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Optimum design of sensor arrays via simulation-based multivariate calibration

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ABSTRACT

This paper is concerned with the optimum design of sensor arrays (i.e., electronic noses or tongues) using simulation experiments. The proposed design method considers multiple criteria simultaneously for the evaluation of sensor arrays, and a multiple objective tabu search algorithm was adapted to search for a number of Pareto optimum array designs in terms of those criteria. The evaluation of a candidate sensor array is based on its multivariate calibration model, which is efficiently estimated from well-designed simulation experiments. The method can be used to optimize the design of both linear and nonlinear sensor arrays.

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1. Introduction

Sensor arrays, also known as electronic noses or tongues, are finding wide applications in areas such as environmental monitoring, quality control, and medical diagnosis [1]. One of the major advantages of sensor arrays is their ability to adapt to specific measurement problems; by carefully selecting component sensors, a sensor array is able to identify/quantify a number of target analytes for a particular application. However, when approaching a new sensing problem, usually a large variety of sensor elements are available for selection to form the desired array. How to design a sensor array that has the best performance and lowest complexity is the subject of “array optimization”, the primary interest of this paper. Optimizing a sensor array is challenging mainly due to the existence of a vast number of alternative configurations (combinations), which makes it impossible to test each single configuration by real experiments. The unbearable cost/time likely involved in optimizing sensor arrays via real experiments can be substantially mitigated – if not completely overcome – by the use of simulation, a computer model that mimics sensor responses in various analyte environments.

This paper intends to take advantage of the benefit of simulation, and to adapt statistical methods and optimization heuristics for the optimum designs of sensor arrays. Our method distincts from the existing array optimization work in the following aspects. (i) To the best of our knowledge, this is the first time that the axiomatic

design criteria [2] were adopted to evaluate sensor arrays. In Section 2.2, the similarities between these criteria and those used in the array design literature will be discussed, and the advantages of axiomatic design criteria will also be identified. (ii) A multi-objective tabu search algorithm was adapted to search for a set of Pareto optimal configurations/solutions [3]. Compared to the uniformly used single-objective algorithms in the array optimization literature (e.g., [4,5]), the multi-objective optimization method has clear benefits (detailed in Section 2.4). First, it overcomes the practical difficulties of using a single-objective optimization algorithm to accommodate multiple criteria. Second, instead of giving a single “optimum” design which may well not provide a good balance between multiple criteria, the multi-objective method leads to a set of designs that are diverse and non-dominated to each other, that is, a set of optimum designs in the Pareto sense. The resulting designs allow for further evaluation and selection based on real experiments, and/or non-performance factors such as cost. (iii) Design of experiments (DOE) techniques were used to carry out simulation experiments efficiently for the calibration of candidate arrays. (iv) The proposed method can be applied to optimize both linear and nonlinear sensor arrays.

This work utilizes computer simulation to efficiently select among a potentially large number of sensor combinations the most promising array configurations for a target application. The proposed simulation-based method is intended to perform a pre-selection of array designs, and the resulting small set of selected designs can be further evaluated through other venues such as real experiments, which is beyond the scope of the current work. This is similar in spirit to Lei’s research [6], which shares the same objective but differs in the four aspects above. To illustrate the proposed

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method of array optimization, the class of sensors investigated by Lei and Pitt [6], conductive polymer composite sensors, are used as examples in this paper.

The remainder of the paper is organized as follows. Section 2 details the simulation-based method for optimizing a sensor array. In Section 3, the proposed method was applied to the design of arrays consisting of conductive polymer composite sensors. A brief summary is given in Section 4.

2. Methods

Suppose that the sensor array is designed to quantify p different analytes, the concentrations of which are represented by the $p \times 1$ vector $\mathbf{c} = (c_1, c_2, \dots, c_p)$. Let q be the number of distinct sensors included in the array, and denote the sensor responses by the $q \times 1$ vector $\mathbf{r} = (r_1, r_2, \dots, r_q)$.

Generally, it is required that $q \geq p$, since otherwise \mathbf{c} cannot be identified even from an error free \mathbf{c} [7]. In this work, we assume $q = p$, i.e., the number of distinct sensors is equal to its minimum, the number of different analytes to be detected. This assumption is made out of the following considerations. In this work, the sensor responses \mathbf{r} are simulated from the analytical models (Appendix C), and hence are deterministic. In the deterministic domain, $q = p$ distinct sensors are able to identify p analytes. Recall that our simulation-based array design serves as a preliminary selection for a subsequent optimum design based on real experiments. The latter is beyond the scope of this work, and the goal here is to use simulation to identify potentially promising configurations with each one consisting of p distinct sensors. These p -sensor arrays will further be evaluated through real experiments which, unlike simulation, are subject to random errors that may be caused by measurement variability, temperature shifts, sensor failures, etc. Thus, we consider that sensor redundancy (i.e., $q > p$) will only be explored at the stage of real experiment-based design (unless realistic errors are also part of the simulation model, which is not the case here); that is, through real experiments, each p -sensor array obtained from the simulation approach will be evaluated and possibly expanded to include repeated sensors for improved robustness against random errors. Lastly, the expanded array designs can be evaluated with respect to their accuracy, robustness, complexity, cost, etc., and the one that is best in terms of all those aspects will be chosen for the application.

Assuming $p = q$ in our simulation-based approach, the relationship between \mathbf{c} and \mathbf{r} can be approximated by the multivariate calibration model:

$$r_i = f_i(\mathbf{c}, \boldsymbol{\theta}_i), \quad i = 1, 2, \dots, p \quad (1)$$

where $\boldsymbol{\theta}_i$ represents the unknown parameter vector. The objective of array optimization is to identify p sensors, associated with which a good calibration model $\{f_1, f_2, \dots, f_p\}$ can be obtained and used for accurate and precise prediction of the analyte concentrations of an unknown sample.

