



Calibration transfer between different analytical methods

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ABSTRACT

The procedure for transfer of calibration models between different analytical methods is suggested. It is based on the direct standardization (DS) algorithm earlier suggested for data conversion between physically different instruments of the same type. As a result, multivariate regression models obtained e.g. for NIR spectroscopic measurements in one wavelength range can be successfully applied for predictions from the data obtained with another NIR spectrometer in another wavelength range. The performance of the suggested method was tested with two simulated and two real datasets. In the latter case calibration models constructed for energy-dispersive X-ray fluorescence, UV–Vis spectrometry and NIR spectrometry were addressed. The observed performance of the method implies that it can have a broad range of possible applications in analytical chemistry; some of them are suggested in the paper.

1. Introduction

A problem of calibration transfer is well-known in analytical chemistry. Most of the works addressing this issue 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 with 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 works [1,2]. 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 can be based on single wavelength standardization [3,4], when a response of the second instrument at each individual wavelength is converted into corresponding response of the first instrument so that the response of the second instrument can be used together with the

regression model from the first instrument. This approach allows for correction of linear shifts and intensity differences between the instruments; however it does not take into account possible peak broadening effects. In order to address these effects so called direct standardization (DS) [5] and piecewise direct standardization [6] approaches were developed. In the first method instrumental response conversion between two devices is done simultaneously for the whole wavelength range by means of the transformation matrix. This matrix is calculated from the measurements in a small transfer set and sometimes may contain the information which is not related to the differences between the instruments but to the calibration modelling instead. The piecewise direct standardization circumvents this issue by relating the response at particular wavelength of the first instrument to the certain window of responses around this wavelength on the second instrument. The piecewise direct standardization is probably the most popular and widely applied method of calibration transfer between spectrometers.

Nowadays approaches are suggested which allows for calibration transfer between NIR spectrometers having different wavelength range and different digitization [7]. Another series of studies is devoted to the use of latent variable space for calibration transfer [8–10] and various further developments [11–13].

At the same time the problem of calibration transfer can be considered in a broader context – as calibration transfer between two instruments operating on different physical principles. These different

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analytical instruments will have different response shape and different number of response variables, different sensitivity and intensity scale, etc.

Although numerous studies show that piecewise direct standardization outperforms direct standardization, the latter has an advantage of potentially being applicable for the case when two instruments have different lengths of response vectors with different shape and location of analytical signals in spectra.

The purpose of this research was to perform a feasibility study of direct standardization protocol as a potential tool for calibration transfer between different analytical instruments capable of addressing the same analytical task. Obviously, such kind of transfer is only possible when corresponding reliable analytical signals from target analyte are present in the responses of both instruments. Being validated such an unusual transfer approach can be widely employed in analytical chemistry e.g. for transferring of global multivariate calibration model constructed with a very large number of samples for one particular instrument to numerous other instruments based on other detection principles. This may have particular importance for transferring models between older and newer versions of the same analytical device having various analytical resolution and interferences, or for transferring reliable calibrations models from full-scale spectrometers to optical sensors employing limited number of LEDs.

This report is organized as follows: first we will briefly describe direct standardization mathematics; then we will show the performance of the approach with two simulated datasets of various complexities in terms of interfering species; finally we will address two real datasets. Projection on latent structures (PLS) regression model derived for energy-dispersive X-ray fluorescence spectrometry (EDX) measurements will be employed for prediction of Co, Ni and Cu content from UV–Vis spectroscopic data; PLS model for sugar content in marzipan samples based on NIR measurements in one wavelength range will be applied for predictions from NIR data in another wavelength range. The discussion on the appropriate choice of transfer set will be done addressing this latter case study.

2. Experimental

2.1. Direct standardization procedure

Our approach to data conversion between two instruments is based on classical DS procedure described in details in [5]. Briefly, let us consider two analytical instruments: the first one, for which we have developed calibration model based on its responses in a set of calibration samples (X_1); and the second one, for which we plan to use this calibration model after adjusting its response in the format of the first instrument using appropriate transfer set (X_{2tr}).

