

Characterization of the ability of polymeric chemiresistor arrays to quantitate trichloroethylene using partial least squares (PLS): effects of experimental design, humidity, and temperature

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Abstract

Polymeric chemiresistors are a class of chemical sensor that have promise for being practical in situ sensors of volatile organic compounds (VOC) in various environmental monitoring applications. However, these devices may undergo changes in response due to changes in temperature or humidity that must be taken into consideration when developing calibration models. The devices can also display significant hysteresis effects after exposure to VOC vapor. These effects are complicated by the fact that each sensor within an array is coated with a different polymer, each with a different response to temperature, humidity, and VOC exposure. It is shown that partial least squares (PLS) can provide quantitative predictions of trichloroethylene (TCE) using an array of chemiresistors through appropriate experimental design. Effects of humidity and temperature on the response of chemiresistor arrays and predictive ability of PLS are also discussed. It is also shown that to truly assess the quality of a calibration model it must be first tested through prediction of a test set at a time separated from the acquisition of the calibration data. Using only leave-one-out cross-validation results from the calibration can lead to unwarranted confidence in a model that is not stable with respect to changing environmental conditions and device drift.

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1. Introduction

Numerous sites that are either contaminated with toxic chemicals or have the potential to release contaminants into the environment require characterization and long-term monitoring to protect the environment (air, soil, or water) and to determine when remedial measures are needed. Current monitoring methods that require grab samples and off-site analysis are costly and time-intensive, and limitations in sampling and analytical techniques exist. Measured concentrations using these ex situ methods can therefore be lower than actual in situ concentrations.

An attractive alternative is the use of real-time sensors that can be placed in situ, which would reduce the need for sample collection and expensive off-site analyses. Emerging technologies and sensors are becoming available that may be viable for these long-term in situ applications [1,2]. However,

the development and demonstration of these new microsensors and systems have been typically conducted under well-controlled laboratory environments. Few have been tested under realistic conditions of varying temperature, pressure, and humidity induced by diurnal or seasonal fluctuations.

A promising technology for in situ environmental monitoring involves the use of polymeric chemiresistor arrays. Chemiresistors are manufactured by dissolving a chemically sensitive polymer in an appropriate solvent and mixing the dissolved polymer with conductive carbon particles. The resulting “ink” is then deposited and dried onto thin-film platinum traces on a solid substrate (i.e., a microchip). When chemical vapors come into contact with the polymers, the vapor absorbs into the polymers, causing them to swell. The swelling changes the resistance of the electrode, which can be measured and recorded. The amount of swelling correlates to the concentration of the chemical vapor in contact with the chemiresistor [3]. The process is reversible if the chemical vapors readily desorb, but some hysteresis and drift can occur [4,5] and is similar to what is seen for similar

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polymer coatings on surface acoustic wave (SAW) sensors. Chemiresistors coated with different polymeric materials can be placed in an array to provide a pattern of responses specific to a chemical or class of chemicals. An attribute of chemiresistors is that they are simple devices with no mechanical parts, which reduces the chances of failure during applications in remote environments. Current applications of the technology include those for groundwater remediation efforts at sites with high TCE contamination. Detection of TCE vapor in the several hundred to several 1000 ppm range is desirable and readily obtainable with the chemiresistors described in this paper [6]. To further improve the quantitative results, preconcentrator technology is currently being explored in our labs to make the device practical for remote atmospheric sensing.

Many previous studies involving the use of polymeric chemiresistors for detection of organic vapors have focused on qualitative multivariate pattern recognition techniques that aim to identify analytes of interest [7–12]. While this is an extremely valuable application of the sensors, for the purposes of environmental monitoring it is necessary to both identify the compound and give information about its concentration. Multivariate data analysis techniques such as partial least squares (PLS) are well suited to this type of problem and have been used for understanding and pattern recognition of SAW response to organic vapors [13–15]. Data from all chemiresistor sensors, including the internal temperature sensor, can be efficiently used simultaneously to calculate the concentration of the analyte. In addition, since all the sensors are analyzed simultaneously PLS can reject extraneous signals, i.e. outlier responses, very efficiently. To date, most of the reported results for chemiresistor arrays have focused on calibration behavior. The next step is to determine the predictive behavior of these arrays. In this paper we focus on three areas of concern for long-term prediction: experimental design, validation and changing environmental conditions.

An important issue in developing robust calibration models for polymeric-based sensors is developing an experimental design that does not allow sensor drift or hysteresis to be confused with analyte signal. Proper experimental design can greatly enhance the predictive ability of multivariate calibration models [16]. This is particularly important with polymeric chemiresistors where irreversible swelling caused by exposure to solvent vapor increases the baseline offset in the sensor response. Often, due to the time involved in equilibrating sensor arrays, no experimental design is followed during the calibration phase. Rather, concentration of an analyte is increased or decreased in sequential order. Models resulting from a sequential (non-designed) experiment will incorrectly associate sequential hysteresis and drift with the change in concentration. The end result is a model that shows good behavior in calibration but is much less robust in prediction. By simply randomizing the sample sequence and including repeat samples the robustness of the model can be greatly improved.

It is also important to develop calibration models that take into account changing environmental conditions such as temperature and humidity. Changes in temperature and humidity effectively act on the array as non-target analytes, since changing these conditions induces a volume change in the polymer films similar to what is caused by sorption of organic vapors. Such volume changes are proportional to the change in DC voltage measured by the chemiresistor [3]. To our knowledge only one study has explored the effects of humidity, using univariate methods to correct for changes in the sensor response with humidity [19].

