

A Methodology for Monitoring Concentrations of Complex Waste Solutions-14182

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ABSTRACT

In this contribution, a methodology for calibrating infrared absorbance readings to solution composition is presented. While this methodology has been specifically developed to track in-solution solute concentration profiles during crystallizations, it can be applied more generally to establish on line solution composition analysis. In particular, the calibration method is expected to be of use in establishing robust *in situ* measurement techniques for characterizing high salt content nuclear waste solutions.

INTRODUCTION

Much of the liquid nuclear waste stored at Hanford is saturated with solutes. Handling this waste may therefore result in unwanted crystallization and solid precipitation that disrupts downstream operations. The solutes of concern are predominantly sodium salts with the following anions: NO_3^- , NO_2^- , SO_4^{2-} , CO_3^{2-} , OH^- , $\text{Al}(\text{OH})_4^-$, and PO_4^{3-} [1-3]. To develop and run waste treatment operations successfully, it is important to establish automated, *in situ* measurement techniques for monitoring the concentration of these solutes in solution [4, 5].

Spectroscopic measurements can be made rapidly and *in situ* and, accordingly, provide a potential route for establishing automated, real-time monitoring. However, accurately calibrating spectroscopic measurements to give the concentration of multiple solution components can be difficult. Despite challenges associated with multicomponent calibration, Bryan et al. [6] demonstrated the ability to accurately monitor the concentrations of NO_3^- , NO_2^- , SO_4^{2-} , CO_3^{2-} , OH^- , $\text{Al}(\text{OH})_4^-$, CrO_4^{2-} and PO_4^{3-} in solution using a Raman-based monitoring system. Although this system performed well for single phase solutions, the presence of solids significantly degrades the measured Raman intensity. As we are interested in monitoring solutions with potentially high solid contents, an alternative technique was required.

The development of attenuated total reflectance Fourier-transform infrared (ATR-FTIR) technology has made it possible to measure the infrared absorbance spectrum of a solution even when solids are suspended in that solution [7, 8]. Although not all of the anions in nuclear waste absorb infrared light, in this study we have limited our attention to monitoring four anions that are likely targets for fractional crystallization of nuclear waste (NO_3^- , NO_2^- , SO_4^{2-} , and CO_3^{2-})—each of these anions strongly absorbs infrared light.

Even for this reduced set of anions, developing a calibration model that accurately predicts the concentration of each anion simultaneously is a challenging task, with difficulties arising due to overlap of the characteristic IR absorbance peaks and a number of disturbance variables. To overcome these challenges we have constructed a tailored calibration methodology that utilizes a novel regression algorithm, termed robust parameter support vector regression (RPSVR). This paper briefly describes the developed methodology, examines the accuracy of established

calibration models, and compares the performance of RPSVR with more common linear regression algorithms like partial least-squares regression (PLSR).

CALIBRATING INFRARED MEASUREMENTS

IR-to-Concentration Calibration Models

Infrared absorbance measurements can be used to identify the type and amount of molecules present. However, to derive quantitative concentration information from infrared absorbance spectra, a calibration model is needed.

In many cases a single spectrum feature (typically “peak height” or “peak area”) can be correlated with the solute concentration in a straightforward manner. In this case, however, multiple infrared-absorbing anions are present in the solutions of interest and the characteristic infrared absorbance peaks for these anions overlap (Figure 1).

