \quad (6.5)$$

where \mathbf{I} is the identity matrix.

This case is similar to the case where the SAW sensor response conforms to Equation 4.1 with n greater than one.

The solution for this specific case is obtained by augmenting \mathbf{V} to contain the log of $(\mathbf{I} + m \mathbf{Y}) \mathbf{C}$, giving \mathbf{V}_c (see Table 2.1), and augmenting \mathbf{P} with a vector of ones as usual to get \mathbf{P}_a .

Then the response model and solution are

$$\mathbf{R} = 10^{(\mathbf{V}_c \mathbf{P}_a)} \mathbf{D}^{-1} \mathbf{F} \quad (6.6)$$

$$\{\log (\mathbf{R} \mathbf{D} \mathbf{F}^{-1})\} \mathbf{P}_a^T (\mathbf{P}_a \mathbf{P}_a^T)^{-1} = \mathbf{V}_c \quad (6.7a)$$

$$\{\log (\mathbf{r} \mathbf{D} \mathbf{F}^{-1})\} \mathbf{P}_a^T (\mathbf{P}_a \mathbf{P}_a^T)^{-1} = \mathbf{v}_c \quad (6.7b)$$

Thus one solves for the vapor descriptors and the log of the concentration-containing term. The fact that there is a volume sensitivity and it is dependent on varying vapor-specific volumes does not prevent independent determination of the vapor descriptors for this case.

Equations 6.5 and 6.7 match the forms of the general Equations 3.3 and 3.4.

If this special case does not pertain, then there is no exact closed-form solution for the mass-plus-volume-transducing case in Equation 6.1. A SAW sensor array where some sensors have a greater modulus contribution than others, as is likely, would not fit the special case. However, it is possible to assume that the specific volumes of the vapors as liquids are unity so that \mathbf{Y} is taken as the identity matrix. Given this assumption, estimates can be determined for the vapor descriptors using following closed-form solution

$$\{\log (\mathbf{R} (\mathbf{D}^{-1} \mathbf{F} + \mathbf{S})^{-1})\} \mathbf{P}_a^T (\mathbf{P}_a \mathbf{P}_a^T)^{-1} = \mathbf{V}_a \quad (6.8a)$$

$$\{\log (\mathbf{r} (\mathbf{D}^{-1} \mathbf{F} + \mathbf{S})^{-1})\} \mathbf{P}_a^T (\mathbf{P}_a \mathbf{P}_a^T)^{-1} = \mathbf{v}_a \quad (6.8b)$$

where \mathbf{V}_a is defined as before. As we shall show below, this approach generally gives satisfactory values for the vapor descriptors if the measurement noise is low. Descriptor values can be obtained that are within the precision with which they were originally determined for vapors.

Assuming that the overall sensitivity is a combination of the mass and volume sensitivities without consideration of vapor-specific parameters like the vapor-specific volume is similar to the SAW response in Equation 4.1 where the mass response is amplified by n without assuming that the value of n is the same for all the sensors in an array. The solution in Equation 6.8 is similar to the general solution in Equation 3.4 and the mass-transducing solution in Equation 4.4.

If desired, this initial estimation can be refined by using direct fitting of the sensor responses to the model with a non-linear least-squares optimization procedure to determine \mathbf{V}_a and \mathbf{Y} . The use of this optimization will be demonstrated below. It can improve the determination of vapor descriptor values when the volume sensitivity is quite variable from one sensor to another in the array, and the measurement noise is low. However, if the volume sensitivity across the array is a single scalar multiple of the mass sensitivity, i.e., $\mathbf{S} = \mathbf{D}^{-1} \mathbf{F} m$, there is no need or point to doing such an optimization, even if the descriptors have been found using Equation 6.2 rather than Equation 6.7.

7.0 Simulations of Mass-Plus-Volume-Transducing Sensors

7.1 Simulation Approach

Simulations were performed to investigate the determination of descriptor values from arrays of mass-plus-volume-transducing sensors. The primary objectives of these simulations were to determine if these methods can be applied to SAW array responses in a similar manner to their application to purely mass-transducing sensor arrays and to demonstrate the use of nonlinear least-squares optimization to improve upon vapor-descriptor estimations.