Note that in this paper, two different models were developed to quantify the \mathbf{c} - \mathbf{r} relationship. One is the simulation model, a sequence of complicated mathematical equations (Appendix C). The other is a calibration model denoted as (1), which is linear/nonlinear derivable equations of straightforward functional forms. In this work, to optimize array designs without actually building the sensors, simulation models were developed quantifying the \mathbf{c} - \mathbf{r} relationship for sensor arrays with sufficient accuracy. From simulation data, calibration models were obtained providing a good and simple functional approximation to the underlying relationship implied by simulation. The evaluation of each array configuration is based on its multivariate calibration models, as will be seen in Section 2.2.

2.1. Simulation-based multivariate calibration

In this work, the calibration model for a sensor array is estimated from the data collected by running simulation. We discuss two cases, linear and nonlinear arrays.

2.1.1. Linear multivariate calibration

If the sensor responses are linearly dependent upon the concentration of analytes, then a calibration model of the form $\mathbf{r} = \mathbf{A}\mathbf{c}$ is adequate to describe the \mathbf{c} - \mathbf{r} relationship, with $\mathbf{A} = [A_{ij}]_{p \times p}$ being a square matrix estimated from simulation data. Each element A_{ij} is the response of the i th sensor in the array to the j th analyte in the sample. The j th column of the matrix, A_j , includes the responses of the p sensors to the j th pure component analyte.

2.1.2. Nonlinear multivariate calibration

The sensor arrays are much more difficult to calibrate if the dependence of sensor responses upon the multiple analyte concentrations is nonlinear. The nonlinearity mainly stems from two sources: (i) the presence of one analyte affects the way a sensor component reacts to another analyte; (ii) over certain concentration range (typically at relatively high concentration levels), the sensor responds to pure analyte following a nonlinear pattern.

Nonlinear calibration, as general nonlinear regression, is difficult due to the various complications involved in model identification, convergence of nonlinear fitting, etc. [8]. In the literature, a variety of models such as artificial neural nets (e.g., [9]) have been used to calibrate sensor arrays. In such works, efforts are rarely made to provide guidance on the design of experiments (i.e., the efficient data collection), or to ensure that a good model of the simplest functional form is achieved. This is mainly because that these statistical issues are difficult to address for complicated nonlinear models. In this paper, our simulation-based multivariate calibration is to assist the design of sensor arrays at relatively early stage, rather than to provide a highly accurate \mathbf{c} - \mathbf{r} model which can well predict sample components from sensor responses in operational use. In light of this, we chose to use a full quadratic model (2), instead of complicated nonlinear models, to approximate the \mathbf{c} - \mathbf{r} relationship.

$$r_i = \sum_{m=1}^p \theta_m^{(i)} c_m + \sum_{m=1}^p \theta_{m,m}^{(i)} c_m^2 + \sum_{m=1}^{p-1} \sum_{n=m+1}^p \theta_{m,n}^{(i)} c_m c_n \quad (2)$$

$$i = 1, 2, \dots, p$$

Here, $\boldsymbol{\theta}^{(i)} = (\theta_1^{(i)}, \dots, \theta_p^{(i)}; \theta_{1,1}^{(i)}, \dots, \theta_{p,p}^{(i)}; \theta_{1,2}^{(i)}, \theta_{1,3}^{(i)}, \dots, \theta_{p-1,p}^{(i)})$ represents the unknown parameters to be estimated. The interaction terms $c_m c_n$ ($m = 1, \dots, p-1; n = m+1, \dots, p$) intend to capture the possible effects on sensor responses due to the coexistence of two analytes. The quadratic terms are meant to capture the curvature effects of changing an analyte concentration upon sensor responses. Thus, model (2) is able to describe the main characteristics of the \mathbf{c} - \mathbf{r} surfaces. At the same time, (2) is linear with respect to the unknown parameters and thus is much easier to estimate than its complicated counterparts.

To calibrate a sensor array using a model of the form (2), simulation experiments will be carried out at certain values of \mathbf{c} following the central composite design (CCD), which was particularly developed to efficiently collect data for the estimation of a full quadratic model [10]. A graphical illustration of the CCD for a two-analyte case is given in Fig. 1. Once the simulation data has been collected, multivariate least square regression [11] will be performed to obtain the fitted calibration model (2).

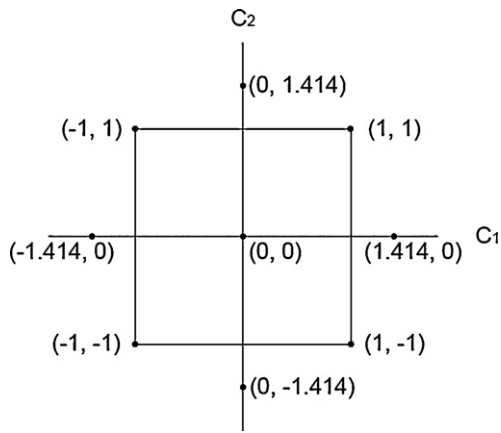


Fig. 1. Central composite design (CCD) for nonlinear calibration model.

2.2. Sensor selection criteria

In this part, we introduce the criteria for evaluating the array configurations based on their multivariate calibration models.

2.2.1. Independence across individual sensors

An ideal sensor array consists of $q = p$ sensors with each component sensor reacting to changes in one of the p analytes exclusively. For such an ideal array, the calibration model (1) can be written as follows (assuming linearity for the model):

$$\begin{pmatrix} r_1 \\ r_2 \\ \vdots \\ r_p \end{pmatrix} = \begin{pmatrix} a_{11} & 0 & \cdots & 0 \\ 0 & a_{22} & \cdots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \cdots & a_{pp} \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ \vdots \\ c_p \end{pmatrix} \quad (3)$$

In the ideal case represented by (3), each individual sensor reacts exclusively to its corresponding analyte independent of the existence of other analytes. Whereas practically, almost all sensors react to multiple analytes to some extent, in which case we need to know the degree of independence among individual sensors in order to evaluate the array configuration. Here, we use the measures of independence developed by [2].

