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Robust calibration model transfer

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ABSTRACT

Calibration model transfer is an important issue in infrared spectra analysis. For identical sample, spectra collected with master and slave spectrometers share same components. In the sense of mathematics, they share same basis. If the basis and corresponding coefficient matrices can be obtained, the model transfer can be efficiently realized. On the other hand, the performance of calibration model transfer method will degrade if there are outliers and noise in samples. In this paper, a robust calibration transfer model is proposed. Cauchy estimator are employed to learn same basis shared by master and slave spectra robustly. Transformation matrix can be calculated with the two corresponding coefficient matrices. Slave testing spectra are represented with the common basis and corresponding coefficients are then transferred using the transformation matrix. The slave testing spectra can be transferred using common basis and the corrected coefficients. The convergence property and bound of proposed model are also discussed. Extensive experiments are conducted, experimental results demonstrate that our robust calibration transfer model can generally outperform the existing methods.

1. Introduction

Multivariate calibration model transfer is the key problem in infrared spectral quantitative analysis [1–3]. Multivariate calibration techniques are commonly employed but in practice the model is invalid if an existing model is applied to spectra measured under different circumstances (temperature and humidity) or on a separate instrument [4]. Recalibration can be utilized to break the limitation, but it is expensive and time consuming. This motivates calibration transfer method which refers to the transfer of quantitative analysis model between different instruments or conditions [5, 6]. Calibration transfer plays an important role, because of the possibility of using an existing model to analyze new samples obtained in new conditions or with an new instrument without the need to build the calibration model again [7–10].

Various calibration model transfer methods have been proposed, which have been comprehensively discussed [11, 12]. These methods fall into three categories. The first category is the pre-processing methods which eliminate or decrease the differences between master and slave spectra, including baseline elimination, derivative techniques, multiplicative scatter correction (MSC) [8], FIR filtering [9], orthogonal signal correction (OSC) [10], and generalized least squares (GLS). The second is to find a transformation matrix that maps the response of the slave instrument onto the master instrument, including direct standardization (DS) and piecewise direct standardization (PDS). The third is based on subspace learning. The transforation matrix is built in subspace.

Direct standardization (DS) and piecewise direct standardization (PDS) methods are the representative approaches of second category [13, 14]. DS uses the whole spectrum on the slave instrument to fit each spectral point on the master instrument. While in PDS, a small window from the slave spectrum is used instead of the entire spectral range.

CCA is a widely employed subspace learning tool in machine learning and pattern recognition, which is successfully applied to correct the differences between spectra measured on different instruments because of its ability to reveal the correlations between them [15]. CCA is first employed to reduce the dimensionality of master and slave spectra. The transformation matrix is calculated in lower subspace. Peng pointed out that the CCA is a linear subspace learning method. There are many subspace learning techniques, such as PCA, locality preserving projections (LPP) [16, 17], and neighborhood preserving embedding (NPE) [18]. However, the dense matrices eigenvalue decomposition in these algorithms is expensive in both time and memory, and the solution of the optimization problem

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is usually unstable when the number of features is larger than the number of samples. Thus spectral regression based model transfer method is proposed by Peng [19] to cast the problem of learning an embedding function into a regression framework, which avoids eigenvalue decomposition. The difference between the CCA based model transfer and Peng's method is that the direction vectors for master and slave spectra are calculated with spectral regression.

Calibration model transfer is to find the relationship between master and slave spectra. For simplicity, master and slave spectra are obtained using same sample. According to Lambert–Beer's Law, mixture spectrum is weighted sum of pure substance spectra. Thus, if the pure substance spectra are obtained, calibration model transfer can be implemented efficiently. Unfortunately, to obtain pure substance spectra of complex mixture is impossible. In the sense of mathematics, master and slave spectra share same basis. If the basis and corresponding coefficient matrices can be obtained, the model transfer can be efficiently realized.

To obtain high accuracy, spectra acquisition is one of the most important stage in quantitative analysis. It would be desirable to eliminate or minimize the sources of data variability that are not related to the analytical property of interest. In fact, the spectra collected with infrared spectrometer are often affected by noise and outliers. Thus, the proposed methods should be robust against the noise and outliers to obtain higher accuracy.

In machine learning and pattern recognition, Cauchy estimator is more robust than least square estimator and ℓ_1 estimator [20, 21]. Compared with least square estimator and ℓ_1 estimator, Cauchy estimator can heavily reduce the influence of large errors. Meanwhile, when an estimator is robust, it is inferred that the influence of any single observation is insufficient to yield a significant offset. Cauchy estimator has been shown to own this property. At this point, we proposed a new robust method based on Cauchy estimator to correct the spectral data.

The rest of the paper is organized as follows. We review general principles of calibration model transfer methods in Section 2. We formulate robust calibration model transfer and provide an efficient algorithm for solving the proposed model in Section 3, where analysis to convergence analysis and bound discussion are also conducted. Experiments and result analysis are provided in Section 4 and conclusions are drawn in Section 5.