A method of generating synthetic data sets that perfectly fit the LSER model was set up according to Equation 6.1. Estimated descriptors were found using the solution in Equation 6.8. This solution is calculated assuming that the vapor specific volumes in \mathbf{V} are equal to 1. This assumption is relevant if there is a volume sensitivity, and it varies from sensor to sensor; this assumption has no consequences if there is no volume sensitivity, or if the volume sensitivity is a scalar multiple of the mass sensitivity and this scalar multiple is constant across the entire array.

The synthetic data set consisted of 102 vapors for which the solvation parameters and densities as liquids were tabulated. Liquid densities range from 0.6 to 3.3 g/mL, a wider range than is typically encountered and hence a rigorous test set. Twelve polymers for which the LSER relationships had been determined previously defined the array. These were the same 12 polymers and LSER relationships used in our original simulations for mass-transducing sensors.[4]

In the simulations, the mass sensitivities in $\mathbf{D}^{-1} \mathbf{F}$ were defined as 1 (i.e., the identity matrix), and volume sensitivities were set to zero or some positive integer value. In this way, the relationship between volume sensitivity and mass sensitivity of each sensor was clear. A number of cases were considered for volume sensitivities.

Gaussian measurement noise proportional to the response[47] with a standard deviation of 1, 2, 5, 10, or 20% was added to the synthetic responses. For each case, 20 replicates were produced for each of the 102 vapors by 12 polymers. Thus, each reported root-mean-square error of prediction for a particular vapor descriptor at a particular imposed noise level was determined from $20 \times 102 = 2040$ simulated determinations.

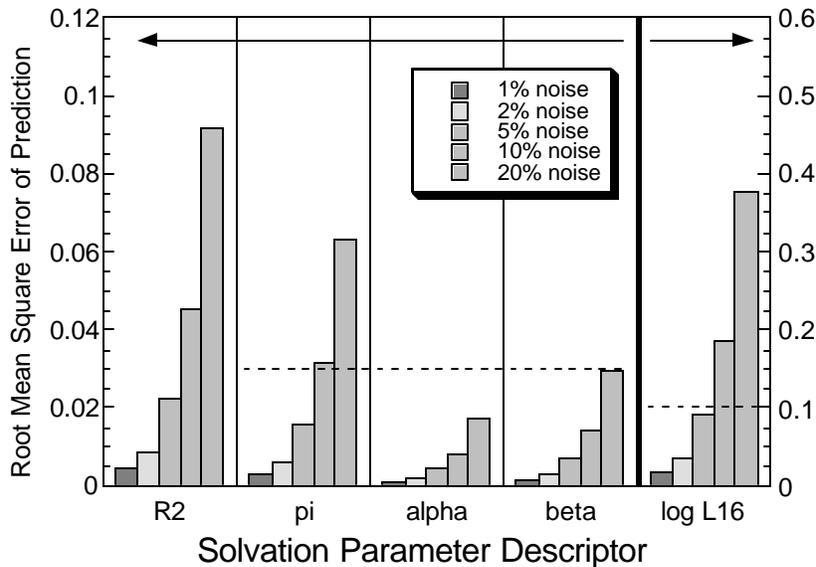
The simulations investigated the effects of the added measurement noise on the errors in the found descriptor values using various methods of obtaining descriptors from mass-plus-volume transducing sensor arrays. The errors are compared with the intrinsic uncertainties in the values of the vapor descriptors. In addition, the results were compared with those for purely mass-transducing sensor arrays as the base case.

In this simulation approach, the LSER models are assumed to be perfect and then measurement noise—up to 20%—is added to calculated sensor responses. For reference, measurement noise of 1% or less for actual polymer-coated SAW vapor sensors has been demonstrated for repeated exposures to the same vapor.[48] In reality, the LSER models will not perfectly match vapor sorption by polymers. To the extent that the models are not a perfect match to reality, the amount of tolerable measurement noise, i.e., the noise required to obtain a given precision in the found vapor descriptors, will be reduced. However, beginning with perfect models and adding measurement noise is a common way to do simulations, and this approach is often used in process-control simulations.

7.2 Mass-Transducing Sensor Array

In the first case considered, all values in the \mathbf{S} matrix were set to zero, i.e., there is no volume sensitivity, and the sensors are simply mass-transducing sensors. Prediction errors for each of the vapor descriptors at each of the simulated noise values are shown in Figure 7.1; the results for $\log L^{16}$ are plotted relative to the scale on the right y-axis while the remaining are plotted against the scale on the left y-axis.