The conversion of the data format between two instruments can be performed using classical direct standardization approach. First we calculate transformation matrix F :

$$F = X_{2tr}^+ X_{1tr}, \quad (1)$$

where X_{1tr} is the response matrix of the first instrument in transfer set of samples. „+“ denotes matrix pseudoinverse. Then we calculate corrected response of X_2 instrument for the whole data set which has to be converted:

$$X_{2cor} = X_2 F; \quad (2)$$

where X_{2cor} refers to the corrected data from the second instrument (converted into the format of the first instrument).

2.2. Simulated datasets

The performance of the DS procedure for inter-instrumental calibration transfer was first assessed with simulated data sets. Spectra were modelled as the mixtures of Gaussians with different

width and amplitude. A normally distributed noise signal was added to each mixture spectrum with variance of 1% from the maximum intensity of the model spectrum. Two different cases were addressed.

The first simulation employed two instruments where no interference from other components was introduced. However, these two instruments (**I1** and **I2**) have different number of variables (1500 and 1000 correspondingly), different shape of signal and different intensity scale. In total the spectra of 40 samples were simulated. 30 samples were used for calibration of **I1**, seven of them were simulated also for **I2** as a transfer set, and 10 samples were employed as independent test set to assess the performance of the regression model with original and transfer data (simulated on both **I1** and **I2**). Concentrations of analyte were varied in the range 1–5 arbitrary units. In all the subsets (calibration, transfer and test set) sample concentrations were uniformly distributed along the concentration range.

The second simulation modelled a more complex situation with significant interference on a target analyte from three other species. Responses from the instruments **I3** and **I4** have different number of variables (200 and 500 correspondingly), different intensity scale, and different interference, which was higher for **I3** and lower for **I4**. In total the spectra of 40 samples were simulated. 30 samples were used for calibration of **I3**, seven of them were simulated also for **I4** as a transfer set and 10 samples were employed as independent test set to assess the performance of the regression model with original and transfer data (simulated on both **I3** and **I4**). In all the subsets (calibration, transfer and test set) sample concentrations were uniformly distributed along the concentration range. Composition of the four-component mixtures employed for the second simulation was designed using the approach suggested in [14] with custom made software. In case of simulated data sets there are no limitations on the number of samples neither in calibration set, nor in a test set. However, with these simulations we were trying to stay close to the real world situation where the number of available samples is usually limited by “time and money” considerations. Moreover, these simulated data sets are not very complex from the point of view of variance structure and thus, they do not require large test sets for reliable assessment of predictive ability.

Fig. 1 represents typical spectra for all simulated data sets. Concentrations of analyte were varied in the range 1–5 arbitrary units. The position of the signal from a target component in **I3** data is shown with the arrows “analyte”.

All simulated data together with corresponding concentrations are available in Electronic [Supplementary Information](#).

2.3. Real datasets

In order to assess the performance of the suggested transfer procedure with the real data we addressed three different datasets.

2.3.1. Co, Ni, Cu quantification in aqueous solutions with EDX and UV–Vis spectroscopy

First, the task of simultaneous quantification of copper, nickel and cobalt in their triple mixtures in aqueous solutions was addressed. The content of each metal was varied in the range 200–1000 ppm. The compositions of these mixtures were designed using the approach suggested in [14] and provided in the [Table S1 \(Supplementary materials\)](#).

The mixtures were prepared from 10 g/L stock solutions of copper sulfate, nickel nitrate and cobalt chloride. The corresponding salts were purchased from Vekton (St. Petersburg, Russia) in *pro analysis* grade.

The mixtures were measured with two spectroscopic methods based on different principles: X-Ray fluorescence spectroscopy and UV–VIS spectroscopy. The resulted spectra from both techniques contain characteristic bands of all three studied elements.