In [2], two measures, reangularity R and semangularity S , were used conjointly to evaluate the functional independence of design alternatives, and they are applicable to both linear and nonlinear design problems. In the general setting of (1), the measures R and S are computed based on the first derivative matrix:

$$\mathbf{D} = D_{ij} = \left[\frac{\partial r_i}{\partial c_j} \right]_{p \times p} \quad i = 1, \dots, p; j = 1, \dots, p \quad (4)$$

The two measures are defined as follows:

$$R = \prod_{\substack{m=1, \dots, p-1; \\ n=m+1, \dots, p}} \left(1 - \frac{\left(\sum_{k=1, \dots, p} D_{k,m} D_{k,n} \right)^2}{\left(\sum_{k=1, \dots, p} D_{k,m}^2 \right) \left(\sum_{k=1, \dots, p} D_{k,n}^2 \right)} \right)^{1/2} \quad (5)$$

and

$$S = \prod_{m=1, \dots, p} \frac{|D_{m,m}|}{\left(\sum_{n=1, \dots, p} D_{m,n}^2 \right)^{1/2}} \quad (6)$$

Reangularity (5) measures the degree of orthogonality of the columns in the \mathbf{D} matrix. The summation in the denominator of (5) are normalization factors, the squared magnitudes of columns; the summation in the numerator is the dot product of the i th and j th columns. Thus, the fraction term can be considered as the cosine of the angle between the i th and j th columns; and the reangularity is the absolute value of the product of the sines of the angles between all pairs of columns in the \mathbf{D} matrix. The measure R achieves its maximum and most desirable value, unity, when the columns are mutually orthogonal. The reangularity measures the ability of a sensor array to discriminate between all the pairs of analytes, and thus is similar in spirit to the selectivity measures used in the chemometrics literature, among which the definition given by Lorber [12] may be the most popular one.

Semangularity (6) measures the degree to which each sensor reacts to one and only one analyte. When all off-diagonal elements are zero, S reaches its maximum and most desirable value, unity. The design quality embodied by the metric S has been largely ignored in the literature of array optimization, regardless of the clear benefits of having S close to one. First, from the perspective of statistical modeling, a calibration model that associates with a diagonal (or close to diagonal) matrix \mathbf{D} , as defined in (4), involves smaller number of unknown model parameters to be estimated since \mathbf{D} includes less non-zero elements. This implies that the estimation of such a calibration model would require a smaller sample [8], and hence save substantial time/cost for data collection. Second, by designing an array in such a way that each sensor is particularly responsive to one analyte, it makes it easy to adapt the current array design to new applications aiming to detect different analyte combinations.

We consider R and S as joint measures of independence among the individual sensors in an array. For an ideal sensor array, both R and S equal to 1, their maximum. When the design deviates from the ideal, the closer the values of R and S and the closer each of them is to 1, the more functional independent is the sensor system [2]. To simultaneously minimize the closeness of R and S as well as maximize their individual values, Thielman and Ge [13] recommended the integrated criterion

$$I = \frac{R + S}{R \cdot S}, \quad (7)$$

which is to be minimized for the optimization of a system's independence property. In our array selection, the criterion I and the sensitivity measure introduced next in Section 2.2.2 will be used as the two criteria to be optimized. The reason that I , as opposed to R and S , is chosen in the optimization problem will be explained in Section 2.4.

2.2.2. Sensitivity to changes in analytes

Sensitivity measures how strongly a sensor responds to analytes of interest. Let D_{ij} be defined as in (4), then the sensitivity of a sensor array to changes in analyte j can be measured as the following root sum square (RSS):

$$RSS_j = \sqrt{\sum_{i=1, \dots, p} D_{ij}^2}$$

The overall array sensitivity to the p analytes is defined as:

$$MRSS = \min_{j=1, \dots, p} RSS_j. \quad (8)$$

The measure (8) is the minimum of the array sensitivity to individual analytes, not the sum of RSS_j used in most literatures. This is to avoid array designs that are highly sensitive to some analytes of interest whereas being insensitive to the others.

2.3. Comparison with the MSE criterion

To evaluate sensor arrays, we use the two criteria defined above, the independence measure I , which integrates R and S , and the sensitivity measure MRSS. The purpose of a sensor array is to quantify analyte mixtures when integrated with its calibration model. So the ultimate criterion for assessing a sensor array should be the ability to accurately predict the analyte concentrations of unknown samples, the measure of which is the well recognized mean square error (MSE):

$$\text{MSE} = E|\mathbf{c} - \hat{\mathbf{c}}|^2 \quad (9)$$

Here \mathbf{c} denotes the true concentration of sample analytes, $\hat{\mathbf{c}}$ the concentration predicted by the sensor array along with the corresponding calibration model, and $|\cdot|^2$ the dot product of a vector. MSE incorporates various types of errors: the bias of the calibration model and the random noise in the calibration and prediction data [14]. Although reflecting the fundamental requirement of sensor arrays, MSE is difficult to evaluate in practice. To estimate (9), the difference $\mathbf{c} - \hat{\mathbf{c}}$ needs to be evaluated via real experiments in a wide range of (if not all possible) values of \mathbf{c} [14], which is unrealistically expensive in terms of time and cost.

Due to the difficulties involved with MSE, alternative criteria have been developed. It has been shown that when the sensitivity (measured by MRSS) and selectivity (measured by R) are good, the deviation of the predicted concentration from the true concentration is small [15]. In our design evaluation, we include an additional measure S , the benefits of which have been explained in Section 2.2.1.

2.4. Array optimization

Different individual sensors can be selected to construct a target sensor array, and the questions that scientists and engineers must answer are: "How does one choose the combination of sensors in the sensor array? Some sensor sets must be better than others, so which set is the best?" In this paper, we are primarily concerned with the pre-selection of array designs using simulation experiments, the role of which in the entire design optimization process has been explained in the beginning of Section 2.

