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Exploration of New Multivariate Spectral Calibration Algorithms

David M. Haaland, David K. Melgaard, Christine Wehlburg, Laura E. Martin, Mark Van Benthem, Robert D. Guenard, and Randy J. Pell

Prepared by
Sandia National Laboratories
Albuquerque, New Mexico 87185 and Livermore, California 94550

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EXPLORATION OF NEW MULTIVARIATE SPECTRAL CALIBRATION ALGORITHMS*

David M. Haaland, David K. Melgaard, Christine M. Wehlburg, Laura E. Martin, and Mark H. Van Benthem

Sandia National Laboratories
Albuquerque, NM 87185-0886

ABSTRACT

A variety of multivariate calibration algorithms for quantitative spectral analyses were investigated and compared, and new algorithms were developed in the course of this Laboratory Directed Research and Development project. We were able to demonstrate the ability of the hybrid classical least squares/partial least squares (CLS/PLS) calibration algorithms to maintain calibrations in the presence of spectrometer drift and to transfer calibrations between spectrometers from the same or different manufacturers. These methods were found to be as good or better in prediction ability as the commonly used partial least squares (PLS) method. We also present the theory for an entirely new class of algorithms labeled augmented classical least squares (ACLS) methods. New factor selection methods are developed and described for the ACLS algorithms. These factor selection methods are demonstrated using near-infrared spectra collected from a system of dilute aqueous solutions. The ACLS algorithm is also shown to provide improved ease of use and better prediction ability than PLS when transferring calibrations between near-infrared calibrations from the same manufacturer. Finally, simulations incorporating either ideal or realistic errors in the spectra were used to compare the prediction abilities of the new ACLS algorithm with that of PLS. We found that in the presence of realistic errors with non-uniform spectral error variance across spectral channels or with spectral errors correlated between frequency channels, ACLS methods generally out-performed the more commonly used PLS method. These results demonstrate the need for realistic error structure in simulations when the prediction abilities of various algorithms are compared. The combination of equal or superior prediction ability and the ease of use of the ACLS algorithms make the new ACLS methods the preferred algorithms to use for multivariate spectral calibrations.

Contents

INTRODUCTION 6

THEORY 7

FACTOR SELECTION FOR PREDICTION AUGMENTED CLS (PACLS) 8

COMPARISONS OF PREDICTION ABILITIES OF AUGMENTED CLASSICAL LEAST SQUARES AND PARTIAL LEAST SQUARES WITH REALISTIC SIMULATED DATA: EFFECTS OF UNCORRELATED AND CORRELATED ERRORS WITH NONLINEARITIES 17

ACLS METHODS FOR IMPROVED MULTIVARIATE CALIBRATION TRANSFER 17

CONCLUSIONS 18

ACKNOWLEDGMENTS 19

REFERENCES 20

APPENDIX A 22

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INTRODUCTION

During this project, we have tested and evaluated the performance of a variety of new multivariate calibration methods for quantitative spectral analysis. Since a number of journal papers have been published (or are in preparation for publication) based on this work, this report will primarily give a description of the new calibration algorithms, provide reference to our published results generated during this project, and briefly summarize the results of a submitted journal paper and several journal papers in preparation. The report will also include a more thorough description of unpublished results for an improved method of factor selection for the new algorithms.

Prior to the start of this Laboratory Directed Research and Development (LDRD) project, we had completed the development and experimental demonstration of our new classical least squares/partial least squares (CLS/PLS) hybrid multivariate algorithm applied to spectral calibrations. [1] In results published from this current LDRD project, we have demonstrated that the new hybrid algorithm can be used both to improve prediction abilities when instrument drift is present [2] and when transferring calibrations between spectrometers [3]. We demonstrated that the new hybrid method is very successful at maintaining and transferring multivariate spectral calibrations and that they performed as well or better than standard partial least squares (PLS) multivariate calibrations when calibration maintenance and/or transfer were required. Although we showed improvement in prediction ability without recalibration using the hybrid algorithm, a procedure that employed recalibration demonstrated further improvements in prediction ability of the hybrid algorithm.

Thus, we investigated the development of a new class of multivariate algorithms that have all the advantages of the hybrid algorithm, but that also have the ability to optimally update the models without recalibration. With the new algorithms developed as part of this LDRD project, we have achieved our goal of optimally updating the calibration models during multivariate predictions of sample spectra. We have called this new class of multivariate calibration methods augmented classical least squares (ACLS) calibrations, and we have recently published the theory behind these algorithms and given results with experimental and simulated data.[4, 5] (See also a review of these methods by Malinowski [6]). These new methods extend the traditional classical least squares (CLS) method to handle data sets where all spectrally active analytes are not explicitly included in the calibration. When used in conjunction with prediction augmented CLS (PACLS),[7] the ACLS calibration models can be efficiently and quickly updated to handle maintenance and transfer of calibration issues without recalibration.[4, 5]

In this report, we will focus primarily on those studies that have not yet been published. Thus, we will present the theory behind the new family of ACLS algorithms, discuss new options for factor selection for these methods, apply ACLS to experiments requiring transfer of ACLS calibration models between different spectrometer configurations, and compare the relative merits of the ACLS with the more commonly used PLS models using a variety of simulated data sets. Developments were also achieved in partial support of this project that yielded improvements in multivariate curve resolution algorithms [8] that can achieve quantitative spectral analysis without standards. However, our developments in this area have been published elsewhere and are beyond the scope of this current report.

THEORY

The CLS multivariate method [9-11] is based on the linear additive model,

$$\mathbf{A} = \mathbf{CK} + \mathbf{E_A}, \qquad (1)$$

where **A** is the n x p matrix containing the spectral intensities for the n samples and p spectral frequencies, **C** is the n x m concentration matrix for the m components, **K** is the m x p matrix of the pure-component spectra at unit concentration for the given data set and $\mathbf{E_A}$ is the n x p matrix of model errors and spectral noise. The notation for the equations in this paper uses bold upper case letters for matrices, bold lower case for vectors, and lower case italic letters for scalars. The calibration model uses the measured or simulated spectral intensities and reference concentrations to estimate the pure-component spectra as:

$$\hat{\mathbf{K}} = \mathbf{C}^{+}\mathbf{A} \qquad (2)$$

where ^ indicates estimated values based on minimizing the sum of squared errors. The $^{+}$ is used to denote a pseudo-inverse of the **C** matrix. The spectral residuals, $\mathbf{E_A}$ are then given by:

$$\mathbf{E_A} = \mathbf{A} - \mathbf{C}\,\hat{\mathbf{K}} \qquad (3)$$

If we perform a principle component analysis (PCA) on the residuals, $\mathbf{E_A}$ can be further separated as follows:

$$\mathbf{E_A} = \mathbf{TP} + \mathbf{E_R} \qquad (4)$$

where **T** represents the n x m_a scores of the PCA, m_a is the number of PCA loading vectors needed to represent all sources of chemical and correlated spectral variation in $\mathbf{E_A}$, and **P** is the m_a x p matrix of loading vectors. As noted by Martens and Naes, [12] $\hat{\mathbf{K}}$ can be augmented with all or some of the loading vectors **P** to help remove the deleterious effects of the addition sources of spectral variation contained in $\mathbf{E_A}$. We refer to this approach as Spectral Residual Augmented CLS (SRACLS).

A very different ACLS approach can be taken by augmenting with concentration residuals rather than spectral residuals. The concentration residuals, $\mathbf{E_C}$ are given by:

$$\mathbf{E_C} = \mathbf{C} - \mathbf{A}\hat{\mathbf{K}}^{+}. \qquad (5)$$

As explained in Ref [5], $\mathbf{E_C}$ is an approximation to linear combinations of the components left out of the model so **C** can be augmented with a vector $\mathbf{e_c}$ from $\mathbf{E_C}$ to compensate for incomplete knowledge of components in the calibration samples. Using an iterative approach of adding successive concentration residual vectors, all the missing components can be accounted for in the model. This ACLS method is referred to as concentration residual augmented CLS (CRACLS).

We can view the ACLS methods using the flowchart in Figure 1. The center boxes 1-5 represent the standard CLS method. The spectra and reference concentration values are used to approximate the pure-component spectra that are in turn used to predict the original reference concentrations. SRACLS, shown as the loop on the left (boxes 4-7), uses the computed spectral residuals from the standard CLS analysis. After performing a PCA analysis of these residuals, one or more of the PCA loading vectors are added as rows to the CLS-estimated pure-component spectra (shown as the shading in the "Estimated Pure-Component Spectra" box) to reduce the spectral and concentration residuals. The PCA analysis is performed only on the residuals from the initial CLS calibration, so the arrow from box 6 to 7 only applies to the first iteration. Each added loading vector results in an additional column in the concentration matrix (represented by

the shading in box 5 in Fig. 1). These loading vectors compensate for the presence of the unknown sources of non-random spectral variation. The curved arrow indicates the process of selecting different sets of loading vectors to minimize the predicted error sum of squares (PRESS) using cross-validation, similar to the approach recommended for PLS in factor selection.[13] In our implementation, successive loading vectors are added one at a time to the estimated pure-component spectra up to the maximum number specified.

