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Calibration transfer in temperature modulated gas sensor arrays

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ABSTRACT

Shifts in working temperature are an important issue that prevents the successful transfer of calibration models from one chemical instrument to another. This effect is of special relevance when working with gas sensor arrays modulated in temperature. In this paper, we study the use of multivariate techniques to transfer the calibration model from a temperature modulated gas sensor array to another when a global change of temperature occurs. To do so, we built 12 identical master sensor arrays composed of three different types of commercial Figaro sensors and acquired a dataset of sensor responses to three pure substances (ethanol, acetone and butanone) dosed at 7 concentrations. The master arrays are then shifted in temperature (from −50 to 50 °C, ΔT = 10 °C) and considered as slave arrays. Data correction is performed for an increasing number of transfer samples with 4 different calibration transfer techniques: Direct Standardization, Piece-wise Direct Standardization, Orthogonal Signal Correction and Generalized Least Squares Weighting. In order to evaluate the performance of the calibration transfer, we compare the Root Mean Square Error of Prediction (RMSEP) of master and slave arrays, for each instrument correction. Best results are obtained from Piece-wise Direct standardization, which exhibits the lower RMSEP values after correction for the smaller number of transfer samples.

1. Introduction

Shifts in working temperature prevent direct calibration transfer between chemical measuring instruments [1]. That is to say that calibration models built for instrument I_1 working at a temperature T_1 experience an important degradation on prediction when applied to data samples of instrument I_2 at T_2 ($T_2 \neq T_1$). This is a matter of the utmost importance for temperature modulated metal oxide gas sensor arrays [2], where tolerances in heater resistances values, variations on the working flow conditions, and environmental fluctuations can give rise to a global shift ΔT of the sensor nominal temperature profile, and therefore of the sensor response waveform. A naïve approach to overcome invalid calibration transfer is to create independent calibration models for each of the arrays. However, this is an impractical solution, since it implies costly and labor-intensive measurement periods. A preferable methodology is the use of instrument standardization techniques [3] to correct the temperature shift in sensor arrays as compared to a reference array (from now on we will refer to these arrays as slave and master arrays respectively) calibrated for a complete set of experimental conditions and a proper temperature profile. The calibration transfer then relies on the measurement of only a small subset of experimental points in the slave array (herein called transfer samples).

According to Marco and Gutierrez-Galvez [4], calibration transfer can be realized following three different strategies: (i) by transforming the slave instrument readings to keep the calibration model of the master instrument still valid on the slave instrument, (ii) by modifying the target labels of the samples from the slave instrument so as to match those obtained from the master instrument, and (iii) by forcing master and slave readings to become more similar before creating the calibration model. Direct Standardization (DS) and Piecewise Direct Standardization (PDS) are the more popular methods to standardize slave instrument response [5,6]. With respect to the second strategy, the most frequently used method is univariate Multiplicative Signal Correction (MSC) [7]. Finally, Component Correction (CC), Orthogonal Signal Correction (OSC) and Generalized Least Squares Weighting (GLSW) are commonly used to remove instrument-to-instrument variability [8–10].

A large number of studies on instrument standardization have been applied to Near Infrared Spectroscopy (NIRS). However, there is a noticeable lack of studies about the standardization of gas sen-

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sor arrays, with the exception of three important contributions. Balaban et al. [11] built a calibration model to identify the age of milk samples with a chemical sensor array of 12 conductive polymers. They transferred this model to a different array with the same sensors. To do so, they transformed the slave array response into master array readings by applying three different types of corrections: Univariate Regression, Multivariate Regression (MLR) and Multilayer Perceptrons (MLP). These calibration transfer methods were evaluated comparing the classification rates of the master and the transformed master arrays. Multivariate regression showed the best performance in standardizing the instruments. In a similar study, Tomic et al. [12] aimed at compensating the effect of sensor replacement in a hybrid sensor array composed of 12 MOS (metal-oxide semiconductor) sensors and 5 MOSFET (metal-oxide semiconductor field-effect transistor). The problem to solve was to distinguish between milk in good condition from off-flavor milk. They acquired twice the complete set of measurements, before and after the sensor replacement. Then they modeled the data of the old sensor array, which was selected as the master instrument. Measurements obtained from the new array were adapted to be used in the master classification model with two different techniques: Component Correction (CC) and Multiplicative Drift Correction (MDC). The later was shown to be slightly more efficient in rectifying the slave instrument response using the classification rate obtained for the test as a figure of merit. In a more recent paper, Carmel et al. [13] showed the possibility of building mappings between two different sensor technology arrays, a 32 conducting polymer array (CP) and an 8 sensor quartz microbalance module (QMB), which were exposed to a set of 23 pure chemicals. The authors built a PCA model for each instrument and tried to classify test samples according to the distance to the centroid of the nearest class. After that, they transformed the projected data from one sensor array to the other in both directions. To perform this task, they investigated three different approaches: Multivariate Regression (MLR, PCR, PLS), Neural Networks (NN) and Tesselation-based Linear Interpolation (TLI). Again, the classification rate was the figure of merit used to compare master and the standardized slave instruments. Their results showed that the performance of the different standardization methods was dependent on the mapping direction, obtaining the best results for the conversion from CP to QMB using NN, and applying TLI in the reverse mapping. In all these previous works the complete set of training samples used to create the data models was transferred from the master to the slave instrument.