2.4.1. Formulation of the array optimization problem

Suppose that p sensors are to be chosen out of a total of K possible ones to quantify p substances. By the criteria introduced in Section 2.2, we formulate the array optimization problem as follows:

$$\begin{aligned} \text{Objective 1 : } & \min_{\mathbf{x}} I(\mathbf{x}) \\ \text{Objective 2 : } & \max_{\mathbf{x}} \text{MRSS}(\mathbf{x}) \\ \text{Subject to } & x_i = 0 \text{ or } 1, \quad i = 1, 2, \dots, K \\ & \sum_{i=1}^K x_i = p. \end{aligned} \quad (10)$$

This is a multi-objective optimization (MOO) problem, where the decision variables are denoted as the vector \mathbf{x} . We have:

$$\begin{cases} x_i = 1, & \text{if the } i\text{th sensor is selected for the array;} \\ x_i = 0, & \text{otherwise.} \end{cases}$$

For a certain sensor array, the I and MRSS metrics depend on the decision vector \mathbf{x} , and can be evaluated based on its multivariate calibration model estimated from simulation experiments (Sections 2.1 and 2.2).

For an MOO problem, there generally does not exist any single solution which can provide the optimal value on all the objectives, and thus it is of interest to generate a set of non-dominated solutions, where no objective can be improved without worsening at

least one other objective. The set of all non-dominated solutions is referred to as the Pareto optimal front [3], and our goal is to find a set of solutions to (10) as close as possible to the Pareto optimal front.

2.4.2. An adapted multi-objective heuristics

To solve (10) by an exhaustive search, a total of $\binom{K}{p}$ array configurations have to be evaluated. The number of all the possible configurations is typically large, and it could be extremely time-consuming, if not impossible, to explore them all even with computer simulation. Thus, we resort to multi-objective optimization heuristics to solve our array optimization problem in search of Pareto optimal (or near Pareto optimal) solutions/designs. For a complete discussion of various multi-objective heuristics, please refer to [3,16–18]. The existing multi-objective heuristics can usually handle a large decision space (e.g., [19,20]) and work very well on *two-objective* problems, but their search ability severely deteriorates with the increase of the number of objectives [21]. Hence, the heuristics in the current literature are expected to have good performance in solving the two-objective problem (10) that may involve a large decision space (in this case, a large number of potential array designs). Due to the difficulty in solving many (more than two)-objective problems, we formulate the array optimization as a two-objective one by using the integrated independence criterion I and the sensitivity measure MRSS.

Among the existing multi-objective heuristics, we chose the multi-objective tabu search (MOTS) algorithm proposed by Baykasoglu [22] for some simple reasons briefed in Appendix A, and adapted it to solve (10). (Other multi-objective heuristics can substitute the adapted algorithm if demonstrated efficient in search of Pareto optimal array designs.) A description of Baykasoglu's MOTS algorithm, along with our proposed modifications, is given in Appendix A as well. As will be shown in Section 3, the resulting solution set from our modified MOTS is close to the Pareto optimal front, and provides a number of array designs that are non-dominated to each other and superior in terms of both criteria I and MRSS. These selected arrays can then be assessed by weighing the relative importance of the two objectives in (10); also, they can be further evaluated through real experiments.

An MOO algorithm has advantages over its single-objective counterparts, which to the best of our knowledge are uniformly used in the existing array optimization literature (e.g., [4,5]). In those single-objective optimizations, multiple criteria are usually accommodated in two ways: One approach is to form one objective function which is a weighted average of all the criteria; the other is to optimize one criterion while moving the others to the constraint set. There are two major drawbacks with such single-objective methods: (i) In practice, it is usually very difficult to specify good weights or constraining values that reflect the practical need, even for someone familiar with the problem domain. Sometimes small perturbation in those parameters can lead to quite different solutions/designs. (ii) These methods only return a single solution rather than a set of non-dominant solutions, and thus does not provide an adequate candidate pool for further evaluation based on real experiments or non-performance factors such as cost. Aiming at overcoming the drawbacks of the single-objective optimization algorithms, we adapted Baykasoglu's MOTS, which leads to a significantly superior design pool containing diverse configurations that perform best in terms of multiple criteria simultaneously—in the sense of Pareto optimality.

It is also worth mentioning that the use of the new independence measure provides a straightforward way to drive down the number of array alternatives by utilizing prior knowledge. The independence criterion, specifically S , requires that the i th sensor in the

array be most responsive to the i th ($i = 1, 2, \dots, p$) analyte of interest. Hence, the candidates for the i th array component can be limited to a subset of the K sensors that respond well to analyte i . This constraint could substantially decrease the number of candidate configurations, and accelerate the search of the MOTS. A rough idea about the relative responsiveness of each sensor to the target analytes is usually available from prior experience.

To conclude this section, we restate that in this paper, the optimum design of sensor arrays is formulated as an MOO problem, to which the solutions are a set of diverse designs close to the Pareto optimal front. The MOO problem is solved by the modified Baykasoglu's MOTS algorithm, and the evaluation of each design is based on its multivariate calibration model estimated via simulation.

3. Empirical results

This section intends to demonstrate the use of the proposed methods in array optimization for conductive polymer sensors (chemiresistors) designed to detect gaseous analytes. Two simple cases were investigated: one assumes a linear calibration model (Section 3.2), and the other involves nonlinear \mathbf{c} - \mathbf{r} behavior (Section 3.3). Note that these small-scale design examples, for which the potential alternatives are limited and can be easily exhausted, are intended to illustrate the proposed optimum design methods without reflecting the actual size of array design problems.

3.1. Simulation

In this work, the evaluation of sensor arrays relies on simulation rather than real experiments. To simulate the \mathbf{c} - \mathbf{r} relationship, we adopted and adapted the model by Lei et al. [23] which assumes that the response of a sensor to an analyte mixture is a linear combination of the sensor responses to individual analytes. Lei's model is briefly described in Appendix C.1. Relaxing the linear assumption, we adapted Lei's simulation model to accommodate the nonlinear behavior of sensor arrays (the interacting effects of co-existing analytes); see Appendix C.2 for specifics.