These results can be compared with the uncertainties with which the values of the vapor solvation parameters were originally determined. The uncertainties in the π_2^H , $\Sigma\alpha_2^H$, and $\Sigma\beta_2^H$ parameters can be taken 0.03 units[4], and a dashed line has been added to the columns for these parameters in Figure 7.1 for reference. The $\log L^{16}$ values have estimated errors of about 0.1 units, and a dashed line is placed at this level for the $\log L^{16}$ results in Figure 7.1. In contrast, R_2 is a calculated parameter without an



BaseCaseL_5Data

Figure 7.1. Simulation Results Giving the Root-Mean-Square Error of Prediction for each Vapor Descriptor at each Imposed Noise Level for the First Case Where There is no Volume Sensitivity, i.e., for a Mass-Transducing Array. The results for $\log L^{16}$ are plotted relative to the scale on the right y-axis while the results for the remaining vapor descriptors are plotted against the scale on the left y-axis. The same results are obtained if the array contains mass-plus-volume transducing sensors were the volume sensitivity is the same scalar multiple of the mass sensitivities across the entire array, i.e., simulation case 2 (see text).

associated uncertainty. In addition, the errors can be compared with the sizes of the descriptor values. The range of descriptor values and approximate uncertainties in the descriptors are listed in Table 7.1. It can be seen that at low imposed noise levels, these simulations on synthetic data return the vapor descriptors to a precision that exceeds the known precision of the actual parameter values. Thus, at up to 5 to 10% noise levels, the estimated solutions are quite satisfactory.

Table 7.1. Minimum and Maximum Values of the Descriptors for the 102 Test Vapors With the Approximate Uncertainty for Each Solvation Parameter

Solvation Parameter	Minimum Value	Maximum Value	Approximate Uncertainty
R_2	-0.24	1.45	
π_2^H	0	1.33	0.03
$\Sigma\alpha_2^H$	0	0.77	0.03
$\Sigma\beta_2^H$	0	1.06	0.03
$\log L^{16}$	1.224	4.95	0.1

7.3 Volume Sensitivities that Are a Scalar Multiple of the Mass Sensitivities

The second case considered was for mass-plus-volume-transducing sensors where the volume sensitivity values were a scalar multiple of the mass sensitivities across the entire array, i.e., $\mathbf{S} = \mathbf{D}^{-1} \mathbf{F} m$ and m is a constant for all sensors. In the first test of this second case, the scalar multiplier m was set equal to 1, such that the volume sensitivity is equal to the mass sensitivity, and the total response is twice the mass response. The results for this case were the same as the first case above (see Figure 7.1) for simple mass-transducing sensors. The same results were obtained again from a second test where the scalar multiplier m was equal to 5 (an unrealistically large value). Thus, if the volume sensitivities across the array are all the same scalar multiple of each sensor's mass sensitivity, then the solution in Equation 6.8 is as good as the closed-form solution for mass-transducing sensors when determining the vapor descriptors. Figure 7.1 represents results for all these cases. There is no reason to use nonlinear least-squares optimization procedures to try to improve the estimates for the vapor descriptors. However, the concentration estimates that are contained in \mathbf{V}_a become worse as the volume sensitivity, \mathbf{S} , increases.