Alternatively, CRACLS, the right loop in Figure 1 (boxes 3-5, and 8), augments the model with concentration residuals. The reference concentration matrix is augmented with one column vector of the concentration residuals (represented by the shading in box 3). New estimated pure components are then computed resulting in changes in the original pure-component spectra and

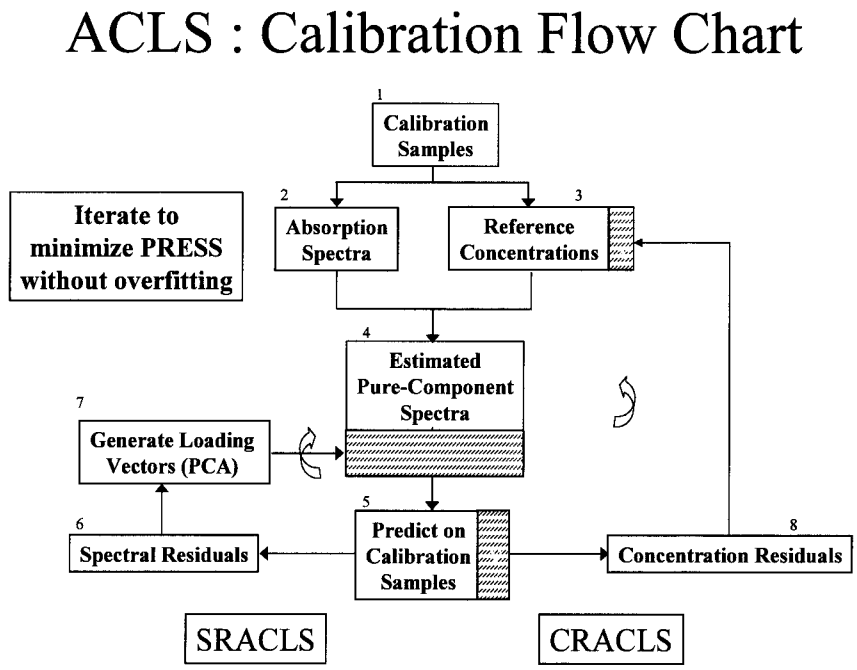

Figure 1. Flow chart of the CLS, spectral residual augmented CLS (SRACLS) and concentration residual augmented CLS (CRACLS) algorithms.

an additional pure-component spectrum (represented by the shading in box 4). Using these new estimated spectra, a new ACLS prediction is made, and the concentration residuals are recomputed including the additional concentrations related to the additional spectra (shown as the shading in box 5). This method differs from SRACLS since the new residuals from each iteration are used in the augmentation whereas only the first set of spectral residuals is used in SRACLS. The number of augmentations used is selected in a similar manor to SRACLS. Since the additional spectra in box 4 are not derived from a single pure component at unit value, the augmented concentrations in box 5 are generally not useful quantitatively.

FACTOR SELECTION FOR PREDICTION AUGMENTED CLS (PACLS)

New approaches for factor selection have been developed for our new ACLS algorithms. In this section of the report, the new factor selection method will be described and demonstrated for the PACLS algorithm using a set of infrared attenuated total reflectance (ATR) calibration and prediction spectra of trace acetone and isopropanol components in aqueous solutions. A similar approach can be used in the selection of factors for the cross-validated ACLS calibrations. The ATR infrared experiments have been described in detail Han et al.[14]. The standard method of factor selection for PLS and all other cross-validated multivariate calibration methods was pioneered by Haaland and Thomas [13]. However, based on the structure of the ACLS and PACLS algorithms, new opportunities exist for more intelligent factor selection. For example, in developing the SRACLS model, after the first CLS calibration is performed, the SRACLS spectral residuals to be augmented during calibration are factor analyzed into a series of orthogonal spectral residual loading vectors using principal component analysis (PCA). Since these PCA loading vectors are orthogonal to each other, the effect of adding each loading vector is independent of the order of adding eigenvectors to the model. Therefore, the order of adding spectral residual loading vectors can be changed at will and does not have to follow the standard order of adding loading vectors based on the magnitude of explained spectral variance. In fact, we can add them in the order in which they most effectively reduce concentration error variance in the calibration or validation samples. The error variance after performing the standard CLS calibration is calculated as $\sum_{i=1}^{n}(\hat{c}_i - c_i)^2$ for each factor derived from the spectral residuals that is to be considered for addition to the model. The $\hat{c}_i$ is the estimated concentration predicted for the analyte of interest for sample i derived from the loading vector (factor) to be added to the model over the n predicted samples. The c_i term is the true concentration of the selected loading vector. Of course, c_i is always zero since the analyte concentrations of mean centered repeat spectra from a single sample are by design always equal to zero. Therefore, the selection of the order of the loading vectors to add to the SRACLS model is simply based upon the magnitude of $\sum_{i}^{n}\hat{c}_i^2$ estimated for each factor.

Since each loading vector added to the model can serve to decrease the net analyte signal of the analyte of interest, it might be desirable to also include a measure of the change in net analyte signal (NAS) by the addition of each factor in the selection criteria. The NAS can be calculated based on the method first described by Lorber. [15] However, if reference error of the calibration samples limits prediction ability, then the change in the net analyte signal (i.e., the spectral signal of the analyte) will not play a significant role in the factor selection process and this effect can be ignored. We have observed empirically that for the majority of industrial applications, reference error rather than net analyte signal limits prediction ability during multivariate calibration. Nevertheless, in those few cases where NAS is limiting, then the effect of the change in NAS might be included in the factor selection process. The proper influence of the error variance reduction and the decrease in NAS will be sample set dependent. However, one possible function to monitor for factor selection might be based on the magnitude of $\sum_{i}^{n}\hat{c}_i^2\left(\frac{\|NAS_i\|^2}{\|NAS_0\|^2}\right)$ where $\|\Delta \mathrm{NAS}_0\|^2$ is the squared magnitude of the net analyte signal before

adding the additional factor and $\|\Delta \mathrm{NAS}_i\|^2$ is the squared magnitude of the net analyte signal after addition of factor *i*. Therefore, factor selection is based upon not only the magnitude of the concentration error but will also be related to the impact of each factor on reducing the NAS. Thus, a combination of reduction in concentration error variance and a small change in NAS are given preference in factor selection for this metric. However, in this report we will ignore the influence of NAS on factor selection since we will assume that reference error dominates. Thus, we can simply base factor selection in this work based solely upon the decrease in concentration error variance as factors are added to the model.

Reference [14] gives the details of the experiments completed to test the new factor selection method and compares the new method with the current standard method of factor selection.[13] Briefly, mid-infrared ATR spectra of trace amounts of acetone and isopropanol in water solutions were obtained with a Nicolet 800 Fourier transform spectrophotometer. The ATR Si plate was coated with a thin sol gel layer (0.25 μm) that had been made hydrophobic to exclude water and to reversibly concentrate the organic analytes. The samples were part of a 2 level, 5factor factorial experimental design with the acetone varying from 0 to 20 ppm and the isopropanol varying from 0 to 100 ppm. The sample representing the center point of the factorial design was run repeatedly during the experimental design in order to understand the repeatability of the data and the drift of the system. The design points were run in random order and the repeat sample was run periodically throughout the experimental run.

The set of all unique sample spectra in the factorial design are shown in the lower plot of Figure 2 after linear baseline correction. The upper plot of Figure 2 shows the linear baseline corrected spectra for the repeat samples. Clearly, instrument drift rather than analyte concentration variation is the major source of spectral variation in these data.
Therefore, accommodating instrument drift into the PACLS prediction is essential for obtaining accurate predictions.

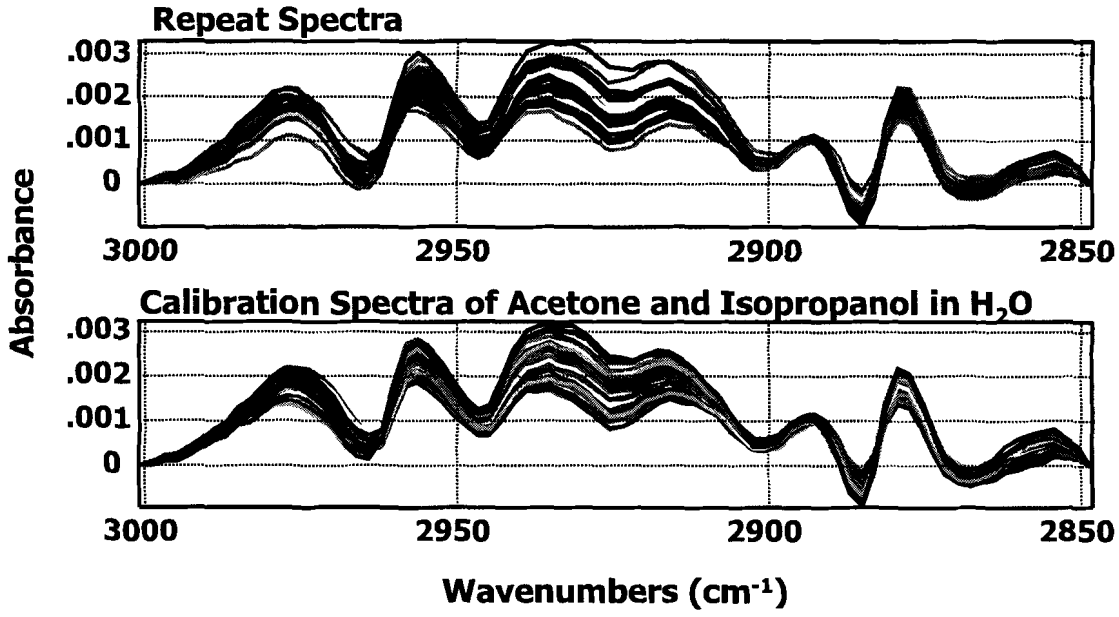

Figure 2. Comparison of linear baseline corrected IR spectra (C-H stretching region used in the analyses) for repeat sample (upper plot) and for calibration samples (lower plot) that contain acetone and isopropanol aqueous solutions on the coated Si ATR plate in the designed experiments. The dry, coated Si ATR plate was used as the spectral background.

