An approach to calibration transfer based on latent variable space

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A problem of calibration transfer is well-known in analytical chemistry. Most of the works addressing this problem are coming from spectroscopy domain. The problem appears every time when one wants to use calibration model developed for one analytical instrument (e.g. near infrared (NIR) spectrometer) with the data obtained by another instrument of the same type (another NIR spectrometer). This is especially relevant to multivariate calibration models since they typically require large number of samples to establish reliable calibration. This large number may be hard/long to measure again on another instrument. Due to the fact that two spectrometers are not identical copies and they may differ in spectral shape, sensitivity, operating conditions, etc. direct application of a calibration model to the data from another spectrometer is normally not possible, since it leads to unacceptable growth of analytical errors in quantification of target sample parameters. Numerous methods were developed to perform calibration transfer and most of them are reviewed in the work [1]. The calibration transfer procedure can be based on correction of regression model parameters (slope and bias) or it can employ correction (conversion) of the second instrument response. The latter case can be considered in a broader context as a calibration transfer between two absolutely different analytical methods.

In this work we suggest the procedure for transfer of calibration models between different analytical methods. It is based on the conversion of analytical signals from one instrument into the format of another instrument. This conversion is performed in latent variable space as follows:

$X_1=T_1P_1^t$ (1), $P_2=T_{1tr}^+X_{2tr}$ (2), $T_2=X_{2data}P_2^+$ (3), $X_{2cor}=T_2P_1^t$ (4).

First we decompose the data X_1 from the first instrument using SVD (singular value decomposition) procedure, then from the score matrix T_1 we choose only the lines corresponding to the samples available in X_{2tr} which yields T_{1tr}. Using T_{1tr} matrix and X_{2tr} we compute P_2 – the

loadings for the second instrument, where T_{1tr}^{+} refers to matrix pseudo-inverse. Then we calculate corresponding score matrix for the data from the second instrument (X_{2data}) which we plan to use for prediction with calibration model from the first instrument and finally we compute corrected response from the second instrument (X_{2cor}) which can be further used with the model from the first instrument.

The performance of the suggested method was tested with simulated data sets and with real data. In the latter case calibration models constructed for quantification of Co, Ni and Cu in their triple mixtures from energy-dispersive X-ray fluorescence measurements were successfully employed for prediction of these three metals from UV-Vis spectrometry data. Moreover the suggested method can be employed for traditional calibration transfer, e.g. between two NIR instruments.

It appears that the method can have a broad range of possible applications in analytical chemistry.

References:

1. S. D. Brown, Transfer of Multivariate Calibration Models in Comprehensive Chemometrics, Elsevier, vol.3, p.345 (2009).