3.2. Case 1: A linear \mathbf{c} - \mathbf{r} relationship

We consider the optimal design of a sensor array for the quantification of five gas analytes: p-Xylene, carbon tetrachloride, acetone, n-hexane and THF. Suppose that the polymer candidates available to construct the array include ten materials: polyisobutylene (PIB), polystyrene (PS), isotactic polypropylene (iPP), polyvinyl acetate (PVAC), polymethyl methacrylate (PMMA), polyethylene glycol (PEG), polytetrahydrofuran (PT), linear low-density polyethylene (LLDPE), poly 4-methyl-1-pentene (PMP) and butadiene rubber (BR). Hence, this simple design example amounts to choosing 5 among the 10 polymers.

In this case, there are a total of $252 = \binom{10}{5}$ possible sensor arrays. For a configuration, simulation (using the model in Appendix C.1) can be performed to estimate its linear calibration model $\mathbf{r} = \mathbf{A}\mathbf{c}$ with both \mathbf{c} and \mathbf{r} being 5×1 vectors. The response \mathbf{r} represents the sensor signals with each element being the change of resistivity in an individual sensor. The concentration \mathbf{c} is measured in terms of solvent activity, and it is restricted to the range $\{c_i \in (0, 0.2); i = 1, 2, \dots, 5\}$, within which a linear calibration model is adequate to capture the \mathbf{c} - \mathbf{r} relationship [23]. Once an array is characterized by its calibration model, it can be evaluated based on the I and MRSS metrics.

For instance, for the array configured as iPP-PVAC-PMMA-PEG-PMP, simulation was performed at

Table 1
 The true Pareto optimal set from an exhaustive search.

Index	Configurations	I	MRSS
1	iPP-PVAC-PMMA-PEG-LLDPE	71.686	10.945
2	iPP-PVAC-PMMA-PEG-PMP	68.758	10.556
3	PIB-iPP-PVAC-PEG-PMP	65.536	9.640
4	iPP-PVAC-PEG-LLDPE-PMP	66.367	9.644
5	PIB-iPP-PVAC-PMMA-PEG	70.676	10.942
6	iPP-PVAC-PMMA-PEG-BR	135.260	11.224

Table 2
 The performance of the modified MOTS algorithm (based on 100 macro-replications).

	MOTS	Exhaustive search
Average number of Pareto optimums found	4.94	6
Average number of array configurations evaluated	89.12	252

values of \mathbf{c} determined by the two-level full factorial design [10]. From the simulation data, the calibration $\mathbf{r} = \mathbf{A}\mathbf{c}$ is fitted as follows:

$$\begin{pmatrix} r_1 \\ r_2 \\ r_3 \\ r_4 \\ r_5 \end{pmatrix} = \begin{pmatrix} 5.62 & 9.86 & 0.91 & 10.10 & 4.53 \\ 11.97 & 3.11 & 8.53 & 1.02 & 7.48 \\ 11.45 & 4.17 & 5.18 & 1.18 & 6.80 \\ 2.62 & 7.94 & 4.36 & 0.92 & 11.48 \\ 1.07 & 4.01 & 0.22 & 2.49 & 1.26 \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \\ c_5 \end{pmatrix} \quad (11)$$

The resistivity r_i ($i = 1, 2, \dots, 5$) is given in terms of $\Omega \text{ cm} \times 10^3$. With the fitted model (11), the \mathbf{D} matrix defined in (4) is simply $\mathbf{D} = \mathbf{A}$, and I and MRSS can be calculated using the formulas in Section 2.2.

With the ability to evaluate an array configuration, the modified Baykasoglu's MOTS algorithm (Appendix A) was used to solve (10) in search of the best alternatives. Since the algorithm is a probabilistic one, a different solution (configuration) set may be obtained every time it is run. To show the effectiveness of the method, we applied the MOTS algorithm on (10) for 100 times, and compared the solution set from each of the 100 macro-replications with the true Pareto optimal set obtained from an exhaustive search. Table 1 provides the six Pareto optimums and their performance metrics. Recall that the purpose of the MOTS is to obtain a solution set close to the Pareto optimal one within a reasonable amount of time. Table 2 summarizes the performance of the algorithm based on the 100 macro-replications. On average, by evaluating about one third of the array configurations required by the exhaustive search, the modified MOTS is able to find five out of six Pareto optimums. In addition, out of these 100 runs only five ends up with a solution set including two or less than two Pareto optimums, while 85% of times a solution set with at least four Pareto optimums was obtained. As pointed out in Section 2.4, the small number of non-dominant configurations resulting from the MOTS can be further judged by designers based on the relative importance of I and MRSS or other performance metrics, or be put through real experiments for evaluation.

In addition, to demonstrate that the array configurations that perform well in terms of I and MRSS are also the ones that have good performance in terms of the prediction errors MSE (9), Appendix B provides a set of empirical results.

3.3. Case 2: A nonlinear \mathbf{c} - \mathbf{r} relationship

In this case, we relaxed the simplified linear assumption and accommodate the nonlinearities present in the array system. As pointed out in Section 2.1.2, such nonlinearities are due to interacting effects of co-existing analytes or nonlinear responses of

sensors to pure analyte over a relatively high concentration range. We consider designing a sensor array to quantify two analytes, toluene and methanol. The six polymer candidates available to construct the chemiresistor array are butadiene rubber (BR), isotactic polypropylene (iPP), poly 4-methyl-1-pentene (PMP), polyvinyl acetate (PVAC), polyisobutylene (PIB) and polystyrene (PS). The optimum design of a nonlinear sensor array is essentially the same as that of a linear one (Section 3.2) except that a nonlinear calibration model of the form (2) needs to be used for calibration and evaluation of the array. Hence, in this small example where only a total of $15 = \binom{6}{2}$ sensor combinations are involved, we focus on presenting the nonlinear calibration results for the purpose of illustration.