The CLS calibrations and PACLS predictions were performed with the use of the PLS2001 Array Basic software written at Sandia National Laboratories. Cross-validated CLS calibration results for isopropanol using all non-repeat samples in the factorial design are shown in Figure 3.

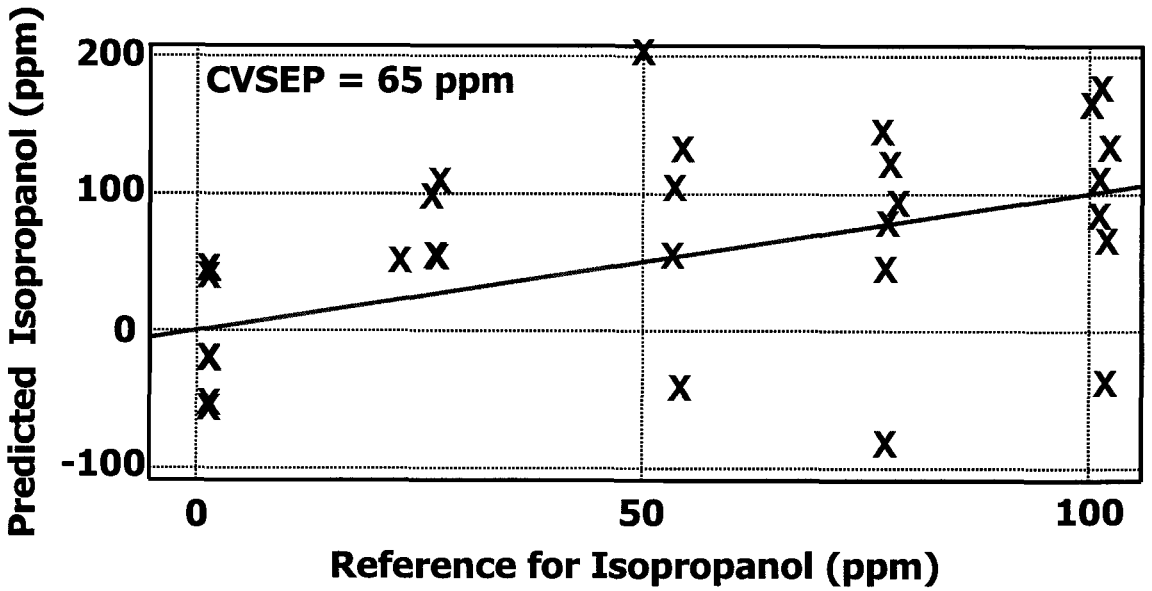

Figure 3. Predicted vs. reference concentrations for isopropanol based upon cross-validated CLS calibrations of the unique calibration samples with acetone, isopropanol, and a linear baseline include in the CLS model.

All calibrations in this portion of the report included a fit of the acetone and isopropanol species and a linear baseline. Only the results for isopropanol will be shown since isopropanol is most sensitive to instrument drift. Clearly there is almost no prediction ability for isopropanol using the CLS calibration method.

To demonstrate that PACLS predictions can improve the CLS calibration with the use of repeat sample spectra to correct for the presence of spectrometer drift, a cross-validated PACLS calibration using augmentation with 8 eigenvectors (selected in order of explained spectral variance) from all repeat spectra is shown in Fig. 4.

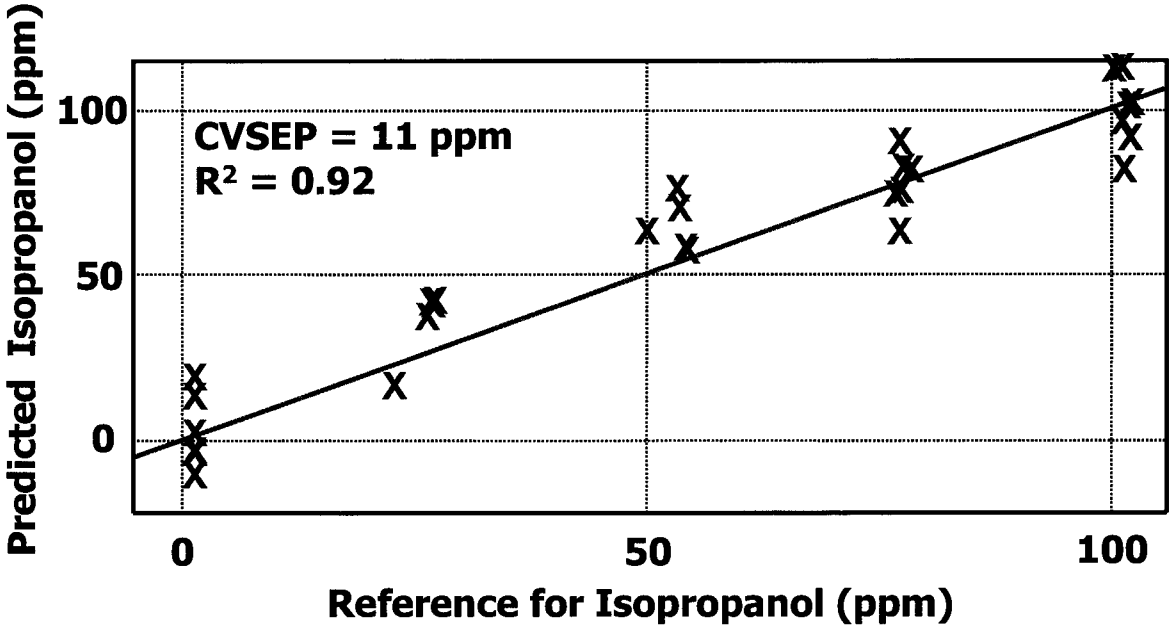

Figure 4. Cross-validated PACLS calibration for the same samples in Fig. 3 but augmented with the first 8 mean-centered eigenvectors from all repeat spectra.

This dramatic improvement in cross-validated prediction ability is similar to the results obtained for SRACLS or PLS calibrations applied to the same spectral data. Thus, for this data set, the PACLS method is competitive with the more powerful SRACLS and PLS calibration methods.

In order to test the new method proposed for PACLS factor selection, CLS calibrations were performed with the use of non-repeat sample spectra and concentrations from data taken during collection of spectra obtained from the first half of the factorial design. PACLS predictions were then performed on the sample spectra taken during the last half of the designed experiments. For the PACLS predictions, all the repeat spectra from both halves of the experiment were used in the PACLS augmentation. Two PACLS predictions were performed. The first PACLS prediction simply used mean-centered eigenvectors from the repeat spectra added in order of explained spectral variance. The second PACLS prediction added mean-centered repeat sample spectra eigenvectors in the order in which they reduced the errors in the repeat sample spectra. Because the repeat sample spectra were mean-centered, the order of added eigenvectors in the latter case can be determined directly by the sum of squared concentration predictions for each

repeat sample eigenvector. The plot of the square root of the error variance vs. unsorted eigenvector number (i.e., sorted only by spectral variance) is shown in Fig. 5.

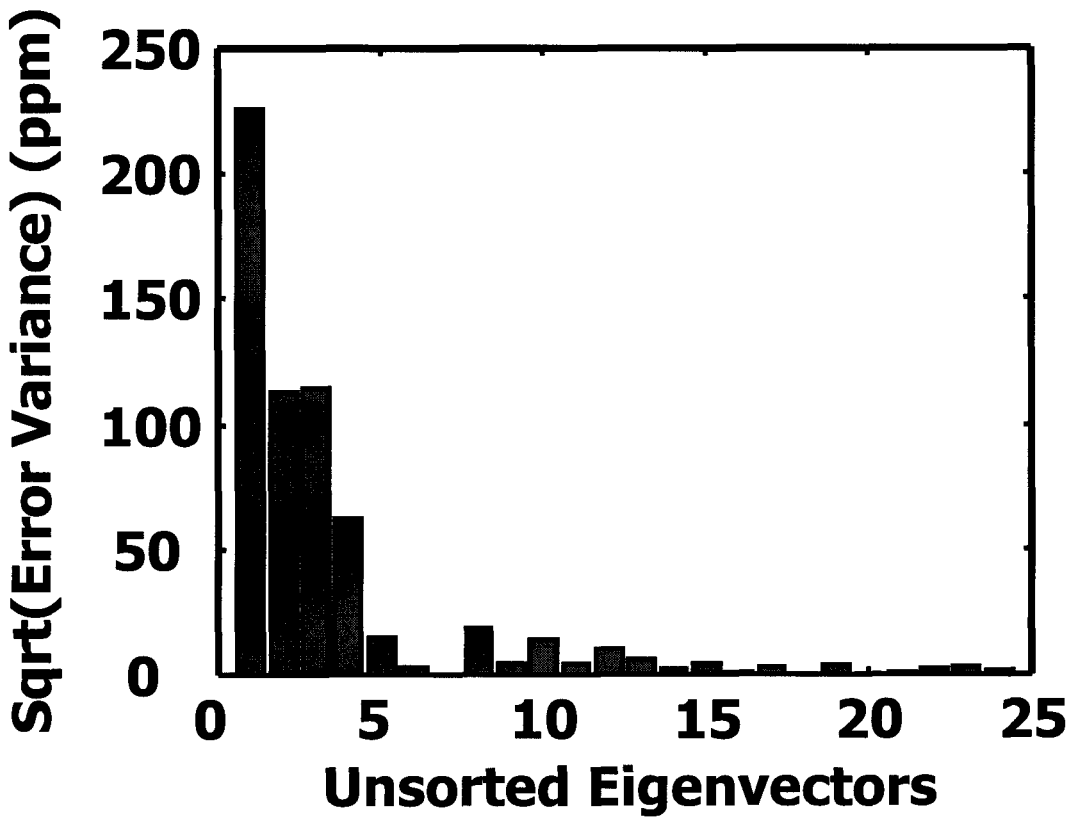

Figure 5. Square root of the concentration error variance from the CLS calibration model for each of the mean-centered eigenvectors from all repeat spectra plotted as a function of the unsorted eigenvectors (i.e., ordered by the spectral variance).