EDX spectra of aqueous solutions were obtained with energy-dispersive X-ray fluorescence spectrometer Shimadzu EDX-800HS

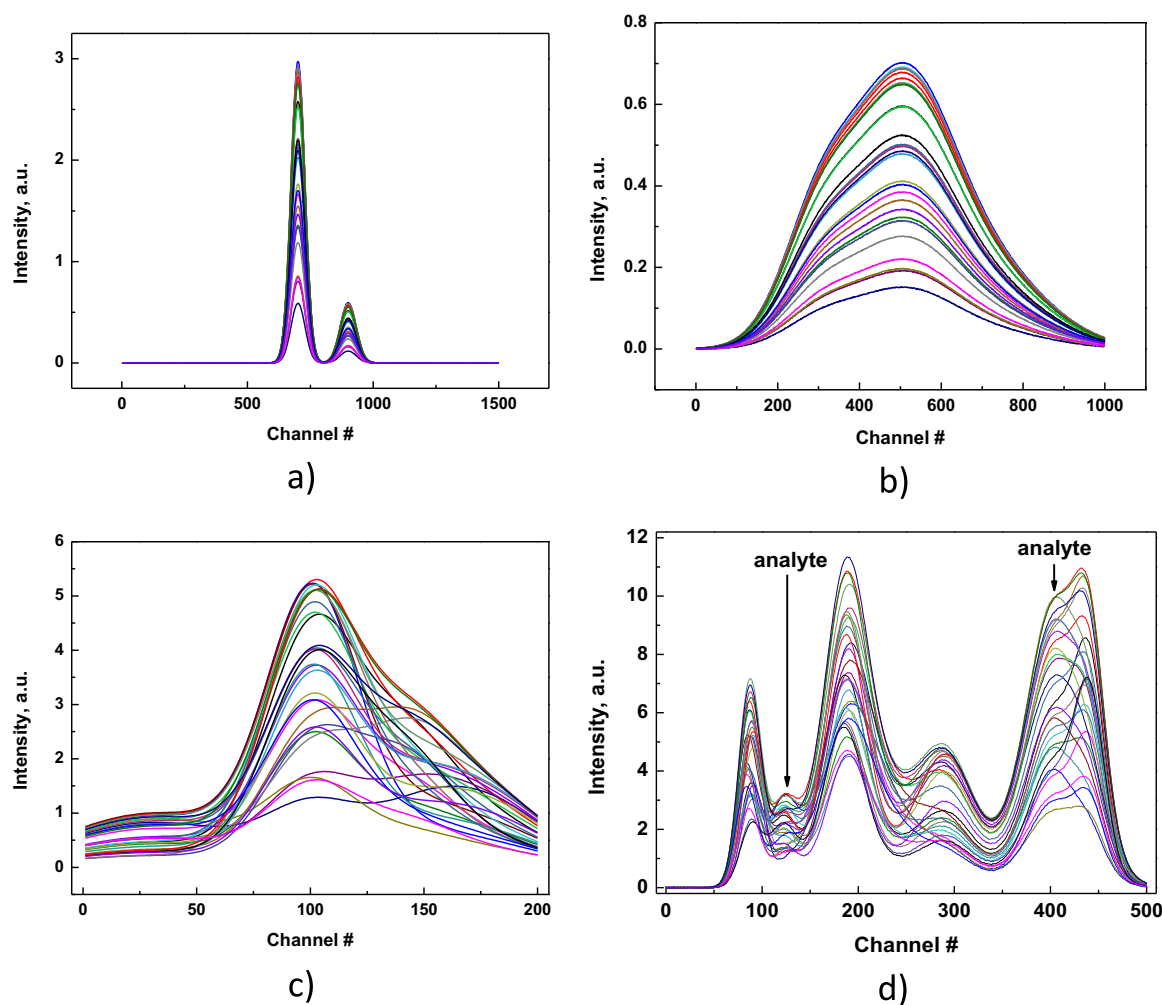


Fig. 1. Response of the simulated instrument a) **I1** with 1500 variables; b) **I2** with 1000 variables, c) **I3** with 200 variables, d) **I4** with 500 variables.