7.4 Varying Volume Sensitivities Across the Array

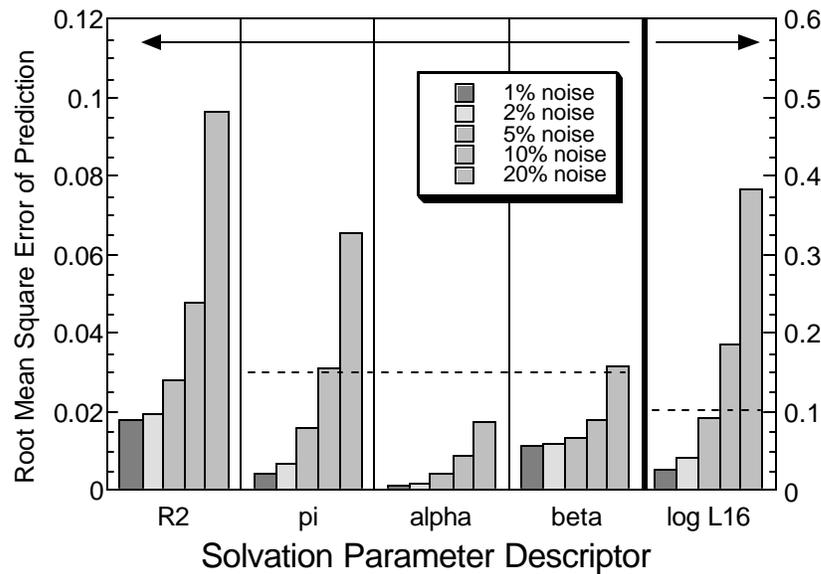
The third and final case considered was where the sensors in the array have variable volume sensitivity across the array. Thus the nonzero elements of \mathbf{S} vary, where some are smaller than the mass sensitivities and others are equal to or larger than the mass sensitivities. This is the most realistic case for an SAW array where some or all of the sensors respond as mass-plus-volume transducing sensors. A number of \mathbf{S} matrices were considered as given in Table 7.2.

Table 7.2. Values for the Volume Sensitivities for the “Third Case” Simulations

Identifier	S matrix ^a
S3	$S = \text{diag}([1\ 1\ 0\ 0\ 0\ 0\ 1\ 0\ 0\ 1\ 1\ 1])$
S4	$S = \text{diag}([2\ 2\ 1\ 1\ 0\ 0\ 1\ 1\ 0\ 0\ 2\ 2])$
S5	$S = \text{diag}([2\ 0\ 2\ 0\ 2\ 0\ 2\ 0\ 2\ 0\ 2\ 2\ 0])$

(a) The volume sensitivity matrices, S , are diagonal matrices with values for the following polymers, respectively: PIB, PECH, OV25, OV202, PVPR, PVTD, PEM, SXCN, PEI, SXPYR, FPOL, SXFA. See reference [4] for more on these polymers.

The volume sensitivities in S3 were set up so that half the sensors have no volume sensitivity, and the remaining half have S values = 1, which means the mass and volume sensitivities are equal. This is a reasonably realistic case for an SAW array where some sensors give observed responses that are twice the mass-only response.[9,34,36] Simulation results are shown in Figure 7.2. Aside from somewhat greater errors at low noise levels for R_2 and $\Sigma\beta_2^H$, there is little difference between this mass-plus-volume transducing array example and the first case of purely mass-transducing sensors. There is essentially no

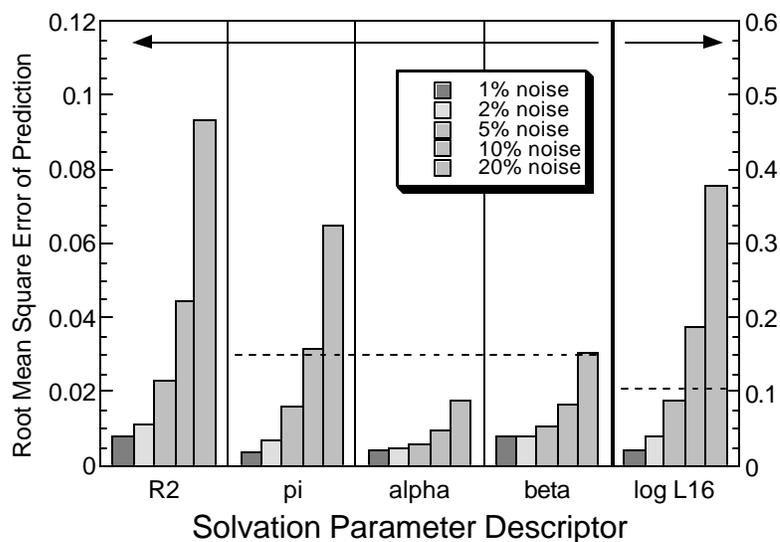


S3Estimated

Figure 7.2. Simulation Results Giving the Root-Mean-Square Error of Prediction for each Vapor Descriptor at each Imposed Noise Level Plotted Relative to the Left and Right y-axes as Noted in the Figure 7.1 Caption. These results are obtained from the third case where there is variable volume sensitivity across a mass-plus-volume transducing array, and the simulations were performed using the volume-sensitivity matrix designated S3 in Table 7.2.

difference with regard to which noise levels yield results exceeding the reference lines on the plot. The conclusion for this test example is that response pattern vectors from mass-plus-volume transducing arrays, such as SAW sensor arrays, can be transformed into vapor descriptors just as effectively as purely mass-transducing arrays.