The corresponding plot with eigenvectors sorted by their error variance is shown in Fig. 6.

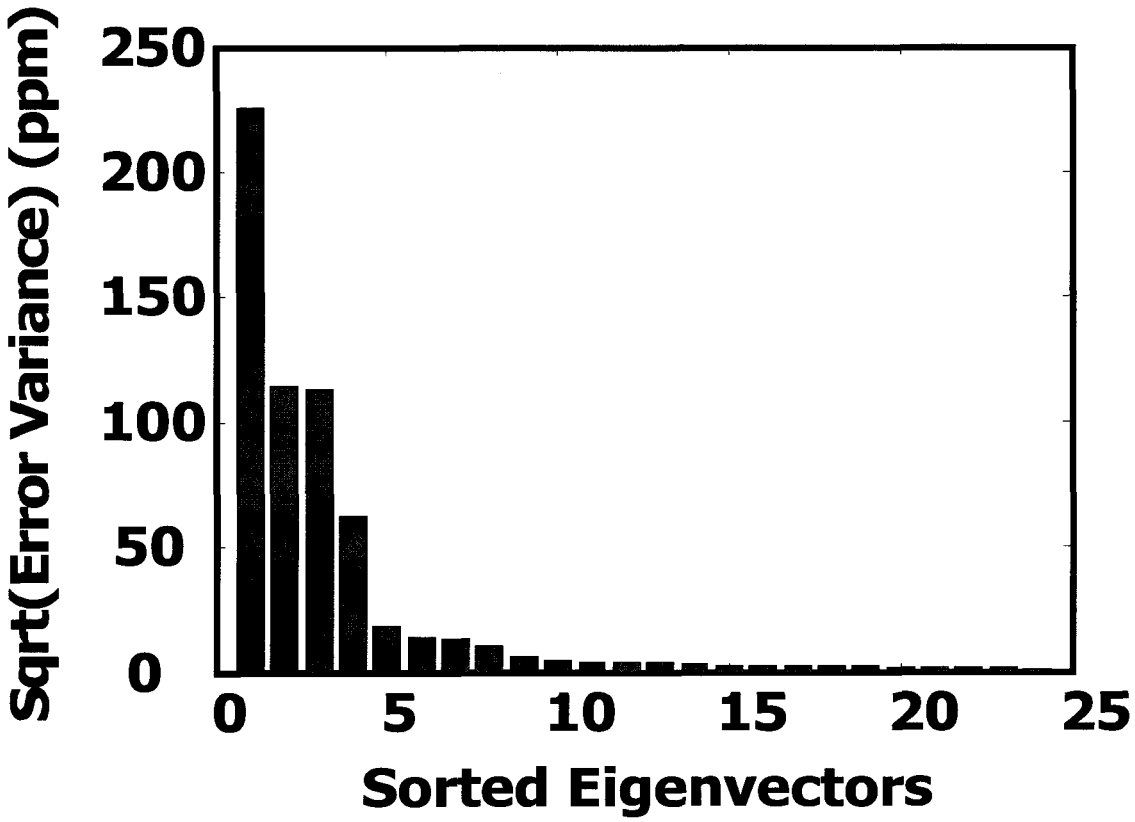

Figure 6. Square root of the concentration error variance from the CLS calibration model for each of the mean-centered eigenvectors from all repeat spectra plotted as a function of the eigenvectors sorted by their concentration error variance.

The impact of the sort order on the PACLS prediction of the second half of sample spectra collected during the factorial experiment can be seen in Fig. 7 where the order of adding unsorted and sorted eigenvectors is seen to affect prediction ability.

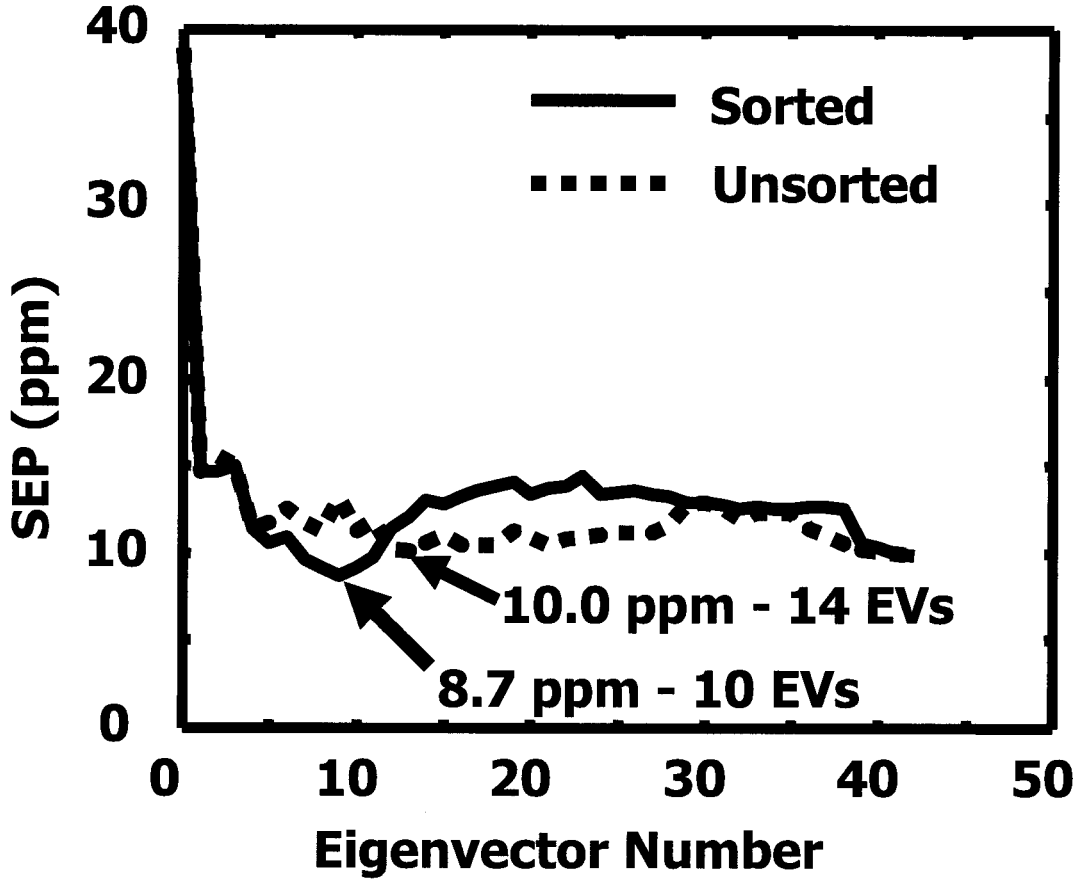

Figure 7. PACLS standard errors of prediction (SEP) as a function of added mean-centered eigenvectors from all repeat spectra for both sorted and unsorted addition of eigenvectors.

For the early factors, the predictions are clearly better for the sorted addition of eigenvectors relative to the unsorted. In addition, the minimum error is lower for the sorted eigenvectors and the definition of the minimum is more distinct. Note that as required, when all factors are added, the two methods yield the same prediction ability. Assuming these results are representative of other data sets, it is clear that PACLS prediction with proper sorting of the repeat sample eigenvectors has an advantage over the addition of eigenvectors based upon their described spectral variance. Similar methods can be used to improve factor selection during SRACLS and CRACLS cross-validated calibrations.

COMPARISONS OF PREDICTION ABILITIES OF AUGMENTED CLASSICAL LEAST SQUARES AND PARTIAL LEAST SQUARES WITH REALISTIC SIMULATED DATA: EFFECTS OF UNCORRELATED AND CORRELATED ERRORS WITH NONLINEARITIES

A manuscript describing this work summarized below has been submitted to Applied Spectroscopy.[16] Comparisons of prediction models from the new ACLS and PLS multivariate spectral analysis methods were conducted using simulated data with deviations from the idealized model. Simulated uncorrelated concentration errors, and uncorrelated and correlated spectral noise were included to evaluate the methods on situations representative of experimental data. The simulations were based on pure spectral components derived from real near-infrared spectra of multicomponent dilute aqueous solutions containing glucose, urea, ethanol, and NaCl in the concentration range from 0 – 500 mg/dL. The statistical significance of differences was evaluated using the Wilcoxon signed rank test.[17] The prediction abilities with nonlinearities present were similar for both calibration methods although concentration noise, number of samples, and spectral noise distribution sometimes affected one method more than the other. In the case of ideal errors and in the presence of nonlinear spectral responses, the differences between the standard error of predictions of the two methods were sometimes statistically significant, but the differences were always small in magnitude. Importantly, SRACLS was found to be competitive with PLS when component concentrations were only known for a single component.

Thus, SRACLS has a distinct advantage over standard CLS methods that require that all spectral components be included in the model. In contrast to simulations with ideal error, SRACLS often generated models with superior prediction performance relative to PLS when the simulations were more realistic and included either non-uniform errors and/or correlated errors. Since the generalized ACLS algorithm is compatible with the PACLS method that allows rapid updating of models during prediction, the powerful combination of PACLS with ACLS is very promising for rapidly maintaining and transferring models for system drift, spectrometer differences, and unmodeled components without the need for recalibration. [4, 5, 16]

The comparisons under different noise assumptions in the simulations obtained during this investigation emphasize the need to use realistic simulations when making comparisons between various multivariate calibration methods. Clearly, the conclusions of the relative performance of various methods were found to be dependent on how realistic the spectral errors were in the simulated data. Results demonstrating the simplicity and power of ACLS relative to PLS are presented in the following section.