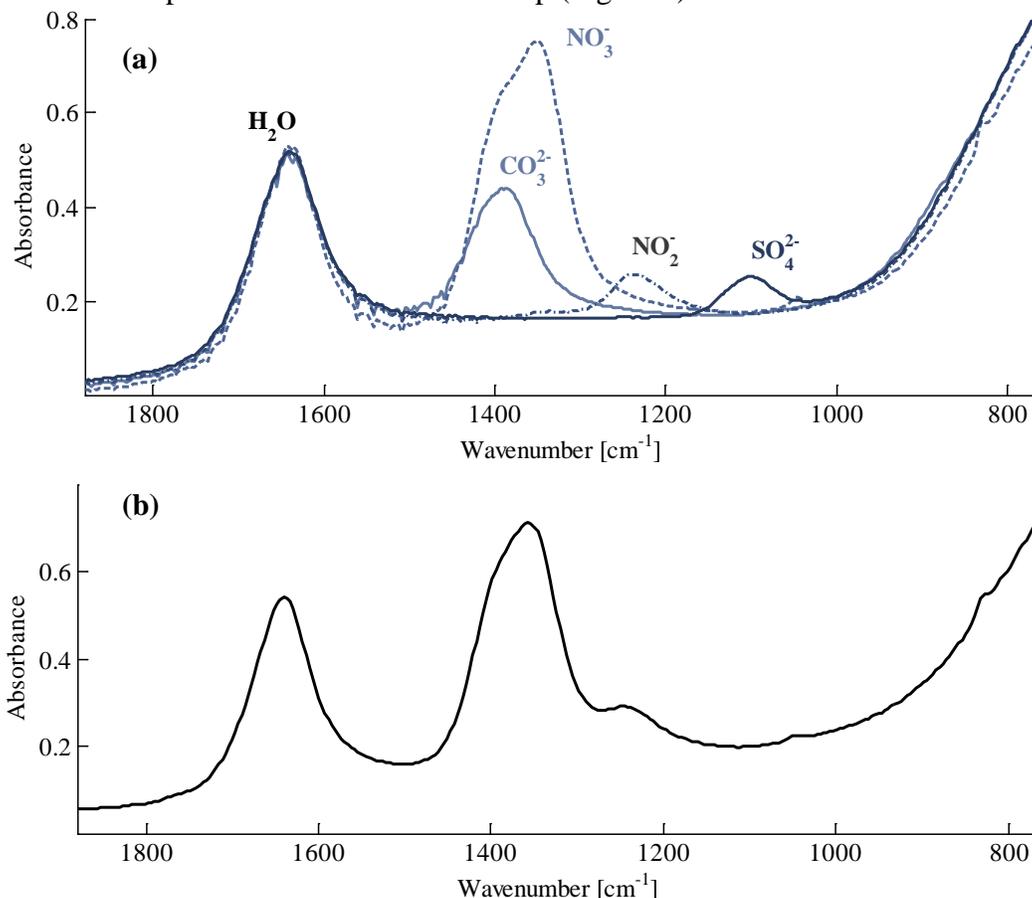


Figure 1: Infrared spectra for single-solute aqueous solutions containing sodium carbonate, sodium nitrate, sodium sulfate, and sodium nitrate (a) and the infrared spectrum of a complex electrolytic solution containing each anion (b)

To capture the intricacies of the convoluted infrared spectrum required to accurately predict the concentration of each anion, a feature *vector* is required. Correlating this feature vector to composition requires multivariate regression techniques and a large, well-formed training data

set. The following sections present the methodology we employed to build accurate and robust calibration models that predict the concentrations of multiple solutes in a complex electrolytic solution.

Linear Multicomponent IR-to-Concentration Calibration Models: Notation

Before presenting the calibration methodology, some notation needs to be introduced and the calibration model defined.

Let $\mathbf{IR} \in \mathbb{R}^m$ represent the digitized infrared absorbance spectrum:

$$\mathbf{IR}^T \equiv [a_1 \quad \dots \quad a_l \quad \dots \quad a_m] \quad (1)$$

Furthermore let $\mathbf{x} \in \mathbb{R}^q$ represent the input feature vector (constructed from the digitized infrared absorbance spectrum for a select range of frequencies):

$$\mathbf{x}^T \equiv [1 \quad \mathbf{IR}_{\text{select}}] \in \mathbb{R}^q \quad (2)$$

Finally, let $\mathbf{y} \in \mathbb{R}^p$ represent the solution composition:

$$\mathbf{y}^T \equiv [C_{\text{CO}_3} \quad C_{\text{NO}_3} \quad C_{\text{SO}_4} \quad C_{\text{NO}_2}] \in \mathbb{R}^p \quad (3)$$

In Equation (1) a_l is the measured infrared absorbance (l denotes the frequency). In Equation (2) the constant 1 is added as the first input feature to include a constant term in the calibration model, $\mathbf{IR}_{\text{select}}$ is the digitized infrared absorbance spectrum for frequencies between 764 cm^{-1} and 1507 cm^{-1} and q is the dimension of \mathbf{x} (201 in this study). Finally, in Equation (3), C_j is the concentration of the of the j^{th} anion and p is the number of anions monitored (4 here).