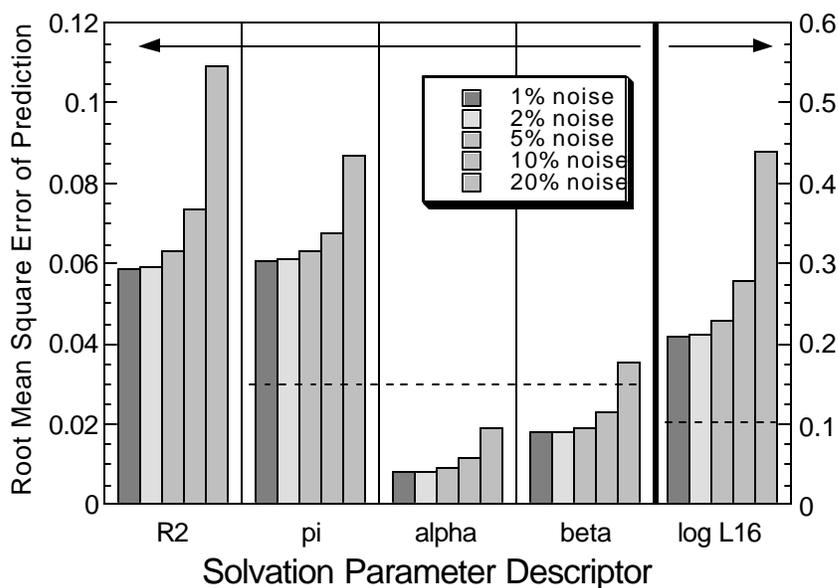
The volume sensitivities in S4 and S5 were set up so that the maximum volume sensitivity was increased to 2 (compared to a maximum value of 1 in S3). Then the total response for sensors with a volume sensitivity of 2 would be 3 times the mass response. This represents the most volume sensitivity that might be expected for realistic SAW arrays and may exaggerate it. For both of these simulations (S4 and S5), the total of the volume sensitivities was 12, but the values were distributed differently among the sensors. For S4, we deliberately tried to make the volume sensitivities for polymers with similar interaction properties similar to one another. Similarity was determined from the authors' knowledge of the polymer properties and from hierarchical cluster analysis. Simulation results for S4 are shown in Figure 7.3. These results are very similar to those for S3, although the errors in R_2 and $\Sigma\beta_2^H$ at low noise are actually less than those in S3, even though some of the volume sensitivities are greater. Relative to the reference lines on the plot, the results for S4 are like S3 and like the mass-transducing first case (Figure 7.1). From such results, one again concludes that the transformation of sensor-array patterns into vapor descriptors can be as effective for the mass-plus-volume transducing case (e.g., for SAW sensor arrays) as for purely mass-transducing arrays.



S4Estimated

Figure 7.3. Simulation Results Giving the Root-Mean-Square Error of Prediction for each Vapor Descriptor at each Imposed Noise Level Plotted Relative to the Left and Right y-axes as Noted in the Figure 7.1 Caption. These results are obtained from the third case where there is variable volume sensitivity across a mass-plus-volume transducing array, and the simulations were performed using the volume -sensitivity matrix designated S4 in Table 7.2.