In addition to employing a sound experimental design it is also best to test the predictive ability of the model on a test set of data acquired some time after the calibration set. Simply relying on the results of a calibration that employs a leave-one-out cross-validation can lead one to believe the model is more robust in prediction than it actually is. For the case of the polymeric chemiresistors, drift is observed as an increase in resistance with time that may be caused by changes in the conductive pathways of the carbon particles due to polymer aging. Polymer aging has also been cited as one of the factors giving rise to drift observed in SAW devices [17], thus it is reasonable to assume that polymeric chemiresistors may suffer similarly. Other types of chemiresistors, however, have been found to be quite stable over time [18].

2. Methods

Fabrication of the chemiresistors used in this study has been described in detail elsewhere [7] but a brief description is warranted. The prepared chemiresistors contained 40% of 20–30 nm size graphitized carbon black (Polysciences) by weight; 0.06 g of polymer to 0.04 g of graphite. The chemiresistor array used in this study consisted of four different materials, polyepichlorohydrin (PECH) (Aldrich), polyisobutylene (PIB) (Aldrich), PECH doped with Spruso (OMG Americas, Inc.) surfactant, and PIB doped with Spruso (OMG Americas, Inc.) surfactant. For typical 5 ml polymer inks, 0.05 g of surfactant was added. Response of each of the materials to trichloroethylene (TCE) (Fisher) was found to be unique. The array also contained an internal temperature sensor, a thin film platinum wire.

Exposure of the chemiresistor array to TCE was accomplished through the use of a nitrogen gas stream passing through gas-washing bottles filled with TCE. A ceramic frit at the bottom of the bottle allows the nitrogen gas to be broken into a fine stream of bubbles (system designed in-house). Intimate contact between the liquid analyte and the gas bubbles allowed the gas stream to exit the bottle in a saturated condition. Analyte concentration was controlled by dilution using a set of mass flow controllers (Brooks Instrument 5850E). Conversion of percent TCE of saturated vapor pressure to parts per million (ppm) was done through the use of Antoine equation [20]. Temperature of the bub-

blers was continuously monitored internally to account for evaporative cooling with time. This temperature was used in the Antoine equation so that effects of temperature fluctuations on the concentration of TCE exposed to the array could be taken into account. The concentration range for this study was 1000 to 10 000 parts per million (ppm) TCE.

Chemiresistor response to an exposure was obtained by recording the changes in two-wire electrical resistance. For all experiments, electrical resistances and thermocouple measurements were taken using a Hewlett Packard 34970A digital multimeter and recorded by a LabVIEW[®] program on an Apple Macintosh[®] computer. Temperature of the chemiresistor array was controlled via a laboratory oven (Fisher Scientific) and temperature was monitored with the temperature sensor internally housed in the chemiresistor array. In order to account for fluctuations and run to run variance of the temperature, temperature measured by the internal temperature sensor in the array was included as a channel in the PLS calibration models. Typical temperature variations are ± 1 °C. The response of the resistors was calculated as a percent change from the baseline resistance to the response to the analyte vapor as shown in Eq. (1) below [7,8]

$$\frac{\Delta R}{R} (\%) = \frac{R_{\text{response}} - R_{\text{baseline}}}{R_{\text{baseline}}} \times 100 \quad (1)$$

R_{baseline} is defined as the average resistance of the last 10 raw response points prior to the rapid increase in resistance due to introduction of TCE to the array (see Fig. 2). R_{response} is defined as the average resistance of the last 10 raw response points prior to the sudden decrease in resistance due to the introduction of pure nitrogen to the array (see Fig. 2). By calculating the R_{response} value just prior to the introduction of pure nitrogen allows for maximum equilibration of the sensors with the TCE vapor and gives improved precision to the results.

Data acquired from the test bed was then transferred to Microsoft Excel[®] and finally to text format for export into Matlab[®] version 6.1. All data analyses were carried out in Matlab[®] 6.1 or in an in-house PLS routine written to operate in a GRAMS32[®] environment [21]. All calibrations and predictions were carried out on a Dell personal computer with a Pentium 3 processor. During PLS calibration, samples were excluded as outliers if their response residuals, predicted data subtracted from all other data, yielded an F -ratio significantly different from the rest of the data (also known as F -test) [21]. The response F -ratio is a comparison of the squared residuals for the responses of all samples minus the one of interest [22]. If this ratio is significantly distinct from the rest of the data then that sample is statistically distinct from the rest of the data and can be treated as an outlier.

At TCE levels of 10% or greater saturated vapor pressure, response of the chemiresistors exhibited nonlinear behavior [7]. In order to improve the reliability of quantitation at these concentrations, the raw response was converted to the \log_{10} of the raw response to reduce the non-linearity in the data,

prior to applying Eq. (1). This is an empirical pretreatment of the data that has provided consistent results for PLS analysis. Since the error in the raw data readout is 50–100 times less than the shot to shot response variance of the array at the lowest concentration this procedure introduces negligible error into the concentration predictions.