For an array configuration, the quadratic model (2) is used to calibrate the \mathbf{c} - \mathbf{r} relationship. The analyte concentration (i.e., activity) range is set as 0 to 0.4. To estimate the calibration model, simulation experiments are performed (using the model in Appendix C.2) at the 9 different values of \mathbf{c} following the CCD design (Section 2.1). The location of the design points in the two dimensional space of analyte concentration is shown in Fig. 1, where the three levels of analyte activity, 0.1, 0.2, and 0.3 are coded as -1 , 0 , and 1 respectively. From the simulation data collected, multivariate regression methods are used to estimate the calibration model (2). For instance, the fitted model for design BR-PMP is as follows (with the resistivity response given in terms of $\Omega \text{ cm} \times 10^3$):

$$\begin{aligned} r_1 &= 2.44 + 4.53c_1 + 5.21c_2 - 11.78c_1^2 - 10.65c_2^2 + 11.29c_1c_2 \\ r_2 &= 2.86 + 1.75c_1 - 0.28c_2 - 1.26c_1^2 + 0.82c_2^2 + 1.73c_1c_2 \end{aligned} \quad (12)$$

Based on the fitted calibration model (12) of array BR-PMP, the \mathbf{D} matrix (4) is obtained as:

$$\mathbf{D}(\mathbf{c}) = \begin{pmatrix} 4.53 - 23.56c_1 + 11.29c_2 & 5.21 + 11.29c_1 - 21.30c_2 \\ 1.75 - 2.52c_1 + 1.73c_2 & -0.28 + 1.73c_1 + 1.64c_2 \end{pmatrix} \quad (13)$$

Unlike the linear case (Section 3.2) where $\mathbf{D} = \mathbf{A}$, which is independent of analyte concentrations, the matrix \mathbf{D} for the quadratic model depends on \mathbf{c} . Hence the matrix \mathbf{D} (13), and thus the evaluation criteria, can only be numerically evaluated at a given analyte concentration. To compare different configurations based on these criteria, a set of values for \mathbf{c} , say $C = \{\mathbf{c}_1, \mathbf{c}_2, \dots, \mathbf{c}_n\}$, has to be selected and used to compute $\mathbf{D}(\mathbf{c})$ and subsequently the measures $J(\mathbf{c})$ and $\text{MRSS}(\mathbf{c})$ with $\mathbf{c} \in C$. The selected values in C should be representative in the range of analyte concentrations considered, and the evaluation criteria could be set as the (weighted) average of the measures across the set C .

The optimization scheme is the same as that in Section 3.2. Due to space constraint, we do not provide the details of the optimization results. Interested readers are referred to [24].

4. Summary

This paper integrates a set of system design criteria, a multi-objective tabu search algorithm, experimental design techniques, and multivariate regression to approach the optimum design of sensor arrays based on simulation experiments. For illustration, the proposed methods have been applied to two small design problems, one for a linear array and the other for a nonlinear array.

Table B.3

A comparison of three array configurations.

	Array configurations	J	MRSS	$\widehat{\text{MSE}}$
Worst	PIB-iPP-LLDPE-PMP-BR	2,546,931	2.88	0.8617
Average	PIB-PS-PMMA-PEG-BR	529	8.04	0.0221
Best	iPP-PVAC-PMMA-PEG-LLDPE	72	10.95	0.0072

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Appendix A. The multi-objective tabu search algorithm

In this part, we briefly describe the MOTS algorithm, which is a slightly modified version of the one developed by Baykasoglu [22]. Fig. A.2 outlined the MOTS applied to solve the array optimization problem (10), and is directly modified from the “the flowchart of MOTS algorithm” in [22]. For specifics of the original algorithm, please refer to [22]. The modifications made particularly for our array optimization will be explained later in this section.

We chose Baykasoglu’s MOTS out of the following considerations. First, in the array optimization (10), the search space of the decision variables is clearly defined, and a neighborhood solution can be easily generated by replacing one sensor with another. Hence, applying a tabu search method is fairly straightforward. Second, comparing to other multi-objective tabu search algorithms (e.g., [25,26]), Baykasoglu’s algorithm does not involve a weighting scheme for different objectives, and requires no extra parameters to be specified other than those in the original single-objective tabu search algorithm [3,27].

However, in our experience, running Baykasoglu’s algorithm directly often leads to premature termination of the search with two or less Pareto optimums in the solution set. In light of this, we incorporate in Baykasoglu’s algorithm a modification, which is given in the dotted square in Fig. A.2. The modified MOTS leads to substantial improvement in the sense that more Pareto optimums can be found. (The detailed comparisons are given in [24].) As can be seen from Fig. A.2, two actions are taken to avoid the premature termination of the algorithm: (i) temporarily increase the size of the neighborhood, and (ii) empty the tabu list. Both of them provide a more aggressive search scheme when the current neighborhood is not that promising. Since this scheme requires more candidate evaluations, we may want to control the times of using it depending on the total computational time available at hand.

Appendix B. Empirical comparison of array configurations

As shown in Table B.3, three array configurations were selected representing the worst, average, and best configuration in terms of the adopted design criteria, J and MRSS. Recall that the proposed array optimization seeks to minimize J and maximize MRSS.

The last column of Table B.3 provides the estimated MSE for each configuration, which is obtained as follows. A test data set, denoted as $\{\mathbf{c}_n, \mathbf{r}_n; n = 1, 2, \dots, N\}$, is obtained by performing simulation experiments (subject to random errors) at $N = 4^5$ evenly spaced grid points in the 5-dimensional feasible region for the concentration vector \mathbf{c} . For each array configuration, the N array responses $\{\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N\}$ were fed to its multivariate calibration model to obtain the predicted concentrations $\{\widehat{\mathbf{c}}_1, \widehat{\mathbf{c}}_2, \dots, \widehat{\mathbf{c}}_N\}$. The MSE of the array,