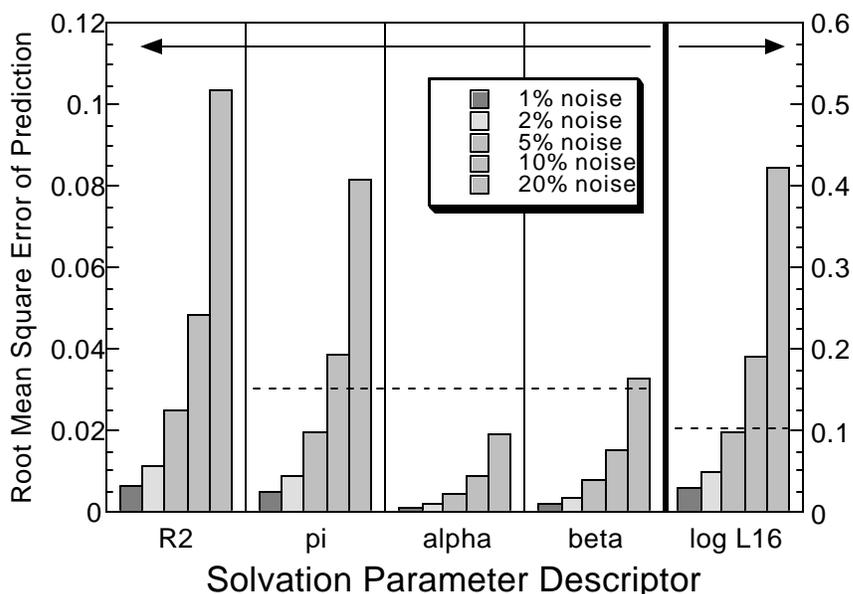
For S5, we deliberately made volume sensitivities for similar polymers as different as we could within the bounds of the simulation. Therefore, for each pair of similar polymers, one had a value of 0 and the other a value of 2. These results for this simulation are shown in Figure 7.4. It can be seen that this case gives the greatest errors of any simulation considered thus far. The errors at low noise levels are significantly increased for all the parameters, especially for π_2^H and $\log L^{16}$. Errors at all noise levels for these parameters exceed the reference lines. On the other hand, they are at most about twice the reference lines at 5 to 10% measurement noise and still much less than the overall values of the descriptors (see Table 7.1 for descriptor ranges). Thus, even for the challenging conditions of S5, it appears that determining reasonable estimates for descriptor values is feasible.



S5Estimated

Figure 7.4. Simulation Results Giving the Root-Mean-Square Error of Prediction for each Vapor Descriptor at each Imposed Noise Level Plotted Relative to the Left and Right y-axes as Noted in the Figure 7.1 Caption. These results are obtained from the third case where there is variable volume sensitivity across a mass-plus-volume transducing array, and the simulations were performed using the volume-sensitivity matrix designated S5 in Table 7.2.

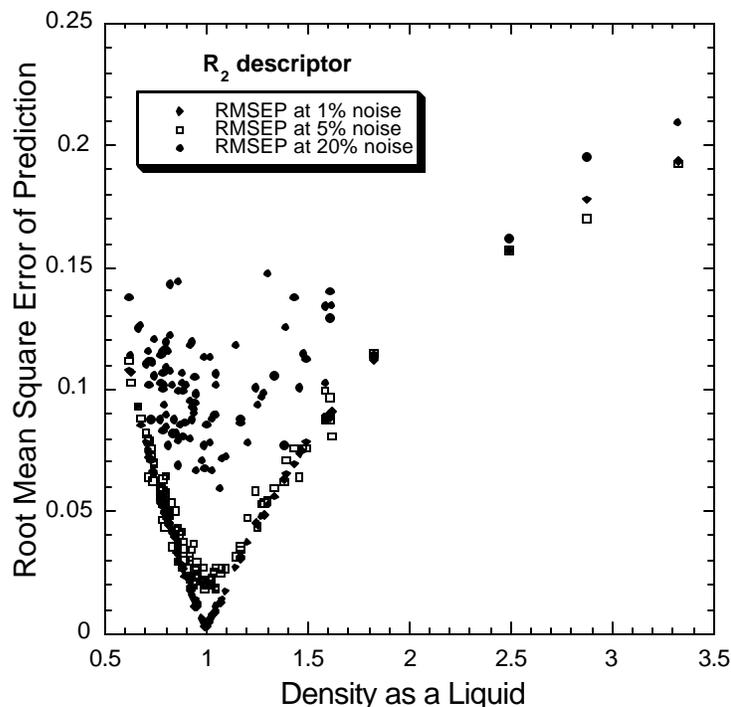
The descriptor-estimation results from S5 obtained using the method in Equation 6.8 were used as initial values for a nonlinear least-squares optimization to obtain better values for the descriptors. These results are shown in Figure 7.5. The optimization gives a rather minor improvement at 20% noise levels, but it provides dramatic improvement in descriptor estimations at low noise levels. Indeed, the results are that the lower noise levels are nearly as good as those for the mass-transducing only case and well below the reference lines on the plot. Thus, optimization can be beneficial at low noise levels but is of little value at high-measurement noise levels.