Using this notation, a linear calibration model can be defined as follows:

$$\mathbf{g}(\mathbf{x}) \equiv \mathbf{x}^T \mathbf{B} = \hat{\mathbf{y}} \approx \mathbf{y} \quad (4)$$

where \mathbf{g} is the vector-valued calibration model, $\mathbf{B} \in \mathbb{R}^{q \times p}$ contains the model parameters, and $\hat{\mathbf{y}}$ is the model-predicted concentration vector.

Calibration Methodology

There are two basic steps in building a calibration model: collect data to compose a training data set and use a regression algorithm to fit a calibration model to the training data (Figure 2).

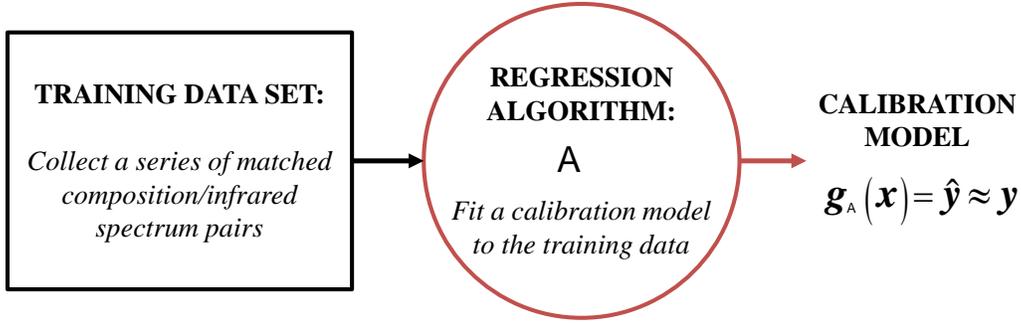


Figure 2: Schematic outline of the basic calibration steps

Training Set

To build a training data set, a series of matched concentration/infrared spectrum pairs (Figure 3) must be collected.

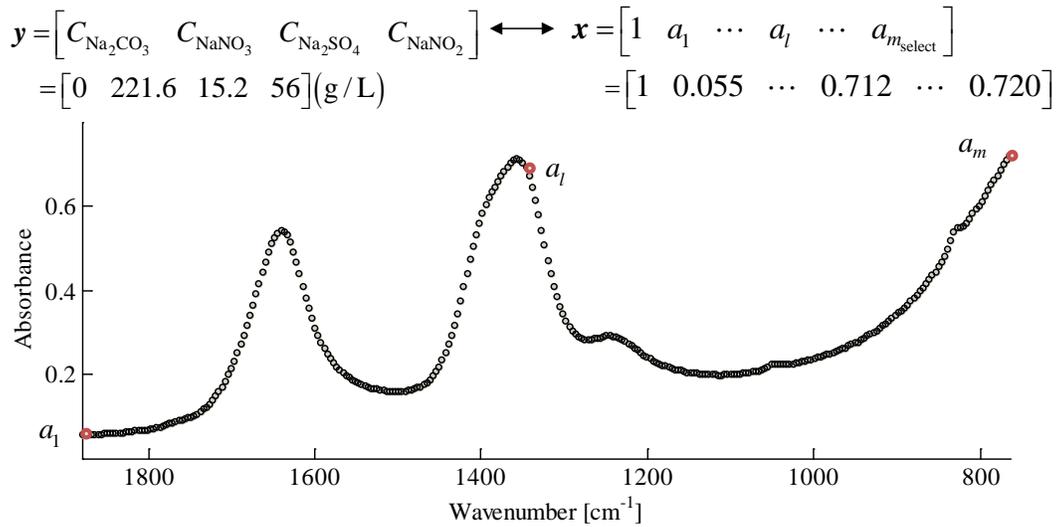


Figure 3: Example IR spectrum solution/composition (\mathbf{x}/\mathbf{y}) pair in the training set