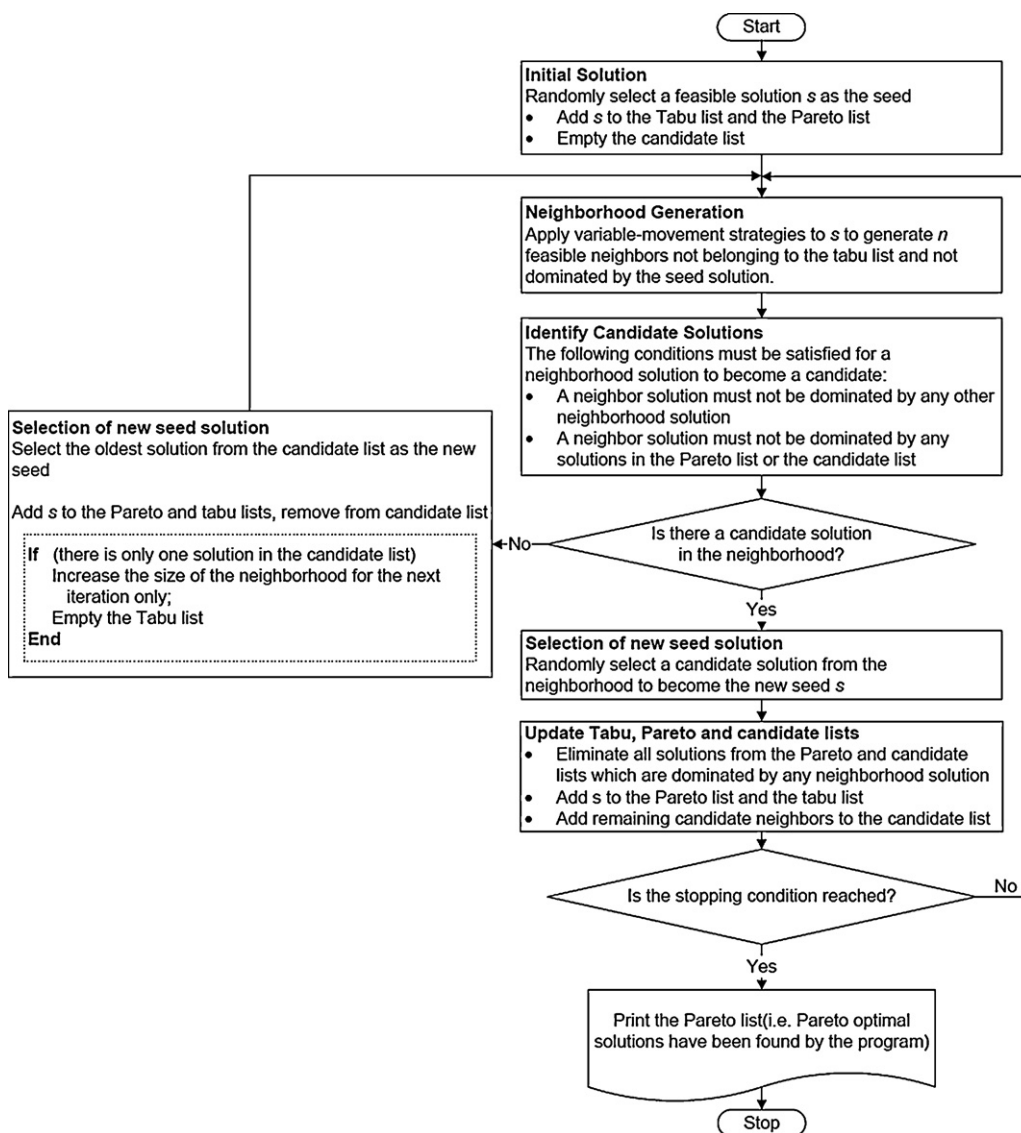


Fig. A.2. The flowchart of the modified MOTS algorithm (adapted from Baykasoglu's work [22]).

which is defined in (9), is estimated as follows:

$$\widehat{MSE} = N^{-1} \sum_{n=1}^N |\mathbf{c} - \hat{\mathbf{c}}|^2$$

Note the relative size of the estimated MSE for the three configurations (Table B.3). The empirical results show that the sensor arrays that perform well in terms of the *I* and MRSS metrics are also likely to be the ones that are superior in terms of MSE.

Appendix C. Simulation models

We present the simulation model for the conductive polymer composite sensors (chemiresistors). A chemiresistor responds to analytes by producing a change in the composite resistivity in exposure to a vapor environment containing the analytes, and the sensor responses depend on the conductive and thermodynamic properties of the composite and analytes. To simulate the responses of a chemiresistor, Lei et al. [23] developed a model consisting of two sub-models, as illustrated in Fig. C.3. The thermodynamic model relates the vapor concentration to the volume fraction of each com-

ponent (the polymer and the analytes absorbed by the polymer) in the composite. The conductivity model associates the volume fraction of the different components in the the composite with the resistivity of the composite, which is the sensor signal. With these two sub-models combined, the relationship between analyte concentrations in the vapor and the resistance changes in the composite sensor can be simulated.

The rest of the appendix is divided into two parts. In Appendix C.1, we briefly describe the simulation model in Lei et al. [23], which assumes that the sensor response to a mixture of several analytes is a linear accumulation of the influence from each individual analyte. In Appendix C.2, we inherit the sub-model scheme (Fig. C.3), and adapt Lei et al.'s model to accommodate the interacting effects between two analytes due to their co-existence in a sample. The

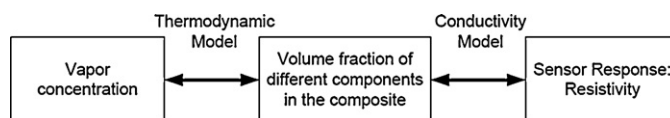


Fig. C.3. Associating the inputs and outputs of the chemiresistor by combining the two sub-models.

models in Appendix C.1 and Appendix C.2 will be referred to as linear and nonlinear simulation models respectively.

C.1. The linear simulation model

The simulation model of Lei et al. [23] is based on the assumption that in the presence of more than one analyte, each analyte acts independently and the resulting sensor signal is a linear accumulation of the effects of multiple analytes. Hence, the basic building block of the simulation model in Lei et al. [23] is an analyte–polymer binary system, for which the two sub-models are detailed as follows.

C.1.1. Thermodynamic model

The thermodynamic model is based on three assumptions [23]: air absorbed by the carbon black does not change the resistivity of the carbon black; non-reactive carrier gas (e.g., air) has negligible solubility in polymer and thus no effect on polymer swelling in the composite; and polymer swelling reaches equilibrium.