S5Optimized

Figure 7.5. Simulation Results Giving the Root-Mean-Square Error of Prediction for each Vapor Descriptor at each Imposed Noise Level Plotted Relative to the Left and Right y-axes as Noted in the Figure 7.1 Caption. These results are obtained from the third case where there is variable volume sensitivity across a mass-plus-volume transducing array, the simulations were performed using the volume-sensitivity matrix designated S5 in Table 7.2, and optimization was performed.

The results reported so far are averaged over all vapors in the simulation. However, the estimated solution using Equation 6.8 assumes all vapors have a specific volume as a liquid with a value of one, and hence the density as a liquid is also one. It stands to reason that the closer the actual liquid density is to one, the better the estimates should be. This was confirmed in the simulation using the S5 set of volume sensitivities. Figure 7.6 shows the root-mean-square error of prediction for all the vapors plotted as a function of the density. A clear minimum appears at a density of one, with much larger errors at extreme densities, such as those large values for brominated and iodinated compounds. The effect of density is prominent at 1% and 5% noise; estimates at 5% noise show that estimates at a density of one are ten times better than those at high densities. At the 20% noise level, the density effect is less significant.



S5 Estimated

Figure 7.6. Root-Mean-Square Error of Prediction for each Vapor as a Function of the Vapor's Density as a Liquid, from the same Simulation as in Figure 7.4, i.e., Using the Volume Sensitivity Matrix Designated S5 in Table 7.2

7.5 Array Size

Smaller arrays were also considered. Principal-components analysis of large and small polymer-coated SAW arrays with very diverse polymers have shown that there are at most six principal components.[6] Hence, the responses of well-designed small arrays of six sensors can, in principle, contain chemical information on all the vapor/polymer interactions. However, six sensors is the minimum number with which one can attempt to solve for the five descriptors and log of concentration (i.e., solving for six unknowns with six equations). If there were only five sensors, the $\mathbf{P}_a\mathbf{P}_a^T$ term would be rank deficient and could not be inverted (without using some form of pseudoinverse). One of the requirements for this approach is that the sensor array must be sufficiently diverse to cover all the chemical interactions, and \mathbf{P} must be full rank so that the set of sensors display independent variations in all five polymer parameters.[4] In general, larger numbers of diverse sensors result in \mathbf{P}_a matrices that are better conditioned numerically. Furthermore, combined mass-plus-volume sensitivity complicates the situation considerably for small arrays.

Even in the purely mass-transducing case, simulations with only six sensors gave poor results. Adding more sensors significantly improves the results if one starts with only six. For example, when using nine diverse sensors (leaving out PVPR, OV202, and SXPYR) for the mass-transducing case, the results obtained are much closer to the results originally obtained for twelve mass-transducing sensors (Figure 7.1). Solutions to systems that are just determined (number of equations equals number of

unknowns) are much more sensitive to changes in the data, such as measurement noise, than overdetermined systems. Thus, while having more sensors does not necessarily add new kinds of chemical information, the signal-to-noise is much better.

Simulation (using the estimation method of Equation 6.8) with six diverse polymers with volume sensitivities of either zero or two (i.e., similar to S5 but with fewer sensors) returned very poor results, as expected. Indeed, errors were at least a factor of 10 worse at all noise levels compared to the same simulation with 12 sensors. Optimization does not work in this case to improve results because the problem is solved exactly via Equation 6.8 with no residuals because of the minimum number of sensors in the system. Even with no noise, the solution is perturbed considerably by variation in vapor-specific volume. The volume-sensitivity effect is illustrated in Figure 7.7, which shows the errors of the solutions for a set of hypothetical single vapors, all with the same fixed solvation parameters but varying in vapor-specific volume. The solution is essentially perfect if the vapor-specific volume is one, but errors increase as specific volumes are different from one. If the sensor array were purely mass-transducing, the solution in this no-noise simulation would be perfect at all vapor-specific volumes.