It is convenient to represent the training set with matched “X” and “Y” matrices:

$$\mathbf{X}^{\text{tr}} = \begin{bmatrix} \mathbf{x}_1^T \\ \vdots \\ \mathbf{x}_N^T \end{bmatrix} = \begin{bmatrix} 1 & a_{1,1} & \cdots & a_{1,m_{\text{select}}} \\ \vdots & \vdots & & \vdots \\ 1 & a_{N,1} & \cdots & a_{N,m_{\text{select}}} \end{bmatrix}, \quad \mathbf{X}^{\text{tr}} \in \mathbf{R}^{N \times q} \quad (5)$$

$$\mathbf{Y}^{\text{tr}} = \begin{bmatrix} \mathbf{y}_1^T \\ \vdots \\ \mathbf{y}_N^T \end{bmatrix} = \begin{bmatrix} C_{1,\text{CO}_3} & C_{1,\text{NO}_3} & C_{1,\text{SO}_4} & C_{1,\text{NO}_2} \\ \vdots & \vdots & \vdots & \vdots \\ C_{N,\text{CO}_3} & C_{N,\text{NO}_3} & C_{N,\text{SO}_4} & C_{N,\text{NO}_2} \end{bmatrix}, \quad \mathbf{Y}^{\text{tr}} \in \mathbf{R}^{N \times p} \quad (6)$$

In order to obtain an accurate calibration model, Y^{tr} must be carefully constructed. In particular, the effects of each solute on the infrared spectrum should be decoupled and the training set should be unbiased. This can be accomplished with an orthogonal and balanced experimental design [9, 10]. In the present work, we built the training set using a 3^{4-1} fractional factorial design using the concentration levels shown in Table 1. These concentration levels are chosen to be representative of high salt content nuclear waste solutions [11-13], however it should be noted that the training set solutions contain only the target solutes. To extend the presented calibration methodology to monitor actual nuclear waste, the training solutions should be modified to include the additional components of nuclear waste and the concentration levels should be adjusted to reflect those observed for the different classes of nuclear waste to be monitored.

Table 1: Training set design

Factor (solute)	Level 1 (concentration g-solute/100-g H ₂ O)	Level 2 (concentration g-solute/100-g H ₂ O)	Level 3 (concentration g-solute/100-g H ₂ O)
Na ₂ CO ₃	0	6.500	13.0
NaNO ₃	0	27.75	55.5
Na ₂ SO ₄	0	1.850	3.70
NaNO ₂	0	3.500	7.00

Multivariate Regression

For an unbiased training set the relationship between Y^{tr} and X^{tr} should be representative of the general relationship between the solution composition and the infrared absorbance spectrum. Therefore we would expect the solution to the set of equations $X^{\text{tr}}\mathbf{B} = Y^{\text{tr}}$ to give a linear calibration model. Of course, measurement error and small nonlinearities make this set of equations over-determined and impossible to solve exactly. Consequently, regression techniques must be used to find the “best” model for which $X^{\text{tr}}\mathbf{B} \approx Y^{\text{tr}}$.

To accurately predict the concentration of multiple solution components from a convoluted spectrum, a high-dimensional input feature vector must be used; however the features used are often collinear and therefore specific multivariate regression techniques are required to identify a calibration model that accurately correlates these features vectors to the concentration. Most commonly, collinear variables are handled with projection-based regression methods. Of these, partial least-squares regression has been extensively applied to develop multicomponent Raman-to-concentration calibration models [14-18] and single component IR-to-concentration calibration models [19-22].

While projection-based methods successfully navigate collinear variables, these methods do not explicitly take into account errors in the variables. In exploring the use of ATR-FTIR to monitor the concentration of multiple solution components, we noted a number of disturbance variables (temperature, infrared probe fiber optic cable alignment, liquid/probe window contact, and background infrared absorbance) that affected the infrared absorbance and can cause significant variance in the concentration prediction accuracy. To build a robust calibration model that was insensitive to these disturbance variables, we developed a customized regression algorithm. This

algorithm, which we term robust parameter support vector regression (RPSVR), blends ideas used in robust estimation [23] and support vector regression.