ACLS METHODS FOR IMPROVED MULTIVARIATE CALIBRATION TRANSFER

The research summarized in this section has been prepared for submission as a journal paper to Applied Spectroscopy. [18] Calibration transfer involves using a spectral calibration model developed on one spectrometer to predict sample spectra obtained after changing components on the instrument or for predicting concentrations based on sample spectra acquired on an entirely

different spectrometer. Without compensating for the instrument change, applying the original model to the spectra of samples obtained on the second spectrometer often leads to a significant degradation the prediction ability due to differences induced in the sample spectra by the instrument changes. This study was conducted to explore the calibration transfer options provided by the new SRACLS algorithm and to compare its transfer ability to that of the PLS algorithm. The spectral data for this study were obtained on a Nicolet near infrared FT-IR spectrometer at Thermo Nicolet (Madison, WI) from a set of 31 organic solutions using statistically designed mixture concentrations of the chlorobenzene and toluene major components and the minor hexane component (see reference for a more complete description of the samples used in this study). The spectra were obtained on two Nicolet near-infrared spectrometers using several different sampling configurations. SRACLS significantly extends the capabilities of CLS to handle spectral problems that formerly could be addressed only with the implicit multivariate methods such as PLS. SRACLS is especially effective in the solution of transfer of calibration problems because it is compatible with the PACLS algorithm. PACLS directly incorporates spectral information into the prediction model without recalibration and without requiring concentrations for the samples used to transfer the calibrations. SRACLS also provides a variety of approaches for quickly including transfer spectral information in the model.

Because of the speed and ease of updating the SRACLS model, we have found that it is even reasonable to update the model for each new sample. For PLS, the transfer spectra are included in the calibration model, so updating the model requires the time consuming process of recalibration with cross-validation implemented for factor selection. In the course of this work, the flexibility of SRACLS has been demonstrated. Also, during the comparison of SRACLS and PLS, we found that SRACLS generally provided equal or superior prediction abilities during calibration transfer. Since the SRACLS results were competitive with PLS and has greater flexibility and speed, we recommend it as the preferred multivariate method for transferring spectral calibration models.

CONCLUSIONS

This LDRD project has demonstrated the ability of the CLS/PLS hybrid algorithm to maintain a calibration on a drifting spectrometer and to transfer multivariate calibrations between spectrometers from the same or different manufacturers. In addition, a new family of ACLS algorithms was developed that have all the advantages of the PLS and hybrid algorithm, but have the added benefit when combined with the PACLS algorithm that they can be rapidly updated during prediction without the need for recalibration. The updating can be used for maintaining a calibration in the presence of spectrometer drift, transferring calibrations between different spectrometers, or to correct for the presence of unmodeled spectral components in the sample spectra to be predicted. The theory behind the ACLS algorithms (both SRACLS and CRACLS) was presented and prediction ability comparisons were made between the SRACLS and PLS algorithms using both simulated data and experimentally-derived spectra. SRACLS was found to be as good as or better than PLS in prediction ability, and the ease of use and the ability of SRACLS to be updated during prediction without recalibration make it the preferred multivariate method. The fact that the performance abilities of PLS and SRACLS were different for simulated data depending on whether ideal or realistic spectral errors were included in the simulations clearly demonstrates that simulations need to be performed using errors with

characteristics representative of experimental data (i.e., non-uniform and correlated errors). SRACS was found to outperform PLS when the simulated spectra included realistic spectral errors.

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APPENDIX A

INTER-VENDOR MULTIVARIATE CALIBRATION TRANSFER OF FIBER-OPTIC BASED ON-LINE FT-NIR ANALYZERS

Christine M. Wehlburg and David M. Haaland
Sandia National Laboratories, Albuquerque, NM 87185-0886

Robert D. Guenard
Process Analytics Regulatory and Analytical Sciences,Merck & Co. Inc.,
WP 78-110, P.O. Box 4, Sumneytown Pike, West Point, PA 19486

Randy J. Pell
The Dow Chemical Company
Analytical Sciences Laboratory 1897S, Midland, MI 48667

Introduction

Fourier transform near infrared (FTNIR) technology has brought value in many areas of process analysis because of its high precision, speed, multi-component capability and sampling flexibility. Many process FTNIR applications use multivariate calibration models to relate spectral measurements to process stream properties with the goal of predicting those properties from the spectral measurements. Transfer of these calibration models in a global chemical company is of absolute necessity when replicating the same analytical technique at various sites and, possibly, on instruments from different vendors. For process FTNIR technology to be cost effective, it is expected that calibration models will be transferable from one analyzer to another with a minimal amount of spectral preprocessing or data collection. In the world of industrial process analytical chemistry, personnel and monetary resources can be limited thus necessitating a non-intensive implementation and maintenance strategy for FTNIR technology. Part of this strategy is the implementation and maintenance of multivariate calibrations through the mathematical transfer of calibration models rather than complete recollection of the calibration data. Besides resource limitations, other reasons requiring calibration transfer of process FTNIR models include modification of the optical train (alignment, part replacement); environmental health and safety issues; samples are difficult to handle or reproduce; globally standardized calibrations; and cost (some models can cost up to 1 million dollars to develop). With an increased emphasis on global quality within large chemical companies, transfer of multivariate calibration models for process analyzers become essential for producing product at all sites with the same quality specifications.[1]

Our group has been involved in the development of a novel chemometric hybrid algorithm Prediction Augmented Classical Least Squares/Partial Least Squares (PACLS/PLS). The spectral interferences or spectral "shapes" of unmodeled components such as instrument drift and

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instrument response changes are explicitly added to the algorithm during calibration.[2] By combining improved experimental designs and this new algorithm, we have developed near-IR calibration models that require fewer samples, are stable over time and can be transferred to secondary spectrometers. Our previous FTNIR studies in maintaining and transferring spectrometer calibrations showed that the hybrid algorithm, without exception, outperformed standard benchmark techniques currently used in industry.[3,4] This calibration transfer study examined the intra-vendor (same model spectrometer) scenario. Based on the results of that research, a collaborative study with the Dow Chemical Company was facilitated to investigate inter-vendor (same type of spectrometer, different vendors) calibration transfer. Inter-vendor calibration transfer is more challenging than intra-vendor and would more rigorously test the transfer methods, including the new hybrid algorithm.

There is a strong interest to study calibration transfer and much research has been devoted to the problem. De Noord presents a good tutorial of the strategies and techniques for standardizing multivariate calibrations.[5] In that paper, the strategies are broken down into six major categories including instrument matching, robust calibration models, bias correction, correction of measurement data, correction of calibration model and subset recalibration. Much of the literature is devoted to the development of chemometric methods that correct the measurement data. Early methodologies were based upon univariate techniques, such as those developed for agricultural applications.[6] Multivariate techniques such as direct standardization and piecewise direct standardization[7] were developed, with the latter becoming somewhat of a standard upon which others have been benchmarked. Other methods use neural networks[8,9], transfer in the wavelet[10] and in the Fourier domains.[11] Transfer of calibration without standards in common between the parent and child instrument has been shown through a technique using a finite impulse response (FIR) filter.[12] The statistical methods of Procrustes analysis have been applied to calibration transfer.[13] Work has also been done to investigate the strategy of building robust models in order to address instrument standardization.[14,15] Improvements in PLS model transfers

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through robust wavelength selection has also been shown.[16] Adhihetty et al. have recommended the transfer strategy of instrument matching of interferometric spectometers.[17]

Theory

Transfer of calibrations can be performed by estimating a transfer function to match both analyzers spectral response function

$$\mathbf{R_c} = \mathbf{F}\,\mathbf{R_p} \qquad (1)$$

where $\mathbf{R_p}$ is the spectral response matrix of the parent instrument (on which training set was collected), $\mathbf{R_c}$ is the spectral response matrix of the child instrument (target instrument) and F is an appropriate transformation function. Or, the regression vectors can be transferred

$$\mathbf{b_c} = \mathbf{F}\,\mathbf{b_p} \qquad (2)$$

where $\mathbf{b_p}$ is the parent model regression vector and $\mathbf{b_c}$ is the transferred regression vector. There are several instrumental parameters that may affect the overall spectral response and ultimately the ability to transfer a calibration model from one spectrometer to another. The major contributors to **R** include instrument-to-instrument:

- Spectral lineshape
- Frequency registration, precision and accuracy
- Optical pathlength
- Photometric accuracy

Given that the foregoing parameters affect **R,** care must be taken to assure that the controllable instrumental parameters, such as apodization, resolution, and phase correction are equivalent between parent and child analyzers. Because of variation in materials, manufacturing, alignment and sample interface types there will be some amount of instrument-to-instrument distortion in **R**. A pure hardware approach, matching spectral responses ($\mathbf{R_c} = \mathbf{R_p}$), requires that analyzers are similar enough such that instrument-to-instrument variation does not degrade the performance of the model. Gauging from the literature, as well as studying and performing calibration transfers, the current methodology used by the process analyzer community for intra-vendor transfer is to match spectral responses as best as possible and then apply mathematical methodologies ranging from simple spectral preprocessing up to and including the more advanced aforementioned techniques. For intra-vendor model transfer, we have found that even with good instrument-to-instrument reproducibility, some spectral preprocessing (software) is necessary for a successful model transfer.[2]