2. Related work

Infrared spectroscopy is an extensively employed analytical technique in many industrial applications because of its rapidness and the fact that it is non-destructive to the samples. Multivariate calibration techniques are commonly used method to build quantitative analysis model, such as partial least squares (PLS) regression [1] and principal component regression (PCR) [2]. However, a problem occurs when an existing model is applied to spectra that were measured under new environmental conditions or on another instrument. New spectra contain variation which can lead to erroneous predictions. A possible solution to this calibration transfer problem is to measure every sample in the new instrument and construct a new model for it. However, this process would be both costly and time consuming. A more acceptable way is to apply chemometrics techniques to correct the difference of spectra measured on two instruments.

2.1. Classical calibration model

Let $\mathbf{X}_s$ and $\mathbf{X}_m$ be the spectral matrices obtained from master and slave instruments respectively. $\bar{\mathbf{X}}_s$ and $\bar{\mathbf{X}}_m$ are subsets of $\mathbf{X}_s$ and $\mathbf{X}_m$ respectively, $\mathbf{C}$ and $\bar{\mathbf{C}}$ are corresponding concentration matrices. $\mathbf{K}_s$ and $\mathbf{K}_m$ are the matrices of sensitivities on both instruments, each row is the pure components spectra. The relationships between the concentration matrices and observed matrices $\mathbf{X}_s$ and $\mathbf{X}_m$ are:

$$\mathbf{X}_m = \mathbf{C}\mathbf{K}_m \tag{1}$$

$$\mathbf{X}_s = \mathbf{C}\mathbf{K}_s = \mathbf{C}(\mathbf{K}_m + \Delta\mathbf{K}) \tag{2}$$

where $\Delta\mathbf{K}$ is the difference matrix between $\mathbf{K}_s$ and $\mathbf{K}_m$. The same relationship is hold for the subsets.

$$\bar{\mathbf{X}}_m = \bar{\mathbf{C}}\mathbf{K}_m \tag{3}$$

$$\bar{\mathbf{X}}_s = \bar{\mathbf{C}}\mathbf{K}_s = \bar{\mathbf{C}}(\mathbf{K}_m + \Delta\mathbf{K}) \tag{4}$$

The difference matrix $\Delta\mathbf{K}$ can be calculated by:

$$\Delta\mathbf{K} = \bar{\mathbf{C}}^{+}(\bar{\mathbf{X}}_s - \bar{\mathbf{X}}_m) \tag{5}$$

Then $\mathbf{X}_s$ is estimated as

$$\hat{\mathbf{X}}_s = \mathbf{X}_m + \mathbf{C}\bar{\mathbf{C}}^{+}(\bar{\mathbf{X}}_s - \bar{\mathbf{X}}_m) \tag{6}$$

with $\hat{\mathbf{X}}_s$ and $\mathbf{C}$, a new calibration model can be built for prediction on the slave instrument. Two assumptions are implied in this method: the linear relationship should hold on both instruments and the concentrations for all analytes contributing to the response must be known. For complex compound, where the concentrations are not known, this method is invalid.

2.2. Direct and piecewise direct standardization

In direct standardization, response matrices on both instruments are related to each other by a transformation matrix $\mathbf{F}$:

$$\bar{\mathbf{X}}_m = \bar{\mathbf{X}}_s\mathbf{F} \tag{7}$$

where $\mathbf{F}$ is calculated as:

$$\mathbf{F} = \bar{\mathbf{X}}_s^{+}\bar{\mathbf{X}}_m \tag{8}$$

Lin [22] studied calibration model transfer between different temperatures. The method is based on direction standardization.

Piecewise direct standardization builds several local regression models to fit the every wavelength of the master spectra using a range of wavelengths of the slave spectra. The ith wavelength of master spectra $\mathbf{X}_m(:,i)$ is regressed on the slave piece $[\mathbf{X}_s(:,i-j),\ldots,\mathbf{X}_s(:,j+k)]$. According to the PLS or PCR regression model, $\mathbf{X}_m(:,i) = [\mathbf{X}_s(:,i-j),\ldots,\mathbf{X}_s(:,j+k)]b_i$. We obtain the matrix $\mathbf{F} = \mathrm{diag}(b_1^T,\ldots,b_p^T)$. The linear relation between master and slave instruments is $\mathbf{X}_m = \mathbf{X}_s\mathbf{F}$.

2.3. CCA based calibration model transfer

CCA based model transfer is proposed by W. Fan [15]. Canonical correlation analysis is employed to analyzed the mean centered standardization sets $\mathbf{T}_m$ and $\mathbf{T}_s$. Direction matrices $\mathbf{W}_m$ and $\mathbf{W}_s$ are obtained and the canonical variables $\mathbf{L}_m$ and $\mathbf{L}_s$ are obtained by projecting the standardization sets on to the direction matrices. The transform matrix $\mathbf{F}_1$ and $\mathbf{F}_2$ are determined by $\mathbf{F}_1 = \mathbf{L}_s^{+}\mathbf{L}_m$ and $\mathbf{F}_2 = \mathbf{L}_m^{+}\mathbf{T}_m$. The transferred prediction set $\mathbf{Z}_s$ is $\mathbf{Z}_s = \mathbf{K}_s\mathbf{F}_1\mathbf{F}_2$ where $\mathbf{K}_s = \mathbf{P}_s\mathbf{W}_s$.