NoNoise 6Sensor Variable Volume Sensitivity

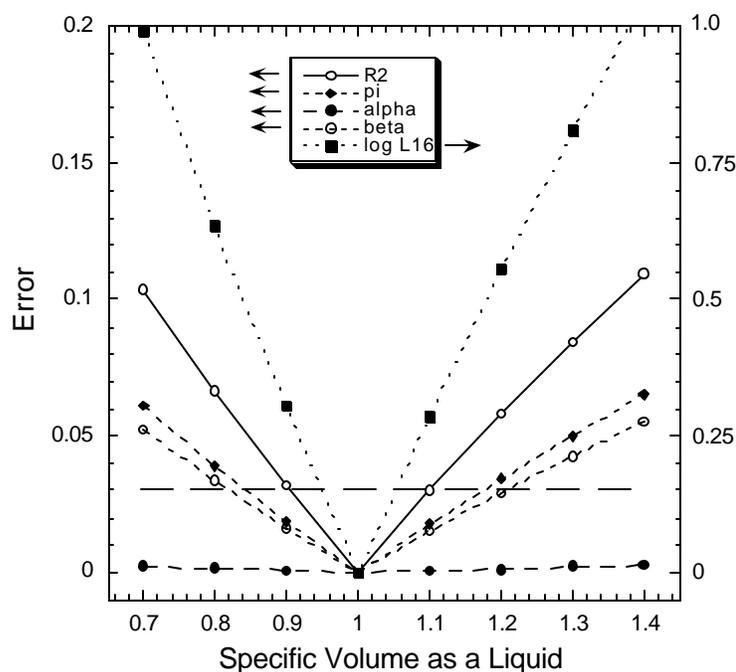


Figure 7.7. Error in the Determination of the Five Vapor Descriptors as a Function of the Vapor-Specific Volume (mL/g) for a Six-Sensor Array with Variable Volume Sensitivity and no Imposed Noise. The specific volume range plotted corresponds to liquid densities from 0.71 to 1.43 g/mL. The horizontal reference line at 0.03 units corresponds to the reference line for the uncertainties in the p_2^H , Sa_2^H , and Sb_2^H parameters as in Figures 3-7.

8.0 Discussion

In general, the results of the derivations and simulations in this paper indicate that these methods can be applied to mass-plus-volume transducing arrays, such as polymer-coated SAW vapor-sensor arrays in the same way the approach is applied to purely mass-transducing sensor arrays. The prediction errors from the estimated solutions depend to some extent on the amount of variation in the volume sensitivities across the array. Thus, some arrays of polymer-coated SAW devices may be better suited for this approach than others. Either minimizing the volume sensitivities (i.e., the polymer modulus change contribution) or matching the volume sensitivities across the array will likely lead to good results. For the case where the volume sensitivities are sufficiently well-matched that the volume sensitivity is a scalar multiple of the mass sensitivities, the method is as good as can be obtained for purely mass-transducing arrays.

Once the descriptors are obtained, they can be compared with descriptors of known compounds as a means of classification and identification. We have previously explored this method using simulations of mass-transducing sensor arrays.[4]

More recently, we used ILS methods to model actual SAW vapor-sensor-array data.[6] In the ILS methods, regression models are developed from training data, where a separate model is developed for each descriptor of interest. Any time a classical least-squares solution exists, inverse least-squares methods should also work. The SAW sensor-array data were correlated very well with each vapor descriptor. At the time the ILS modeling was performed on real data, it was not known to what degree modulus contributions to the observed SAW responses might confound the method. Nevertheless, we found empirically that good ILS models could be developed, and reasonable predictions were obtained in cross-validation experiments.

The derivation and simulation results for classical least-squares methods in this paper indicate that modulus effects should not be a major impediment to estimating vapor descriptors from SAW array data. The results from the simulations demonstrate that solutions, estimations, and/or optimizations exist to obtain results that are as effective as those from purely mass-transducing sensor arrays. The estimation approach (assuming vapor-specific volumes are equal to one) used for obtaining descriptor values has the same form as the closed-form solution for mass-transducing arrays, except that the sensitivity is the total sensitivity rather than strictly the mass-transducing sensitivity. If the estimation method is not precise enough, an optimization approach has been developed to improve the descriptor values obtained.

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