Details of the classical least squares/partial least squares (CLS/PLS) hybrid algorithm have been presented previously,[18] therefore, the following will be an overview. Matrices and vectors are represented as uppercase and lowercase bold letters, respectively. Superscript T denotes row vectors and transposed matrices, while lowercase letters in italics represent scalar values. The

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superscripts "-1" and "+" refer to the matrix inverse and Moore-Penrose pseudoinverse, respectively. The CLS model is

$$\mathbf{A} = \mathbf{CK} + \mathbf{E_A} \tag{1}$$

where **A** is the n x p matrix of absorbances for n samples at p frequencies **C** is the n x m matrix of reference concentrations for the m components, **K** is the m x p matrix of the pure-component spectra at unit concentration, and $\mathbf{E_A}$ is the n x p matrix of spectral residuals. The least squares solution for **K** represented by $\hat{\mathbf{K}}$, is given by

$$\hat{\mathbf{K}} = (\mathbf{C}^{\mathbf{T}}\mathbf{C})^{-1}\mathbf{C}^{\mathbf{T}}\mathbf{A} = \mathbf{C}^{+}\mathbf{A} \tag{2}$$

The CLS/PLS hybrid calibration first performs CLS calibration and prediction steps. During CLS prediction the estimated concentrations, $\hat{\mathbf{C}}$, are calculated by

$$\hat{\mathbf{C}} = \mathbf{A}\hat{\mathbf{K}}^{\mathbf{T}}(\hat{\mathbf{K}}\hat{\mathbf{K}}^{\mathbf{T}})^{-1} = \mathbf{A}\hat{\mathbf{K}}^{+} \tag{3}$$

The estimated pure-component spectra, $\hat{\mathbf{K}}$, are used to predict the concentrations of the known calibration spectra, **A**. Spectral and concentration residuals are obtained during CLS prediction, and these residuals are passed to the PLS portion of the hybrid algorithm for the final steps of the hybrid calibration. The PLS portion of the hybrid algorithm, therefore, builds a model that relates the concentration residuals to the corresponding CLS spectral residuals. Since the concentration errors are modeled, the PLS estimated concentration errors can be combined with the CLS estimated concentrations to obtain an improved concentration estimate. During prediction of unknown spectra, the CLS/PLS hybrid model first estimates concentrations based on the estimated pure-component spectral matrix, $\hat{\mathbf{K}}$, of the CLS front end of the hybrid algorithm. Concentrations based on the PLS portion of the model are estimated from the spectral residuals remaining after the "front end" CLS prediction. The sum of the CLS predictions on the unknown spectra and the PLS predictions of the concentration residuals yields the final CLS/PLS prediction estimates.

The CLS/PLS hybrid algorithm gains an advantage over PLS when it incorporates prediction-augmented CLS (PACLS) during the "front end" portion of the algorithm. The PACLS model allows the unmodeled spectral variations to be added during CLS prediction to the pure-component spectral matrix estimated during CLS calibration.[2] Examples of unmodeled spectral variation include empirically derived spectral variation due to unmodeled analytes, temperature changes, instrument drift, and system response changes due to a change in instruments. We used subset sample spectra collected on both the primary and secondary instruments to capture the response differences between spectrometers. The sources of spectral variation required for the hybrid method to transfer calibration models were chosen to be the eigenvectors of the individual spectral differences between the primary and a secondary instrument for each subset sample and the mean difference of the subset sample spectra on the two spectrometers. The "prediction augmented" pure-component matrix explicitly forces the algorithm to ignore variations in the spectra that contain these same sources of spectral variation. During CLS prediction, the $\hat{\mathbf{K}}$ matrix in Eq. 2 is augmented with rows representing the new spectral shapes resulting in the augmented estimated pure-component spectral matrix, $\hat{\tilde{\mathbf{K}}}$. According to Eq. 3, the augmented, estimated PACLS-predicted concentrations matrix becomes

$$\hat{\tilde{\mathbf{C}}} = \mathbf{A}\hat{\tilde{\mathbf{K}}}^{\mathbf{T}}(\hat{\tilde{\mathbf{K}}}\hat{\tilde{\mathbf{K}}}^{\mathbf{T}})^{-1} = \mathbf{A}\hat{\tilde{\mathbf{K}}}^{+} \tag{4}$$

As explained for the CLS/PLS hybrid, in the PACLS/PLS hybrid calibration, the spectral and concentration residuals calculated in the PACLS 'front end' of the algorithm are then subjected to a PLS calibration. Likewise, the predicted concentrations for unknown spectra will be the sum of the PACLS predictions on the unknown spectra and the PLS predictions on the residuals.

EXPERIMENTAL

Hardware

To study inter-vendor calibration transfer, four different FTNIR analyzers were utilized to collect training set data: an ABB-Bomem Advance (Quebec, Canada), a NetworkIR (ABB Bomem, Quebec, Canada), a Bruker Vector 22/N (Billerica, MA) and an Orbital (formally Analect, Irvine, CA) DS-20. These analyzers were chosen based on availability and breadth of process robustness. All analyzers had optics optimized for the near infrared, used InAs detectors and were coupled by fiber optics. The experimental configuration was devised to closely simulate a process analyzer installation by using a sample interface (fiber coupled probe) typically used in an *in-line* application. Figure 1 illustrates the multiplexed analyzer configuration used for spectral data collection on samples in the training set. All of the analyzers were coupled to a single sampling point via an optical multiplexer. This setup was devised in an effort to minimize variability due to sample integrity and probe-to-probe differences. In this manner, it was assured that a spectrum of the same sample is collected on all analyzers. Also, this ensured that all analyzers were operating under the same environmental conditions (temperature, humidity, etc) over the course of the study. While probe to probe and fiber variations may be significant, the focus of this study was instrument-to-instrument variations. Spectra were collected with all analyzers in a period no longer than 10 minutes for any given sample in this configuration. The multiplexer was connected to a standard process 2-mm pathlength single-sided transmission (SST) probe (Guided Wave, El Dorado Hills, CA). Equal lengths of low hydroxyl content fiber (550 um core, Spectran, Avon, CT) were used to propagate the modulated light between the analyzers, the multiplexer and the probe. Fiber multiplexing was accomplished using an Axiom FMX-206A (Irvine, CA), bi-directional unit, which was capable of switching up to 6 fibers. The channel-to-channel matching specified from the manufacturer is $\pm 0.05\ cm^{-1}$ and $\pm 10\%$ in amplitude.

Data Set

To study the transfer of calibration models between analyzers built by different vendors, an ideal sample was chosen to further minimize the effect of sample variation. The ideal system chosen was a mixture of chlorobenzene (MCB, CAS[108-90-7]), 1,2-dichlorobenzene (ODCB, CAS[95-50-1]) and ethylbenzene (EB, CAS[100-41-4]) diluted in tetrachloroethane (TCE, CAS[127-18-4]). These constituents were chosen as ideal because of the following:

- clear and colorless liquids
- low volatility (boiling point > 120 C)
- low chemical reactivity, i.e. refractory in the time scale of the experiment
- low quantum yield of photodecomposition

- spectral features typical of many process analyzer applications

TCE was used as a solvent and is transparent in the NIR. We used a simple centroid mixture design that was constructed using JMP software (SAS Institute Inc. version 3.2.5). The concentrations were converted from mole fraction to weight per volume to ease sample preparation. The 24 standards were prepared gravimetrically by weighing out the components in a 100 mL volumetric flask and filling to volume. This ensured accurate reference values, which are essential to creating well performing quantitative models. Each sample was placed into a 250 mL jar, capped and refrigerated until analyzed. A cap was modified to accept and seal the SST probe in the jar. The sample was equilibrated in the water bath prior to spectral collection. Once the probe was placed into the jar and the temperature equilibrated, spectra were collected in a sequential manner using each analyzer. Specifically, a spectrum (1 min observation) was collected on the Advance, the multiplexer switched to the next channel, a spectrum collected on the Bruker and so on.

The inset of Figure 2 reveals the spectral region used for modeling purposes (5450 – 6300 cm^{-1}). Wavelength selection was done by using a-priori knowledge of the spectral transitions, response of the spectrometers in a process situation as well as trial and error. The signal-to-noise ratio was found to be highest in this region as a result of spectrometer responsivity and band intensity. Spectra for the primary instrument calibration model were preprocessed by performing a linear baseline correction, pinned at the extremes of the modeled region and then mean-centered. No other preprocessing, such as derivatives, was done so that noise and ultimately prediction errors were minimized. Cross-validated calibration results for both PLS and the hybrid CLS/PLS hybrid algorithm are shown in Table 1. As expected the cross-validated standard errors of prediction (CVSEP's) and corresponding R^2 values were very similar for both methods.

Data Analysis

Spectra from the secondary spectrometers first had to be put on a common frequency scale because of slight differences in point spacing and terminal wavenumber values between the primary and secondary spectrometers. These differences arise from instrument-to-instrument variation in absolute resolution and interferogram sampling. Wavenumber axis registration was achieved by performing a cubic spline interpolation of the secondary instrument spectra to match the primary instrument's wavelength axis. As such, this is the most basic method of inter-vendor calibration transfer in that the only transform that is done is to put all of the spectra on a common wavelength scale. Figure 3 shows the point-by-point spectral differences between the transfer subset spectra on the primary spectrometer and those collected on one of the secondary instruments. Subtracting two consecutively collected spectra on any of these FTNIR spectrometers yields very similar results. A spectrum from each analyzer is only an approximation of the "true" spectrum. Therefore, unless the spectrometers have equivalent spectral responses, there will always be some differences. There are several differences seen in these residual spectra including derivative shaped bands, water vapor spectra as well as baseline offset, tilt and curvature.