2.1. Sampling sequence

Simply increasing concentration exposures in sequential order, 1000, 3000, 5000 ppm of TCE, etc. during calibration, can incorporate drift, such as changes due to sensor electronics or unmonitored changes in the experimental apparatus, into the calibration model. This can lead to the correlation between the response from these interferent variables and the response of the analyte. If the correlation changes or is absent when the model is used for prediction, a systematic error will occur. Randomization of the sampling sequence can help force the relationship between sensor drift and the response of the analyte to be independent within the calibration model. Also, hysteresis (sensor response not returning to the baseline after exposure to analyte) in the sensor is less likely to be confounded with analyte signal. Addition of repeat samples at long and short intervals can allow the calibration model to compensate for shot-to-shot imprecision and effects of long-term drift or hysteresis. In order to demonstrate the effect between experimental designs that are non-designed to those that are designed, the experimental designs in Table 1 were used. The designed experiment was proposed to improve the analytical significance of calibration data (Table 1b). Included in the designs were four different environmental conditions, E1–E4, listed in Table 1. The temperatures listed in Table 1 are design points. Experimental temperatures were recorded. The sequential (non-designed) calibration method (Table 1b) was what had

Table 1

Non-designed experiments were acquired in the order E3, E1, E2 and E4 and designed sequences^a

Environmental condition	TCE \times 1000 (ppm)
Non-designed sequence	
E1	1 1 1 1 3 3 3 3 5 5 5 5 10 10 10 10
E2	1 1 1 1 3 3 3 3 5 5 5 5 10 10 10 10
E3	1 1 1 1 3 3 3 3 5 5 5 5 10 10 10 10
E4	1 1 1 1 3 3 3 3 5 5 5 5 10 10 10 10
Designed sequence	
E1	5 10 3 7 1 5 5 10 3 7 1 5
E1	5
E2	1 5 7 3 10 1 1 5 7 3 10 1
E1	5
E3	10 3 5 1 7 10 10 3 5 1 7 10
E1	5
E4	3 1 10 5 3 7 3 1 10 5 3 7
E1	5

^a E1 is 31 °C and 0% relative humidity; E2 is 31 °C and 100% relative humidity; E3 is 23 °C and 0% relative humidity; E4 is 23 °C and 100% relative humidity.

been previously used to calibrate the chemiresistor arrays. Check standards of 5000 ppm TCE at condition E1 were also run to check the stability of the sensors after exposure to each environmental condition. Building such standards into the experimental design is critical to insure that any hysteresis caused by cycling the chemiresistor arrays through the various environmental conditions can be incorporated into the calibration model. It should be stressed that in order for an experimental to be truly rigorous the range of environmental conditions expected in field operation must be included along with the means of assessing the effect of different environmental conditions on the sensors [16]. Two additional check standards were also incorporated into the PLS calibration of both designed and non-designed runs at 31 °C and 0% humidity (E1), allowing more temperature conditions (29.9 and 30.5 °C) to be sampled. For these conditions, this led to more robust PLS predictions with temperature variations.

While the non-designed (sequential) sampling does contain repeats, they only provide useful analytical information between the first and last repeat at a given concentration. Random drift or severe hysteresis over the entire run cannot be modeled well with this type of repeat sample. The designed experiment has a random sampling sequence that repeats once to give a large number of repeat samples throughout the calibration run. This use of repeats allows drift over both the short term and long term to be incorporated into the calibration model. All sequences listed were run initially over the course of 20 days. The designed sequence was run again 45 days from the mid point of the original calibration runs in order to assess long-term predictive ability of the models created from the original designed and non-designed data.

2.2. Partial least squares

PLS has been thoroughly described in other Refs. [21,23] but a brief discussion is warranted for this study. All data are mean centered, which is simply the subtraction of the mean response of the chemiresistor array for the given responses in a data set from all the response in the data set. Concentration data is also mean centered. Mean centering improves the precision of the PLS analysis. A data matrix of $\Delta R/R$ (%) responses, \mathbf{R} , containing n samples by five rows (number of resistor channels plus temperature) can be written as

$$\mathbf{R} = \mathbf{S}\mathbf{L} \quad (2)$$

where \mathbf{S} is the matrix of PLS scores that contains information correlated to analyte concentration and \mathbf{L} is the matrix of PLS loading vectors that contains information about response of the chemiresistors to the analyte of interest. The PLS algorithm finds the fewest number of factors that describe \mathbf{R} via a factor analysis technique that maximizes covariance between the concentration dimension and the response dimension. The number of response channels in the chemiresistor array, 5, limits the number of factors that can

be determined. In addition, mean centering the data reduces the number of factors by 1. Once the correct number of factors is chosen [21], the resulting PLS regression coefficients are used to predict the unknown concentrations of the analyte through simple matrix multiplication:

$$\hat{c} = r_{\text{unk}}b + c_m \quad (3)$$

where \hat{c} is the estimated concentration, r_{unk} is the vector of chemiresistor responses, and b is the vector of coefficients, and c_m is the mean concentration of the calibration samples.

All calibrations employ a leave-one-out cross-validation routine. This means one sample is left out of the calibration set, a calibration model is constructed using the remaining data, and the concentration of the sample left out is then predicted. This procedure provides some protection against constructing a calibration model that over fits the data. In order to compare the quality of fit between separate PLS models and to estimate the uncertainty in prediction, the cross-validated standard error of prediction (CVSEP) is used, CVSEP is the root-mean-square error between the known concentration and the predicted concentration for a given cross-validated calibration model. For prediction, an SEP is obtained which is just the root-mean-square error between the reference concentration and the predicted values.