Results

Calibration model using RPSVR

To estimate the accuracy of established calibration models, the model-predicted concentrations were compared against the gravimetrically measured concentration for a test data set. The test set used in this study consisted of 310 spectra recorded for 11 solutions not used in the training set. For a calibration model built with RPSVR, the concentration prediction accuracy is shown visually in Figure 4.

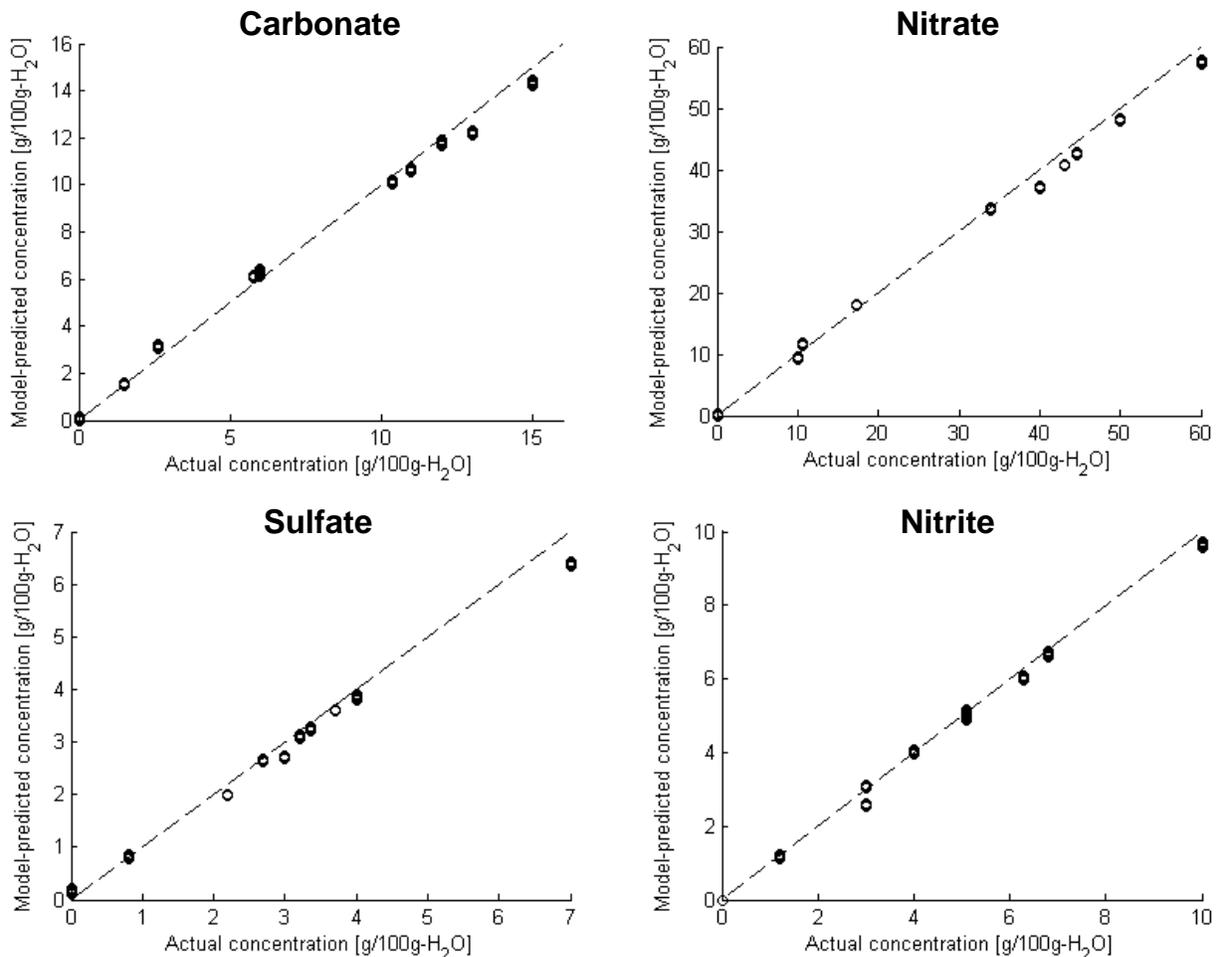


Figure 4: Model-predicted concentrations vs. actual concentrations across the test set for a calibration model constructed using RPSVR