Derivative shaped bands in the regions of EB absorption (2ν CH), e.g., ~ 6000 cm^{-1}, indicate that there is a wavenumber shift between the primary and secondary analyzers. Intensity of these

different bands is related to the extent of the wavenumber shift as well as the extinction coefficient of the band. Shifts from the parent (Bruker) of the 2ν(CH) band were calculated for the Advance, NetworkIR and Orbital to be + 1.13, +0.26 and + 0.33 cm^{-1}, respectively. This shift was determined by finding the shift required to provide a maximum in the cross correlation between the secondary and primary instrument's spectrum over the region from 6300 cm^{-1} to 5450 cm^{-1}. From experience in performing many inter-vendor model transfers, it is known that wavenumber shifts can severely affect model predictions, even if the shift is only a fraction of spectral point spacing.[19] However, the magnitude of this effect is highly dependent upon the application (e.g., peak widths, rate of intensity change across the spectral bands, resolution, number of components, etc) and a general rule of thumb cannot be stated. Frequency (wavenumber) accuracy may be affected by beam aperturing and interferometer alignment. In fiber optic process FTNIR, wavenumber shifts are largely caused by fiber optic connections and sampling devices. The large shift in the Advance spectrum does not reflect the quality of the analyzer, but is caused by differences somewhere in the optical train.

A shift in the wavenumber scale of a FT spectrometer is generally a linear function with wavenumber.[20] Thus, to correctly adjust the wavenumber scale of the secondary spectrometer, some type of wavenumber standard that contains sharp bands across the wavenumber scale, should be scanned on both the primary and secondary spectrometers. In this manner, the linear function of the shift can be fit based upon the position of the bands of the standard across the spectrum. Performing this type of standardization in the process environment is somewhat impractical and problematic. Water vapor bands or neat liquids collected at high resolution are typical standards that can be used to characterize the wavenumber scale. Secondary spectrometer spectra for this study were compared as mentioned previously using EB spectra and then shifted using the constant obtained.

The PACLS/PLS and PLS algorithms were programmed at Sandia National Laboratories using the Array Basic language of the GRAMS 32 software (Version 5.1). Spectra were analyzed over the spectral range from 5450 – 6300 cm^{-1}. The standard F-test method was used to select the optimal size of the PLS models and of the PLS portion of the hybrid algorithm.[21,22]

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[21] D. M. Haaland and E. V. Thomas, Analytical Chemistry **60,** 1202 (1998).
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Results and Discussion

As Table II shows, wavelength shift correction of the secondary spectrometer spectra relative to the primary spectrometer is a way to improve upon the transfer of calibration relative to only placing the two sets of data on the same frequency scale. Using the cross-validated models presented in Table I, the spectra ***must*** be interpolated to the same frequency scale in order to predict the secondary instruments' data with the primary spectrometer's model. Without frequency shift corrections, the predictions are so poor as to indicate that there has been no successful transfer of calibration between the different vendor's spectrometers with either PLS or the hybrid CLS/PLS model. Both the high standard errors of prediction (SEP's) and the number of outliers (indicated in parentheses) support this conclusion. The application of the primary spectrometer's model to the shift-corrected data shows a marked improvement but the SEP's and number of indicated outliers are still too high. No other transfer of calibration technique was utilized in these predictions, hence, the original PLS and CLS/PLS models were compared to the Piecewise Direct Standardization and the hybrid PACLS/PLS methods.

Results in Tables III and IV illustrate the importance of subset selection in applying either (PDS or PACLS/PLS) method for transfer of calibration. For this particular study, PDS performed a better transfer of calibration utilizing the Kennard-Stone algorithm for selection of the subset samples, while the hybrid PACLS/PLS algorithm performed better when subset samples were

selected by concentration profiles discussed in a previous section. In both tables, shift corrected and uncorrected spectra were predicted using PDS and PACLS/PLS. In all cases, the PDS method did not perform well with non-shift corrected data. The hybrid PACLS/PLS method demonstrated marginal transfer of calibration with two of the three spectrometers. Although not conclusive, these results indicate that the use of repeat samples to account for instrument drift coupled with the hybrid PACLS/PLS method may be capable of performing inter-vendor transfer of calibration without shift correcting the secondary spectrometer's spectra.

Table III shows that when the Kennard-Stone algorithm is used to select subset spectra for the transfer of calibration process, the hybrid PACLS/PLS method performed as well as PDS (Advance instrument) or outperformed PDS (Network IR and Orbital). But, as shown in Table IV, PDS was unsuccessful in transfering the calibration from the primary to the secondary spectrometers when the subset sample spectra were chosen based upon concentration profiles. In fact, the hybrid PACLS/PLS algorithm (subset spectra chosen by concentration profiles) significantly outperformed PDS (subset spectra chosen by Kennard-Stone) for transferring the calibration from the primary spectrometer to two of the secondary spectrometers using shift corrected data. The performance measure in this case is reflected in the number of samples labeled as outliers according to the Spectral F-ratio.

Finally, a key observation for the PDS transfer of calibration in Table III of the NetworkIR and Orbital secondary spectrometers is that the SEP for the third component, EB, is very good. However, all 18 samples predicted for this component are identified as spectral outliers according to the spectral F-ratio and, therefore, the transfer of calibration is not considered reliable. Previous and current research by some groups continue to present successful transfer of calibration studies and report only good SEP values. SEP's are calculated based on concentration residuals and cannot be utilized as the sole criteria for a successful transfer of calibration. In a real, on-line application, the actual concentration of samples is unknown and spectral residuals must be the basis for establishing outlier criteria. If a sample spectrum is flagged as a spectral outlier, then its predicted concentration cannot be considered reliable. Thus, if a transfer method yields large numbers of outlier samples, then that transfer method would not be very useful for industrial applications even if it were able to predict validation samples with reasonable accuracy.

Conclusions

As in our previous maintenance of calibration and intra-vendor transfer of calibrations studies, the hybrid PACLS/PLS algorithm outperformed the benchmark method of PDS for an inter-vendor transfer of calibration study. Sandia's collaborative effort with the Dow Chemical Company was initiated after collection of the experimental data and therefore, the study did not profit from our experience in improving transfer of calibration results by correcting for the effects of instrument drift (maintenance of calibration). Through modeling of the data with respect to run order, the data were observed to "drift" over time. The assignment of one outlier sample for the final hybrid PACLS/PLS results on shift corrected data are similar to our previous intra-vendor transfer of calibration study and those results were further improved with the correction for instrument drift. Further inter-vendor transfer of calibration studies that use a

repeat sample or similar experimental method for accounting for instrument drift would be valuable in further improving the transfer results.

Table I. Cross-validated calibration results for data collected on the parent instrument.

Calibration Model for Primary Instrument	Component	# PLS Factors	CVSEP (g/100 ml)	R^2
PLS	MCB	8	0.09	0.9999
	ODCB	10	0.09	0.9999
	EB	12	0.06	0.9999
CLS/PLS Hybrid	MCB	7	0.09	0.9998
	ODCB	7	0.09	0.9999
	EB	8	0.07	0.9998

Table II. PLS and CLS/PLS prediction results from models developed on the primary spectrometer applied to spectra obtained on the secondary spectrometers without using transfer of calibration methods with the exception of a wavelength shift correction.

Secondary Instrument	Component	Standard Error of Prediction (# Outliers*) {g/100 ml}			
		PLS		CLS/PLS	
		no shift correction	shift corrected	no shift correction	shift corrected
B (advance)	MCB	1.08 (18)	0.21 (0)	1.11 (18)	0.20 (4)
	ODCB	3.05 (18)	0.18 (3)	3.89 (18)	0.21 (1)
	EB	0.41 (18)	0.07 (8)	0.39 (18)	0.06 (3)
C (bomem)	MCB	0.26 (12)	0.19 (2)	0.25 (16)	0.17 (6)
	ODCB	0.68 (17)	0.16 (9)	0.82 (16)	0.21 (4)
	EB	0.08 (18)	0.06 (15)	0.08 (16)	0.05 (9)
D (orbital)	MCB	0.40 (17)	0.23 (2)	0.34 (17)	0.21 (7)
	ODCB	1.01 (17)	0.31 (14)	1.31 (17)	0.41 (10)
	EB	0.12 (18)	0.07 (15)	0.12 (17)	0.07 (12)

*Outlier criterion was spectral F-ratio >4

Table III. Piecewise Direction Standardization and PACLS/PLS calibration transfer results utlizing subset samples selected by Kennard-Stone algorithm with and without shift-corrected spectra.

		Standard Error of Prediction (# Outliers*) {g/100 ml}			
Secondary		PDS (win=1)		PACLS/PLS	
Instrument	Component	no shift correction	shift corrected	no shift correction	shift corrected
	MCB	1.0 (18)	0.13 (0)	0.12 (0)	0.12 (0)
B	ODCB	1.9 (18)	0.15 (0)	0.16 (2)	0.18 (0)
(advance)	EB	0.42 (18)	0.06 (0)	0.08 (0)	0.06 (0)
	MCB	0.19 (2)	0.12 (0)	0.18 (1)	0.11 (2)
C	ODCB	0.38 (17)	0.17 (9)	0.19 (14)	0.21 (5)
(bomem)	EB	0.10 (18)	0.05 (18)	0.06 (12)	0.04 (4)
	MCB	0.30 (6)	0.17 (0)	0.16 (0)	0.14 (3)
D	ODCB	0.62 (16)	0.26 (9)	0.15 (3)	0.31 (4)
(orbital)	EB	0.12 (18)	0.06 (18)	0.06 (0)	0.05 (4)

*Outlier criterion was spectral F-ratio >4

Table IV. Piecewise Direction Standardization and PACLS/PLS calibration transfer results utlizing subset samples selected by concentration profiles with and without shift-corrected spectra.

