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Selection of polymeric sensor arrays for quantitative analysis

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Abstract

A novel method has been developed to optimize the selection of polymeric materials to be used within a chemiresistor array for anticipated samples without preliminary experiments. It is based on the theoretical predicted responses of chemiresistors and the criterion of minimizing the mean square error (MSE) of the chemiresistor array. After the number of chemiresistor to be used in an array and anticipated sample chemistry are determined, the MSE values of all combinations of the candidate chemiresistors are calculated. The combination which has the minimum MSE value is the best choice. This can become computationally intensive for selection of polymers for large arrays from candidates in a large database. The number of combination can be reduced by using the branch and bound method to save computation time. This method is suitable for samples at low concentrations where thermodynamic multi-component interactions are linear.

Keywords: Chemiresistor; Sensor array; Carbon black–polymer composite; Mean square error (MSE); Sensor selection; Optimization

1. Introduction

Chemical sensor arrays have attracted significant interest for analyzing volatile analytes [1]. Unlike the traditional "lock-and-key" approach, a single chemical sensor array includes a number of cross-reactive sensors. Each individual sensor can respond in various degrees to widely different analytes. The responses of a sensor array to a sample are analogous to spectrophotometer responses in which samples generate various responses at each wavelength measured in the spectrophotometer. If chemical sensor arrays are well calibrated and used along with some chemometric methods, they can provide both quantitative and qualitative information regarding the composition of an analyte mixture. Since the accuracy, selectivity and sensitivity of computed results for given samples are determined by the individual sensor responses within a sensor set, the sensor selection is critical for designing a sensor array that is selective and sensitive.

An interesting sensor that has received much attention is the carbon black–polymer chemiresistor array [1–6]. Its broad responses to analytes arise from the changes of the resistivity of the diverse carbon black–polymer composites which swell in the analyte vapor environment. These carbon black–polymer composites are the elements of the sensor array, and thus must be selected judiciously to ensure accurate and sensitive performance of the sensor. To date, most research efforts on the selection of polymers for carbon black–polymer chemiresistor arrays focus on qualitative classification and identification of the analytes in samples using linear discriminant analysis (LDA) and principle component analysis (PCA) [1,3,7–13]. To our knowledge, no work has been done to select a priori the best chemiresistor set for quantitative analysis of anticipated samples. Some quantitative analysis methods could be applied for these types of devices, such as principle component regression (PCR) and partial least square (PLS) [5,14–17]. However, they are passive methods that are used after a sensor has been constructed. Exhaustive calibration experiments are still necessary before the sensor can be used.

In our previous work, a carbon black–polymer chemiresistor was modeled, and its responses could be predicted by the model [18,19]. In this paper, we introduce an "a priori" chemiresistor selection method which uses the criterion of minimum mean square error (MSE), combined with an algorithm that had been applied previously to optimize wavelength selection [20]. By applying the model predicted responses in this method, the individual polymer elements within a chemiresistor array can be optimized for quantitative analysis of given samples without

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preliminary experiments. This will save a tremendous amount of "trial and error" experimental work.

2. Theory

2.1. Sensor selection method

The primary assumption of this work is that the relationships between the responses of the sensors are a linear function of analyte concentration. This assumption is valid for samples such as ground water contaminated with low concentrations of organic pollutants. For a sensor array having p different sensors, the response output to a sample which is a mixture of m analytes is given by

$$\boldsymbol{r} = \boldsymbol{S} \cdot \boldsymbol{c} + \boldsymbol{e} \tag{1}$$

where $\boldsymbol{r}$ is a $p \times 1$ vector of responses, $\boldsymbol{c}$ is a $m \times 1$ vector of concentrations of the m analytes (in a mixture), $\boldsymbol{e}$ the $p \times 1$ vector of errors, and $\boldsymbol{S}$ is the $p \times m$ sensitivity matrix of the sensor array to the analytes. The element s_{ij} in the sensitivity matrix is the response of the ith sensor in the array to the jth analyte in the sample. Here we set $p \geq m$, so that the problem is not underspecified.