An F -test was used to determine if the results from the designed sequence were statistically different from the non-designed results. F -test ratio is the variance of two data sets to determine if a statistically significant difference exists between the two data sets. For this study if the F -test between the variance of the two sample sequences yielded a ratio whose value exceeded the 0.05 level it was considered statistically significant.

3. Results and discussion

3.1. Effects of temperature and humidity on chemiresistor response

Effects of humidity and temperature on the chemiresistor response to TCE are clearly shown in Fig. 1. As the humidity increases there is a decrease in the response of the individual chemiresistors to the TCE vapor, Fig. 1a. This decrease in response seems to be due to the uptake of water vapor by the chemiresistors, which causes swelling of the polymer and correlates to a higher baseline resistance [3]. This correlates to a lower percent change in the resistance (see Eq. (1)) since actual change in response to the TCE is less dramatic. The PECH chemiresistor (sensor 2) also shows a very slight decrease with increased humidity, although not evident on the scale of Fig. 1. With an increase in temperature the response of the chemiresistor to TCE decreases, Fig. 1b. This is due to two effects: first as temperature increases the baseline resistance changes due to thermal expansion of the polymer film, with subsequent rearrangement of the carbon

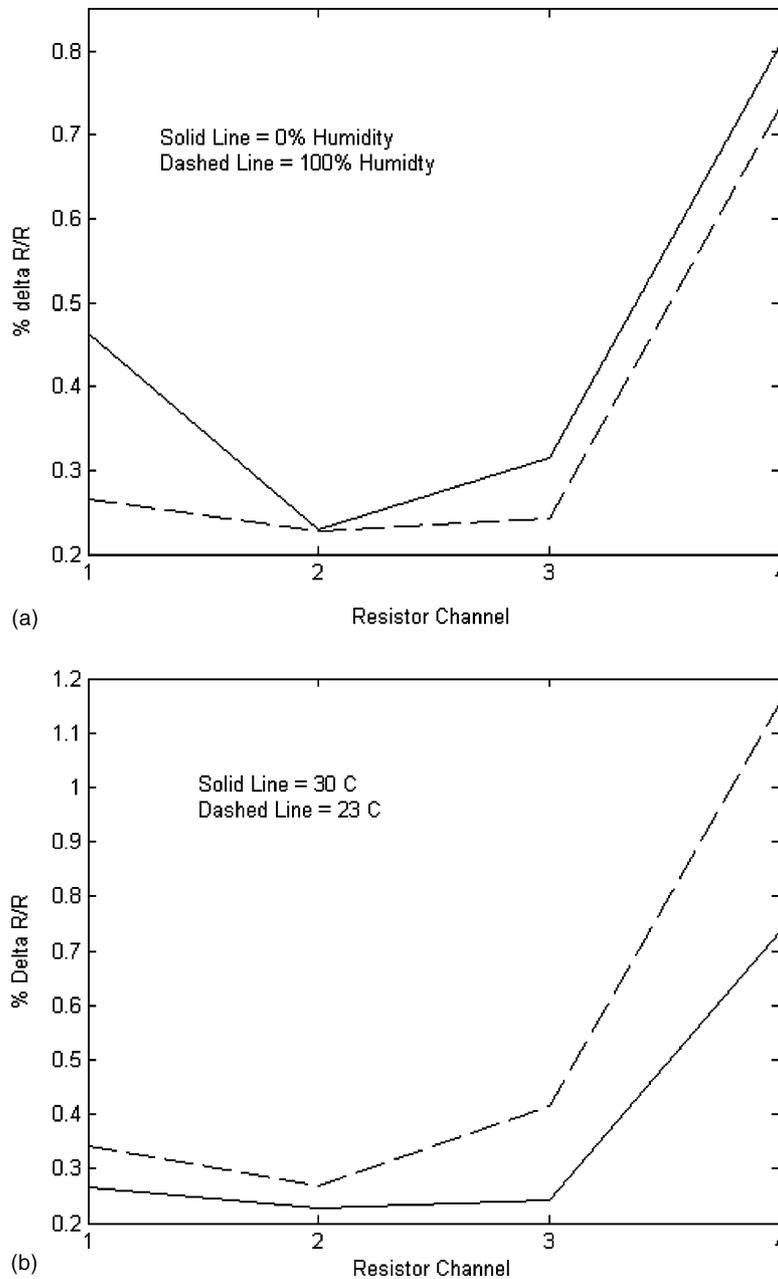


Fig. 1. Response of chemiresistor array to 7000 ppm TCE vapor under the conditions of: (a) 0% (solid line) and 100% (dashed line) humidity at 31 °C, (b) 100% humidity at 31 (solid line) and 23 °C (dashed line). Data are in the form of $\Delta R/R$ (%) of the \log_{10} of raw resistance data, and were taken from the rigorous sequence. The polymers are in the order PIB, PECH, PECH Spruso, and PIB Spruso.

particles. Secondly, at elevated temperatures the adsorption of TCE within the polymer material changes relative to the room temperature results. While adsorption of the TCE vapor into the polymer coatings is expected to obey percolation theory to first order [12], a more complex response due to temperature and humidity changes is not unreasonable to expect. In fact, polymeric resistive devices have shown very non-linear effects with varying humidity [24,25].