For an analyte–polymer binary system, the relationship between the vapor concentration, which is measured as the activity a_{analyte} , and the volume fraction of the analyte absorbed by the composite, which is denoted by ϕ_{analyte} , is quantified by the following equation:

$$\ln(a_{\text{analyte}}) = \ln \phi_{\text{analyte}} + \left(1 - \frac{V_{\text{analyte}}}{V_{\text{polymer}}}\right)(1 - \phi_{\text{analyte}}) + \chi(1 - \phi_{\text{analyte}})^2. \quad (\text{C.1})$$

V_{analyte} and V_{polymer} represent the molar volume of the analyte and polymer respectively, and χ is the analyte–polymer interaction parameter. Eq. (C.1) was derived by Tompa [28] based on the Flory-Huggins theory for polymer solutions. The parameters involved in (C.1) can be obtained from published literature [29,30].

C.1.2. Conductivity model

The conductivity model associates the composite resistivity ρ_m (the sensor response) with the volume fraction of the analyte/polymer in the composite through the general effective media (GEM) equation developed by McLachlan [31]. The GEM equation is given as:

$$\frac{\rho_c(\rho_c^{-1/k} - \rho_m^{-1/k})}{\rho_c^{-1/k} + C\rho_m^{-1/k}} + \frac{(1 - \rho_c)(\rho_p^{-1/k} - \rho_m^{-1/k})}{\rho_p^{-1/k} + C\rho_m^{-1/k}} = 0 \text{ with } C = \frac{1 - \phi_{\text{critical}}}{\phi_{\text{critical}}} \quad (\text{C.2})$$

where ϕ_{critical} is the critical volume fraction of the carbon black or percolation threshold, ρ_c the resistivity of the carbon black, ρ_p the resistivity of the polymer, ϕ_c the volume fraction of the carbon black, $1 - \phi_c$ the sum of volume fraction of polymer and absorbed analyte, and k a constant related to the physical structure of the sensor (e.g. the surface area).

In an analyte–polymer binary system, volume fraction of analyte ϕ_{analyte} absorbed in the composite and the volume fraction of the carbon black has the following relationship [23]:

$$\phi_{\text{analyte}} = \frac{\phi_{0c} - \phi_c}{(1 - \phi_c)\phi_{0c}} \quad (\text{C.3})$$

where ϕ_{0c} is the volume fraction of the carbon black in the dry composite.

Combining (C.2) and (C.3), the relationship between the volume fraction of analyte ϕ_{analyte} and the composite resistivity ρ_m is established. All the parameters involved in (C.2) and (C.3) can be obtained from the empirical results in the existing literature.

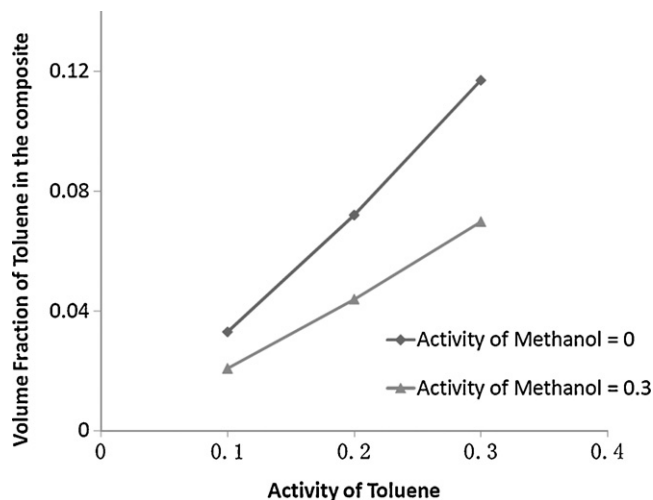


Fig. C.4. Activity of toluene with different vapor concentrations of methanol.

C.2. The nonlinear simulation model

We adapted the linear simulation model in Lei et al. [23] to accommodate the interacting effects due to the co-existence of two analytes in a gas environment. Thus, we consider a system that incorporates two different types of analytes and one polymer sensor.

The thermodynamic model for such a ternary system is given as [32]:

$$\begin{aligned} \ln(a_1) &= \ln \phi_1 + 1 - \phi_1 - \frac{V_1}{V_2}\phi_2 - \frac{V_1}{V_3}\phi_3 + (\chi_{12}\phi_2 \\ &+ \chi_{13}\phi_3)(\phi_2 + \phi_3) - \chi_{23}\frac{V_1}{V_2}\phi_2\phi_3 \\ \ln(a_2) &= \ln \phi_2 + 1 - \phi_2 - \frac{V_2}{V_1}\phi_1 - \frac{V_2}{V_3}\phi_3 + (\chi_{12}\frac{V_2}{V_1}\phi_1 \\ &+ \chi_{23}\phi_3)(\phi_1 + \phi_3) - \chi_{13}\frac{V_2}{V_1}\phi_1\phi_3. \end{aligned} \quad \sum \phi_i = 1 \quad (\text{C.4})$$

Subscripts 1, 2, and 3 refer to the first analyte, the second analyte, and the polymer respectively. Specifically, a_i denotes the activity of the component i , ϕ_i the volume fraction of component i in the composite, V_i molar volume of component i , and χ_{ij} the interaction parameter between component i and j ($i = 1, 2, 3; j = 1, 2, 3; i \neq j$). Note that when the second analyte has little solubility in the polymer, we have $\phi_2 \approx 0$, and the system is reduced to a binary system with Eq. (C.4) simplified to the form given in (C.1).

Take the toluene–methanol–PVAC ternary system as an example. Fig. C.4, which is based on the experimental data obtained in Yilmaz [32], shows that due to the presence of methanol, the solubility of toluene in PVAC is substantially lowered, and the sensitivity of toluene solubility to changes in the toluene activity is also reduced. The linear simulation model given in Appendix C.1 is not adequate to describe the interacting effects due to the co-existence of analytes.

To the best of our knowledge, the simulation model presented here represents the first effort to simulate the sensor responses of a chemiresistor while taking into account the interacting effects of two analytes in a vapor mixture.

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