In addition the concentration prediction errors (Equation (7)) are characterized by the average (Equation (8)), standard deviation (Equation (9)) and relative error (Equation (10)) in Table 2.

$$\varepsilon \equiv C_{\text{predicted}} - C_{\text{actual}} \quad (7)$$

$$\bar{\varepsilon} \equiv \frac{\sum_{i=1}^{N_{\text{Test}}} \varepsilon_i}{N_{\text{Test}}} \quad (8)$$

$$\sigma_{\varepsilon} \equiv \frac{1}{N_{\text{Test}} - 1} \left(\sum_{i=1}^{N_{\text{Test}}} (\varepsilon_i - \bar{\varepsilon})^2 \right)^{1/2} \quad (9)$$

$$\bar{\varepsilon}_{\text{rel}} \equiv 100\% \times \frac{\sum_{i=1}^{N_{\text{Test}}} |\varepsilon_i|}{\sum_{i=1}^{N_{\text{Test}}} C_{\text{actual},i}} \quad (10)$$

Table 2: Concentration prediction errors⁽⁷⁾ observed over the test set using a calibration model built with RPSVR.

Anion	Average Error, ε ⁽⁸⁾ (g/100-g H ₂ O)	Error Standard Deviation, σ_{ε} ⁽⁹⁾ (g/100-g H ₂ O)	Relative Error, $\bar{\varepsilon}_{\text{rel}}$ ⁽¹⁰⁾ (%)
CO ₃ ²⁻	-0.124	0.384	4.42
NO ₃ ⁻	-1.089	1.299	4.71
SO ₄ ²⁻	-0.112	0.211	6.33
NO ₂ ⁻	-0.138	0.163	3.95

These results demonstrate the ability to form an accurate multi-solute IR-to-concentration calibration model using the discussed training data set (large, orthogonal and balanced) and regression algorithm (RPSVR).

Comparison against calibration models build with more common regression techniques

In addition to examining the accuracy of a calibration model built with RPSVR, a number of additional calibration models were constructed using more established multivariate linear regression techniques, including multiple least-squares regression (MLR), principle component regression (PCR) [24, 25], partial least-squares regression (PLSR) [26, 27], ridge regression (RR) [28], dead-zone linear regression (DZLR) [23], and support vector regression (SVR) [29].

Each regression algorithm was then compared based on the performance of the calibration model built using the measure of calibration model accuracy given by Equation (11) as the performance metric. This strategy is shown pictorially in Figure 5 and the results are shown in Figure 6

$$SEP(g_A)_{\text{combined}} \equiv \frac{1}{N_{\text{test}}} \sum_{j=1}^p \left\{ \left(\sum_{i=1}^{N_{\text{test}}} \left(g_{A,j}(\mathbf{x}_i^{\text{test}}) - y_{i,j}^{\text{test}} \right)^2 \right)^{1/2} / \bar{C}_j \right\} \quad (11)$$

where $SEP(\mathbf{g}_A)_{\text{combined}}$ is the weighted standard error of prediction over the test set for the calibration model $\mathbf{g}_{A,j}$ built using the learning algorithm A and \bar{C}_j is the average concentration of the j^{th} species in the training set.