Examples of chemiresistor (PECH) response to TCE vapor at concentrations ranging from 1000 to 10 000 ppm of TCE for both a designed and non-designed sampling sequence are shown in Fig. 2 at condition E1, 31 °C, 0%

humidity. It can be clearly seen that there is a constant hysteresis in the chemiresistor response with increasing TCE concentration in the case of the sequential exposures (Fig. 2a) in that the response does not decay to the baseline. Any method used for modeling the behavior of the chemiresistor would be biased by the hysteresis behavior. Also, if baseline drift underlies the response, due to fluctuations in sensor electronics, the non-designed sequence will not be able to separate it from analyte signal. While the designed sequence also shows some drift with increasing TCE concentration, Fig. 2b, the effects are mitigated by the experimental design. This type of hysteresis is not limited to

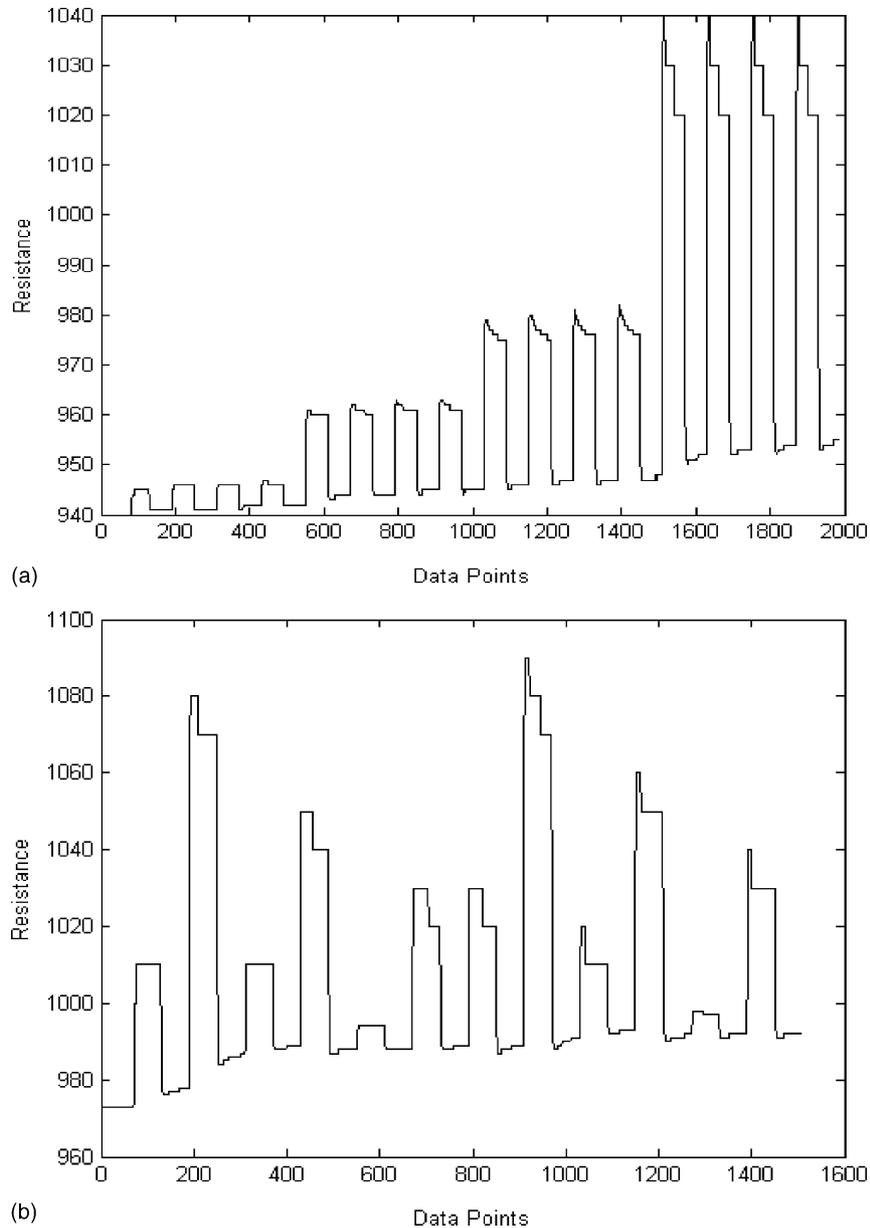


Fig. 2. Response of PECH chemiresistor to TCE vapor employing at condition E1, 31 °C, 0% humidity using (a) the non-designed sequence with exposure to 1000, 3000, 5000 10 000 ppm TCE, respectively and (b) the designed sequence with exposure to 5000, 10 000, 3000, 7000, and 1000 ppm of TCE, respectively.

polymeric chemiresistors, as similar behavior has been seen in polymers deposited onto SAW devices [26].

The appearance of the decreasing steps in Fig. 2 is an artifact of the digitization equipment; the decrease should be a smooth curve. However, the trend of initially high resistance followed by a decrease with time is real and at present is not well understood. It may be due to inhomogeneities in the material that lead to more complex behavior than would be predicted by standard percolation theory.