		Standard Error of Prediction (# Outliers*) {g/100 ml}			
Secondary		PDS (win=1)		PACLS/PLS	
Instrument	Component	no shift correction	shift corrected	no shift correction	shift corrected
	MCB	1.7 (18)	0.37 (5)	0.23 (0)	0.10 (0)
B	ODCB	6.0 (18)	0.08 (11)	0.13 (8)	0.14 (0)
(advance)	EB	4.4 (18)	0.08 (13)	0.11 (0)	0.06 (0)
	MCB	0.18 (18)	0.18 (18)	0.18 (1)	0.10 (0)
C	ODCB	1.3 (18)	0.17 (18)	0.19 (14)	0.16 (1)
(bomem)	EB	0.70 (18)	0.30 (18)	0.06 (12)	0.05 (1)
	MCB	0.67 (18)	0.22 (18)	0.18 (0)	0.12 (0)
D	ODCB	2.0 (18)	0.55 (18)	0.13 (3)	0.24 (1)
(orbital)	EB	0.58 (18)	0.57 (18)	0.07 (0)	0.06 (0)

*Outlier criterion was spectral F-ratio >4

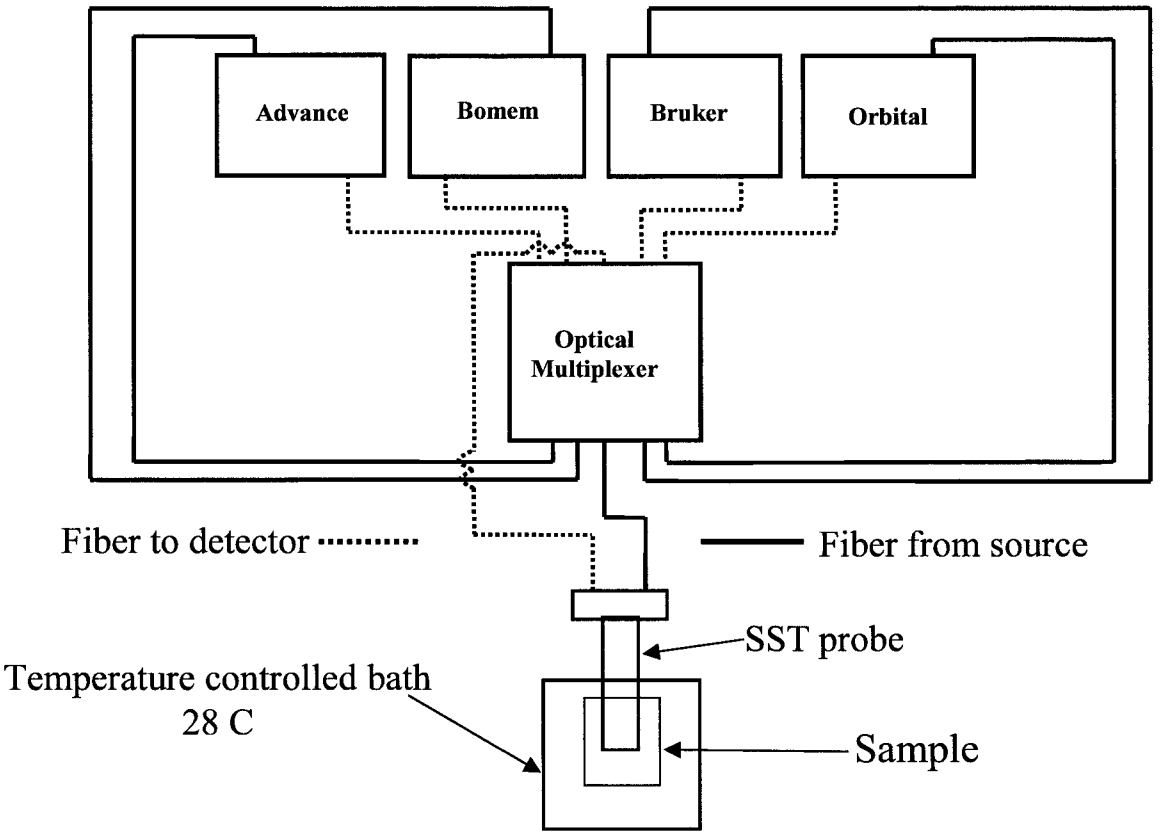
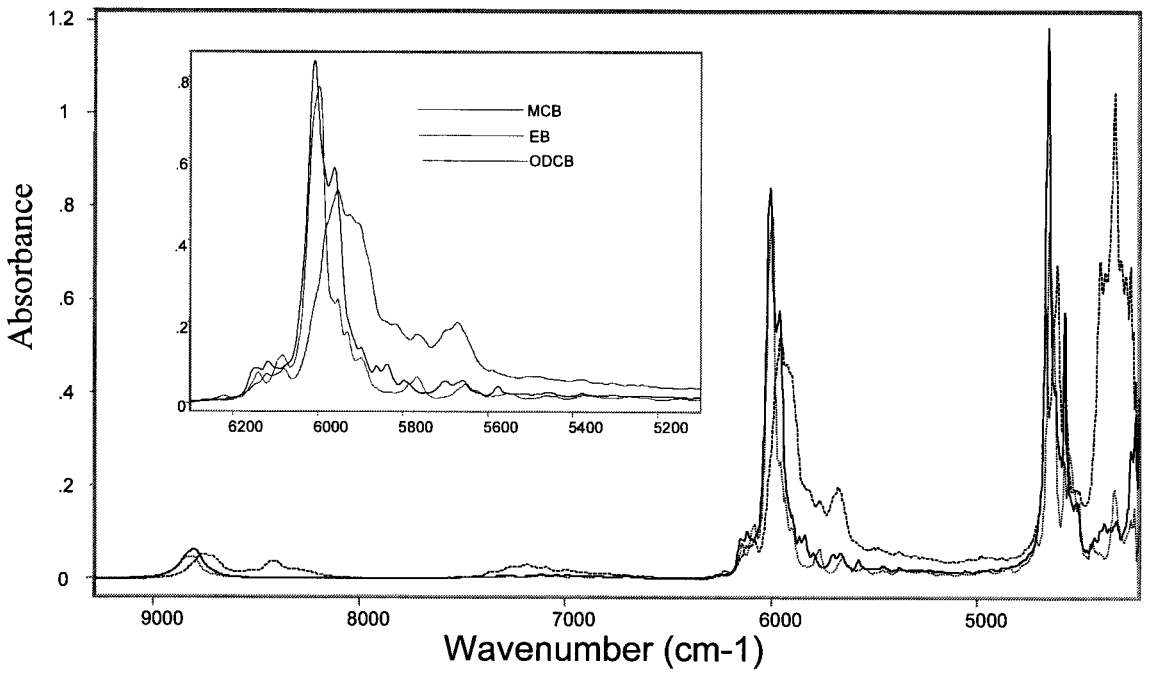


Figure 1. Experimental setup for collection of calibration transfer data on ideal chemical system.

Figure 2. Pure spectra of ideal system components. Inset illustrates modeled region.



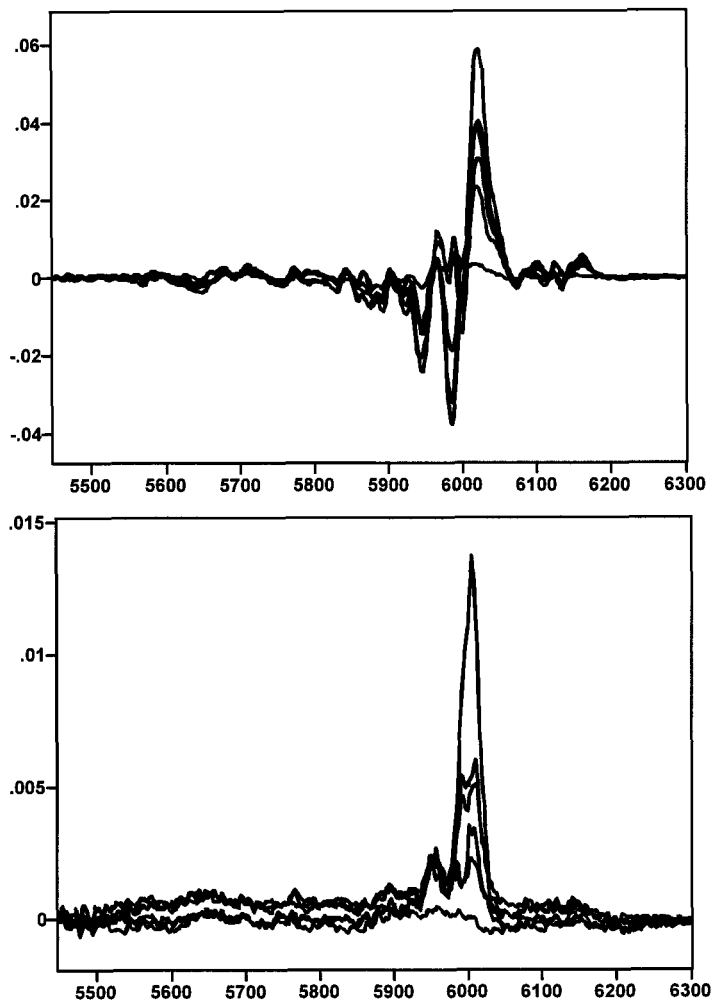


Figure 3. Subset differences without (top) and with shift correction (bottom).

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