with rhodium anode X-ray tube. 5 ml of sample solution were placed in a sample cup (2.5 cm in diameter) and covered with polypropylene film of 5 μm thickness. All measurements were performed in ambient atmosphere. Spectra were obtained at 50 kV voltage and 40 μA current. These conditions are recommended by the instrument producer as optimal for analyzed elements. Spectra acquisition time was 100 s. Raw spectra were smoothed with Savitzky-Golay filter (2nd order polynomial, 15 points, 0th derivative order) and linear baseline correction was performed. The parts of the spectra in the energy range 6.4–9.6 keV (160 variables in total) were employed for further data processing. As an example, Fig. 2a shows the EDX spectra of the first five samples from the Table S1. The first line in the spectra with maximum intensity around 6.9 keV is CoK α , the second line with maximum around 7.5 is a combination of NiK α and CoK β , the line with maximum around 8.2 is a combination of CuK α and NiK β , and the last small peak around 8.9 keV is CuK β . All 29 mixtures were measured with EDX device. The samples # 1–9 were employed as independent test set to assess the predictive performance of PLS regression models constructed from the EDX data for samples # 10–29.

UV–Vis spectra of triple mixtures were acquired with UV–Vis spectrometer Shimadzu UV-1800 in the wavelength range 200–800 nm with 1 nm step in the quartz glass cuvette of 10 mm thickness. Distilled water was used as reference. Raw spectra were cut to keep only the region of interest (300–800 nm, 500 variables in total) and linear baseline correction was performed. Fig. 2b shows the UV–Vis spectra of the first five samples from the Table 1. Copper has a broad band with a maximum around 760 nm, nickel has a signal in the

beginning of the spectra around 300 nm, a distinct band at 395 nm and two broad bands after 600 nm overlapping with copper signal. Cobalt has spectral contribution with maximum around 515 nm and another one in the beginning of the spectra overlapping with nickel signal. All 29 mixtures were measured with UV–Vis spectrometer. The samples # 1–9 were employed as independent test set to assess the performance of the suggested transfer procedure based on different transfer sets constructed from samples # 10–29 used to convert UV–Vis data in EDX format.

All EDX and UV–Vis data together with corresponding concentrations are available in Electronic Supplementary Information.

2.3.2. Sugar content in marzipan samples with NIR spectroscopy

This dataset is described in details in [15] and it is publicly available at <http://www.models.life.ku.dk/Marzipan>. These data are devoted to quantification of sugar content in marzipan samples through NIR spectroscopic measurements. Only the part of the whole dataset was employed for this study, namely the data from Infratec 1255 (“master” instrument), dispersive scanning, 850–1050 nm wavelength range) and from Infraprover II (“slave” instrument, interferometer FT, 1000–2222 nm wavelength range). Both instruments have spectral signal from sugars and while sharing the same physical principle (NIR) differ a lot in spectral registration method and wavelength range. The results of measurements in 32 marzipan samples of nine different recipes are available in the dataset with total sugar content varying in the range 32.7 – 68.7 wt%. Baseline correction using subtraction of the minimal value for each spectrum was applied. The samples were split