3.2. Effects of changing environmental conditions

In order to understand the effects of temperature and humidity on the calibration of the chemiresistors for the

respective calibrations, designed (D) and non-designed (ND), PLS calibration models were created from data grouped according to temperature and humidity. The results are summarized in Tables 2–4. Table 2 lists the calibration results for each environmental condition and designed or non-designed model. Models listed in Table 2 were used to predict data collected under the same environmental conditions for the alternate design and the results are listed in Table 3. For example, models created using the data collected via a designed experiment were used to predict the data collected in a sequential (non-designed) manner. For all environmental conditions, the prediction statistics listed in Table 3 using the non-designed calibration models are poorer than what would be expected from the calibration

Table 2
Calibration (D: designed sequence, ND: non-designed sequence)

Environmental condition	R^2	CVSEP (ppm)	Number of factors
31 °C, 0/100% humidity (E1 + E2)	0.98 (D)	400	2
	0.995 (ND)	230	2
23 °C, 0/100% humidity (E3 + E4)	0.98 (D)	450	2
	0.97 (ND)	480	2
23/31 °C, 100% humidity (E2 + E4)	0.97 (D)	590	3
	0.98 (ND)	430	4
23/31 °C, 0% humidity (E1 + E3)	0.94 (D)	750	2
	0.91 (ND)	980	2

Table 3
Prediction (D: designed sequence, ND: non-designed sequence)

Environmental condition	R^2	SEP (ppm)
31 °C, 0/100% humidity (E1 + E2)	0.96 (D)	730
	0.91 (ND)	840
23 °C, 0/100% humidity (E3 + E4)	0.96 (D)	730
	0.90 (ND)	1000
23/31 °C, 100% humidity (E2 + E4)	0.97 (D)	590
	0.92 (ND)	890
23/31 °C, 0% humidity (E1 + E3)	0.85 (D)	1200
	0.74 (ND)	1600

statistics. The difference in these statistics is statistically significant as measured by the SEP of prediction compared to the CVSEP of calibration. In addition, the prediction of the data acquired 45 days after calibration, listed in Table 4, show consistently poorer prediction results using the calibration model from the non-designed experiment. Prediction results using the model from designed data on both the short-term (Table 3) and long-term (Table 4) data are more in line with what was expected from the calibration statistics. Predictions listed in Table 3 using the models from the designed experiments yield SEPs that are 30% better on average than the SEPs using models created using the non-designed experiment. Prediction of the data collected 45 days after collection of the calibration data using the models from the non-designed data show, in all cases, a statistical difference between the calibration and prediction SEPs. Using models from the designed data to predict the long-term data, only the prediction statistics using the model from

Table 4
Prediction 45 days after calibration (D: designed sequence, ND: non-designed sequence)

Environmental condition	R^2	SEP (ppm)
31 °C, 0/100% humidity (E1 + E2)	0.98 (D)	480
	0.79 (ND)	1600
23 °C, 0/100% humidity (E3 + E4)	0.95 (D)	700
	0.70 (ND)	1700
23/31 °C, 100% humidity (E2 + E4)	0.97 (D)	590
	0.89 (ND)	1000
23/31 °C, 0% humidity (E1 + E3)	0.95 (D)	660
	0.70 (ND)	1680

the designed sequence at the 23/31 °C and 0% humidity condition to predict the same condition are statistically different from the calibration statistics. This indicates that the models created from data collected in the designed sequence are more robust to long-term device drift.

An example of prediction results using the model from the non-designed experiment to predict the designed data is shown in Fig. 3a, and prediction using the model from the designed experiment to predict the non-designed data is shown in Fig. 3b for the 23/31 °C and 100% humidity condition (E2 + E4). This figure shows that prediction with the model from the non-designed data shows a greater spread of data in the 1000–5000 ppm range than the prediction with the model from designed data. For the case shown in Fig. 3, the standard deviation of the predicted data in the 1000–5000 ppm region is 1.9 times greater for the set predicted with the model from the non-designed data compared to the set predicted with the model from the designed data. Similar results were found for the predictive ability of models created for the other environmental conditions. The cause for the reduced variance using calibration models from the designed data at lower concentrations is likely due to the fact that these models are more independent of hysteresis and baseline drift than their non-designed counterparts. In addition, for the prediction of the higher concentration standards, the models from the non-designed data yield predictions that are biased to higher values. Prediction of the high concentration standards using the model from the designed experiment does not produce this bias. The improved performance of the designed experiment at higher concentrations is likely due to the fact that it incorporates a five level design, five concentrations equally spaced, improving the ability of the model to account for non-linearities. The non-designed experiment jumps from 5000 to 10 000 ppm making the modeling of the non-linearities difficult.

Fig. 4a and b show the predictions of the designed sequence, run 45 days after calibration, using the models from the non-designed (Fig. 4a) and designed (Fig. 4b) experiments at 23/31 °C and 100% humidity (E2 + E4). These data clearly show that the model created from a designed data set maintains good predictive ability while the model from the non-designed data loses this ability. The results shown in Fig. 4 are typical for all the environmental conditions assessed.