Beyond these valuable contributions, we have identified three important open questions for calibration transfer in e-noses. (i) E-nose arrays can tune their operational parameters so as to enhance their sensitivity to different compounds [14]. Therefore, instrument dissimilarities due to tolerances on the operational parameters must be corrected accordingly. (ii) In order to make an efficient calibration transfer, a limited subset of experiments should be run in the slave instruments. To the best of our knowledge, no systematic study comparing the performance of different calibration transfer techniques with respect to the number of transfer samples is found in the literature for e-noses. (iii) Continuous calibration models (regressors) provide a more sensitive measure of the calibration transfer performance than discrete calibration models (classifiers). However, in the literature you can only find classification models transferred from one instrument to another.

In this paper, we address these three open questions with the following study. We have explored the calibration transfer problem for temperature modulated metal oxide sensor arrays when a global shift of temperature occurs (i). In an exhaustive study that includes 132 master-slave instrument combinations, we will evaluate the quality of the calibration transfer obtained from several instrument standardization techniques. We will compare master and slave errors (RMSEP) for different temperature shifts and sizes of the transfer sample set (ii) and on concentration prediction (iii).

2. Theory

In this paper, we follow two of the three different strategies proposed in the literature for calibration transfer [Marco and Gutierrez-Galvez [4]]. The first one consists in transforming the sensor responses of the slave instrument so they resemble those of the master instrument. In this way, we can directly use the calibration model built on the sensor responses of the master instrument with the transformed slave sensor responses. In this strategy, we work on the space of responses of the master instrument. To transform the sensor responses of the slave instrument, we used Direct Standardization (DS) and Piece-wise Direct Standardization (PDS). The second strategy consists of transforming not only the sensor responses of the slave instrument but also those of the master instrument to a joint master-slave space. Thus, the calibration model is built in this joint space. The sensor response transformation methods used in this strategy are Generalized Least Squares Weighting (GLSW) and Orthogonal Signal Correction (OSC). Fig. 1 illustrates both strategies.

In addition to this, we realized a sample subset selection to sort out the samples used to study the performance of the calibration transfer in terms of the number of samples considered from the slave instrument. We test two different approaches: select samples before or after creating the calibration model of the master instrument. Next, we describe the main features of the different calibration transfer techniques used in this paper, as well as the two methodologies used to perform sample subset selection.

2.1. Calibration transfer techniques

The purpose of calibration transfer is to correct instrumental differences so that the readings of the slave instrument (X_S) become similar to the readings of the master instrument (X_M). Each of the calibration transfer techniques employed in this work has been trained to perform this task using a subset of samples of the training set of master and slave instruments. These samples are usually called transfer samples S. This notation is employed in the description of the following four calibration transfer techniques.

2.1.1. Direct Standardization (DS)

Direct Standardization [15] is a calibration transfer technique that relates the readings of the slave instrument to those of the master according to the following linear transformation:

$$\bar{S}_M = \bar{S}_S \times F \tag{1}$$

where $\bar{S}_M$ and $\bar{S}_S$ are the mean-centered response matrices of transfer samples of master and slave instruments and F the slave-to-master transformation matrix, which is estimated as the product $\bar{S}_M$ and the pseudo-inverse of $\bar{S}_S$:

$$F = \bar{S}_S^{+} \times \bar{S}_M \tag{2}$$

In this way, new samples from the slave instrument X_S can be projected onto the master instrument response space X_M:

$$X_M^T = X_S^T \times F \tag{3}$$

2.1.2. Piece-wise Direct Standardization (PDS)

The DS method has the limitation of not properly transform the responses from slave to master instruments when the number of variables per sample is greater than the number of samples. Thus, the transformation matrix F (Eq. (2)) becomes underdetermined [7]. Piece-wise Direct Standardization [16] avoids this problem using local PLS models. It creates local linear models f_j that relate the