The fundamental criterion by which a model for quantitative analysis should be evaluated is to estimate the different between the predicted values and true values. In this work, the mean square error is used as the criterion for sensor selection. The MSE is defined as [20]

$$\mathrm{MSE} = E\left\{\sum_{k=1}^{m}(c_k' - c_k)^2\right\} \tag{2}$$

where $E\{\cdot\}$ denotes expectation; c_k' and c_k represent the estimated and true concentrations of the kth component, respectively. When a sample consisting of m analytes is given, one wants to select a set of polymers for the sensor array whose response has minimum MSE value.

Since the responses of sensors are estimated theoretically in this study, noise must be added to simulate real sensors. It is assumed that only normal distributed random noise exists and has a constant variance σ^2. In this case, the MSE is given by [20]

$$\mathrm{MSE} = \sigma^2 \mathrm{Tr}\{(\boldsymbol{S}^{\mathrm{t}}\boldsymbol{S})^{-1}\} \tag{3}$$

where $\mathrm{Tr}\{\cdot\}$ and t represent trace and matrix transpose, respectively. We also assume that all sensors have the same variance. In this example, and for simplicity, we will set $\sigma^2 = 1$. Then

$$\mathrm{MSE} = \mathrm{Tr}\{(\boldsymbol{S}^{\mathrm{t}}\boldsymbol{S})^{-1}\} \tag{4}$$

Eq. (4) shows the main advantage of using MSE as the criterion: the value of MSE can be numerically estimated from the information in the sensitivity matrix. Even when $\sigma^2 \neq 1$, Eq. (3) shows that the MSE is the least for a sensitivity matrix which minimizes the right side of Eq. (4).

In practice, given an anticipated sample composition, one can select the best sensors to use in an array as follows. First the user specifies the number of chemiresistors in the array. Then, a computing algorithm computes the MSE values for all possible combinations of p candidate sensors for the expected sample composition. The combination with the minimum MSE value is the best sensor set in terms of the least error for quantitative analysis of the given samples. Thereafter the user can build and calibrate the sensor array, confident that the best polymers have been used in the sensor.

2.2. Construction of sensitivity matrix

Since the MSE value is calculated from the sensitivity matrix, the estimation of the elements in the sensitivity matrix determines the accuracy of sensor. In our previous work [18,19], we modeled the function of carbon black–polymer chemiresistors. The responses of chemiresistor sensors (resistances) to changes in the vapor pressures of analytes are related by combining two sub-models: a conductivity model and a thermodynamic model (Fig. 1). In this present study, it is assumed that all polymer–carbon composites in these chemiresistor arrays have the same conductive properties and geometry, which means that the similar polymer swelling produces similar change of resistance for various polymer–carbon composites. (We recognize that this may not be true for all polymers–carbon composites, but for the purposes of following discussion, we will adopt this assumption.) Thus, the volume fractions of analytes in the swollen composites are regarded as the responses of sensors. We also assume that each individual analyte in samples (which are analyte mixtures) makes an independent contribution to the polymer swelling. In other words, the analyte–analyte interaction in polymer–carbon composites are omitted, and the contribution to swelling of each analyte to the swollen composite in the analyte mixture environment is same as when only the polymer–analyte binary system exists. We define the concentrations as the activities of analytes. Then the value of element s_{ij} in the sensitivity matrix represents the volume fraction of jth analyte in ith polymer composite in a pure jth analyte environment at unit activity. All elements in the sensitivity matrix can be estimated by using experimental data or some group contribution methods, such as UNIFAC-FV [21,22], Chen's method [23] and High–Danner method [24,25].

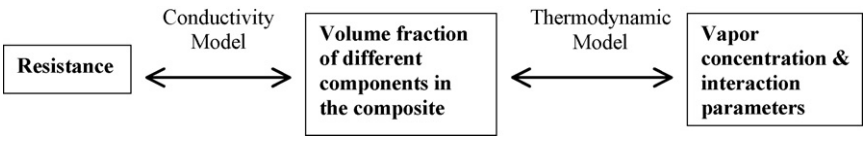

Fig. 1. Modeling chemiresistor by combining the conductivity model and the thermodynamic model.