The temperature at which the non-designed data, condition E2 (Table 1a) was collected was 32.7 °C, which is higher than other temperatures at which data was collected (31 °C). This could be blamed for the poor predictive ability of the resulting model (non-designed, E1 + E2) used to predict the designed sequence, collected 45 days later, at 31 °C and 0 and 100% humidity (Table 4). However, additional samples collected at lower temperatures and 0% humidity were added to the non-designed E1 + E2 data to allow the PLS calibration model to compensate (see Section 2.1) for the missing information and did not alter the

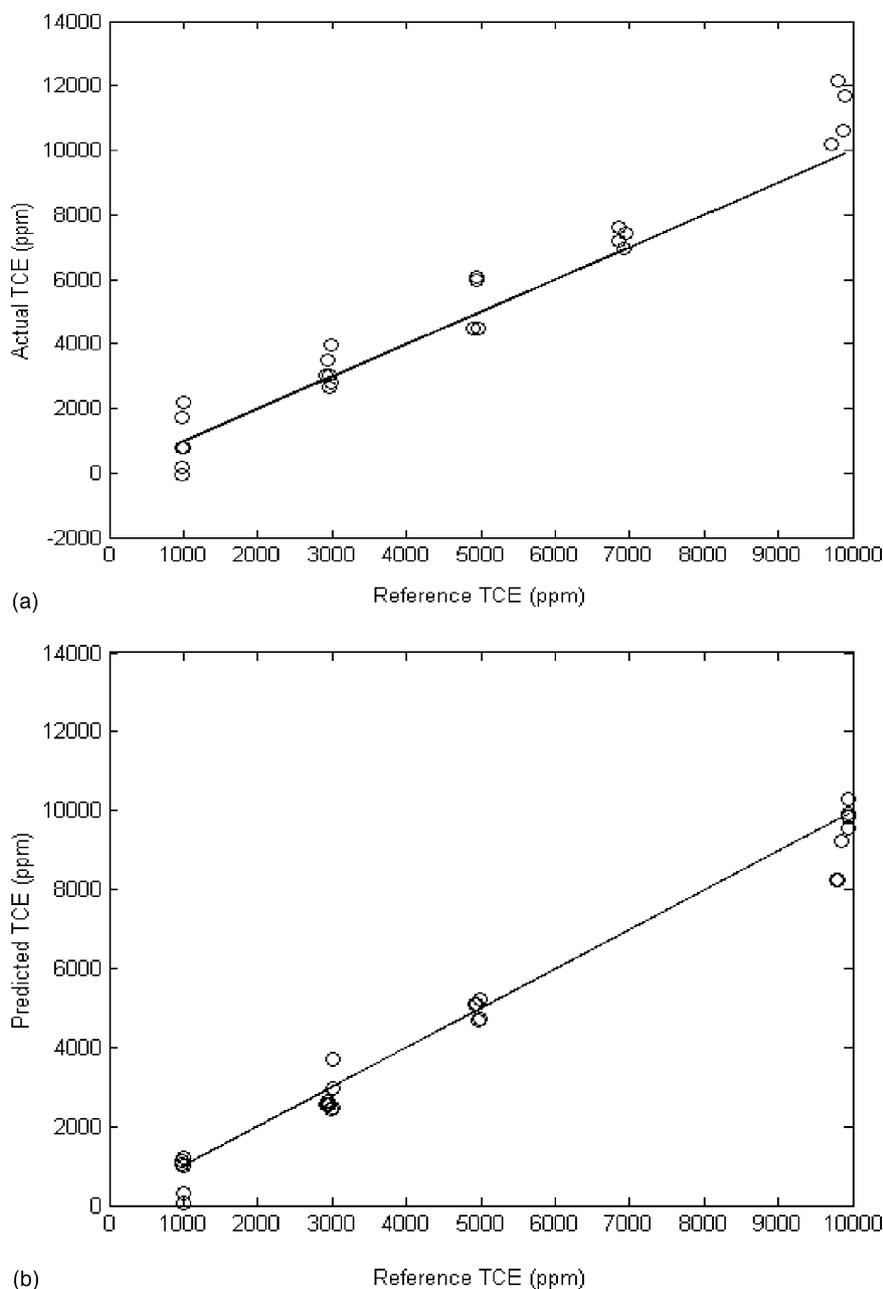


Fig. 3. Predictions using PLS calibrations. (a) Prediction of the first designed sequence at 23/31 °C and 100% humidity using the calibration from the non-designed sequence at the same environmental conditions. (b) Prediction of the non-designed sequence at 23/31 °C and 100% humidity using the calibration from the designed sequence.

predictive results significantly. Analysis of the concentration residuals showed behavior similar to what was seen without inclusion of additional information in the calibration. In addition, use of the higher temperature non-designed E2 sequence in conjunction with non-designed E3 sequence (Table 1a) to predict the long-term E1 + E2 data yielded predictions as good as those listed in Table 4. Analysis of the response residuals, showed that no significant error could be associated with the temperature channel.

Poor predictive ability of the non-designed E1 + E3 combination is not currently understood. When the non-

designed E1 and E3 conditions are individually combined with either E2 and E4 the resulting non-designed calibration models are much better in prediction (Tables 3 and 4) than the E1 + E3 combination.

3.3. Calibration and prediction with all environmental conditions

The most complicated situation is the calibration and prediction of the chemiresistor arrays over all environmental conditions. The calibrations of both the designed and non-