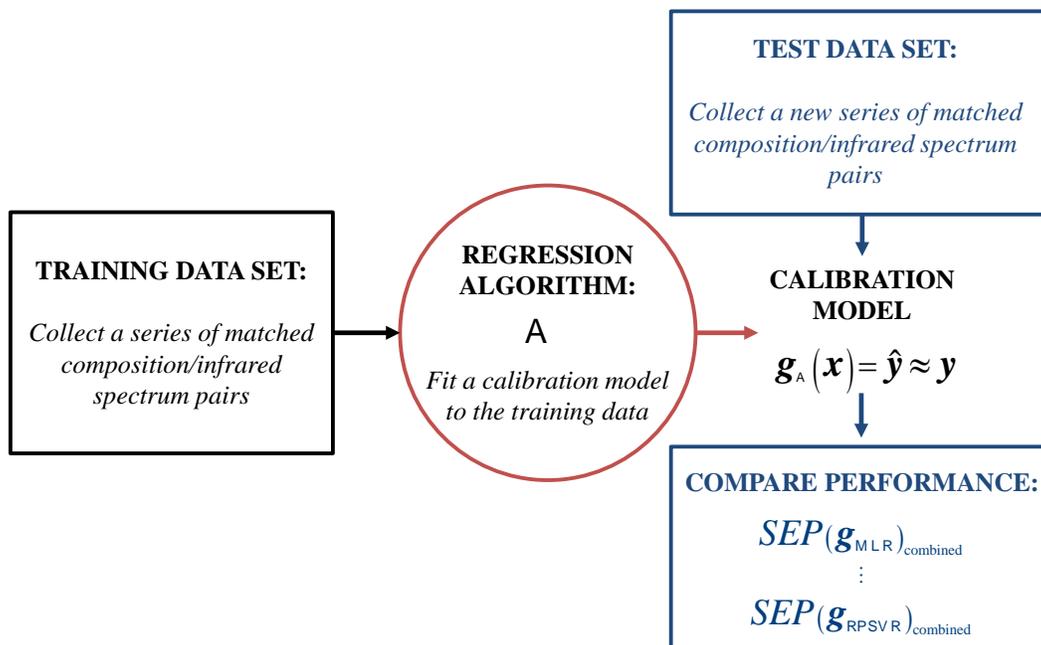


Figure 5: Schematic outline of the strategy used to compare learning algorithms

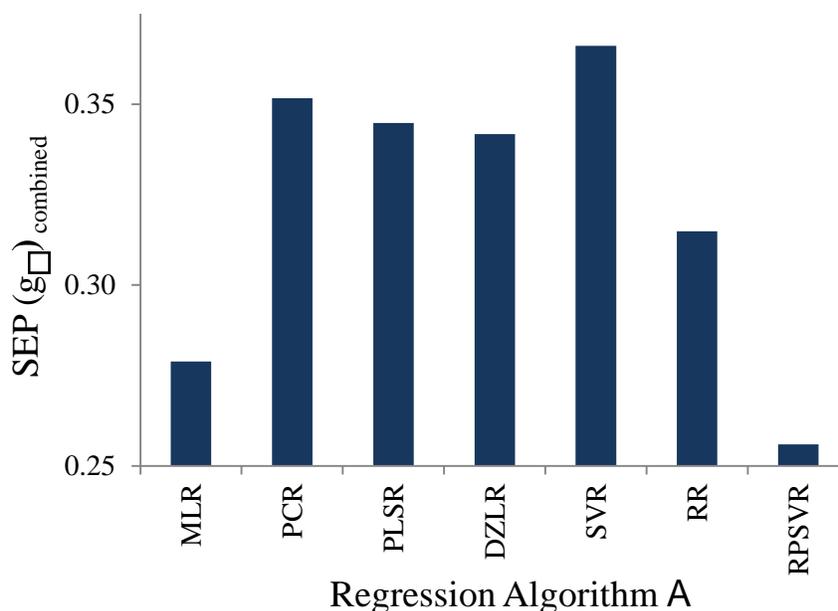


Figure 6: Comparison of the combined SEP for calibration models produced using different regression algorithms

Despite the complexity of the electrolytic solutions probed and the corresponding infrared spectrum, the results in Figure 6 show that the calibration models built with any of the regression

algorithms including the MLR—the simplest regression technique applied—produced calibration models that performed reasonably well. We believe this is attributable to the fact the training set is large, orthogonal and balanced. In addition, Figure 6 indicated that the newly developed robust parameter support vector regression (RPSVR) performed the best of the examined algorithms.

Conclusions

In this work we have presented a tailored calibration methodology and demonstrated the ability to calibrate complex infrared absorbance spectra to give the in-solution concentration of four solutes simultaneously. In addition, we have shown that calibration models produced with a novel regression algorithm, termed robust parameter support vector regression, outperform models built with more standard regression techniques in the case examined.

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