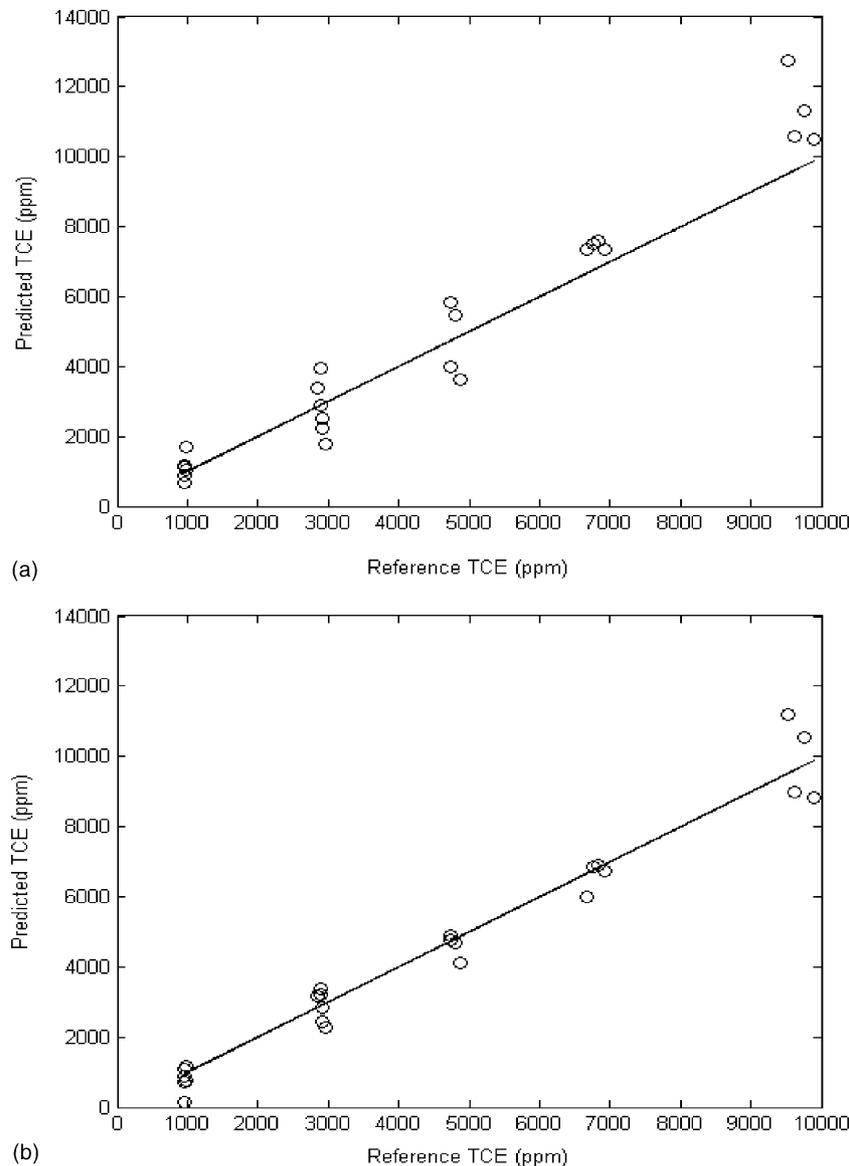


Fig. 4. Predictions using the same PLS calibrations from as used in Fig. 3. (a) Prediction of the designed sequence at 23/31 °C and 100% humidity acquired 45 days after calibration using the calibration from the non-designed sequence. (b) Prediction of the designed sequence at 23/31 °C and 100% humidity acquired 45 days after calibration using the calibration from the designed sequence.

designed sequences are statistically identical in calibration with $R^2 = 0.94$ and 0.96 , respectively and CVSEPs of 750 and 650 ppm, respectively. In short-term prediction, however, the model created from the designed sequences predicts the non-designed data with an $R^2 = 0.93$ and SEP = 900 ppm compared to the model created from non-designed sequences predicting the designed data with an $R^2 = 0.87$ and SEP = 1100 ppm. For long-term prediction (data collected 45 days after calibration), the model created from the designed sequence yields an $R^2 = 0.91$ with an SEP = 920 ppm while the model from the non-designed data yields an $R^2 = 0.81$ with an SEP = 1340 ppm. The prediction statistics between the two models are significant and indicate that models created from the designed data set yields better predictive results for the conditions presented.

4. Conclusions

We have shown the advantages of employing a designed experiment that incorporates a random sampling sequence with repeat samples in the calibration of microsensor data to TCE at various temperature and humidities. This sequence was compared to a non-designed sampling sequence that used both sequential repeats and monotonic increases in concentration for quantitative analysis of TCE vapor using chemiresistor arrays. We have shown that the designed experiment is more robust at predicting TCE concentrations at both short (within 10 days) and long times (45 days) after the calibration.

Effects of humidity and temperature on chemiresistor response and PLS calibration were also shown. Our results

demonstrate the difficulty in quantitating resistor response of a single pollutant over several environmental conditions and the need to use a designed experiment for robust calibration results. It has also been shown that the prediction ability of a calibration model cannot be assessed solely by the leave-one-out cross-validation results of the calibration. Assessment of the predictive ability of a calibration model must be made through true prediction.

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C.K. Ho is a Principal Member of Technical Staff at Sandia National Laboratories. He received a BS in Mechanical Engineering from the University of Wisconsin-Madison (1989), and an MS and PhD in Mechanical Engineering from the University of California at Berkeley (1990, 1993). Dr Ho has performed work as a principal investigator for Yucca Mountain, WIPP, and Hanford in developing models of contaminant flow and transport in porous and fractured media. Dr Ho has also performed experimental and numerical studies for environmental remediation and subsurface contamination problems involving soil vapor extraction, steam injection, and capillary barriers for waste isolation. His current research interests include leading a research project to develop microchemical sensors for continuous, in situ, long-term subsurface monitoring of volatile organic compounds. Dr Ho has published over 30 technical papers in scientific journals and conference proceedings, and serves on the editorial advisory board for the journal sensors.