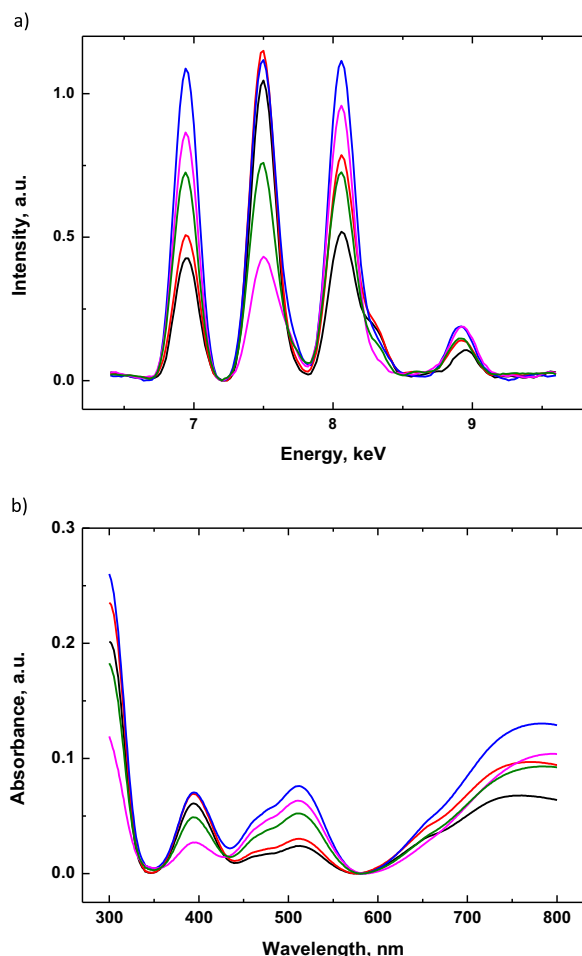


Fig. 2. EDX (a) and UV-Vis (b) spectra of samples #1–5 (Table 1).

Table 1.

RMSEP values obtained for test sets using converted data. The concentration range of target analyte is 1–5 arbitrary units.

Number of samples in transfer set	3 (#3,4,6)	5 (#1,3,4,6,7)	7 (#1–7)
I2 response converted into I1 format (I1 RMSEP=0.059)			
RMSEP obtained with I2 data	0.049	0.049	0.047
I4 response converted into I3 format (I3 RMSEP=0.15)			
RMSEP obtained with I4 data	2.96	0.27	0.25

into the calibration set (11 samples) and the test set (21 samples) using Kennard-Stone algorithm [16]. Sample spectra are shown in the Fig. 1S in Supplementary material.

2.4. Data processing

All matrix calculations described in the Section 2.1 were performed with R software [17]. PLS modelling and prediction was done using The Unscrambler 9.7 (CAMO Software AS, Norway) software package. Root mean squared error of prediction (RMSEP) was employed as a figure of merit to compare different PLS models:

$$RMSEP = \sqrt{\text{sum}(y_i^{\text{pred}} - y_i^{\text{real}})^2 / n},$$

where y_i^{pred} is an analyte concentration value derived from the PLS model, y_i^{real} – actual analyte concentration in the mixture and n is the number of samples in the test set.

3. Results and discussions

3.1. Performance of the DS transfer procedure with simulated data

3.1.1. Simulated instruments I1 and I2

At first a simple case of two analytical instruments providing signals clear from interference was addressed. Instruments **I1** and **I2** have different number of variables in the spectra, different shape of the signal and different intensity scale. Spectra of 10 samples from independent test set measured with **I2** were converted into the format of **I1** using DS procedure described in the Section 2.1 with different transfer sets. Fig. 3a shows the results of such conversion for the 10 samples from the test set. One can see that the shape and intensity of the spectra can be restored well. These converted spectra were employed to predict the analyte concentrations in the test set using PLS model constructed for **I1** instrument. In this particular case ordinary least squares regression will also perform well since there are no spectral interferences; however for the sake of uniformity we use PLS regression throughout the paper. In principle, since we convert the data format, any type of model (classification or regression) derived for **I1** can be further employed with **I2**.

Table 1 shows RMSEP values obtained for the test set data simulated for **I2** and converted into **I1** format when different number of samples is employed for transfer set. The “native” RMSEP value for the test set simulated for **I1** was 0.059 (in 1–5 a.u. concentration range).

In the simple case of **I1** and **I2** instruments the particular choice of the transfer set is not very important and reasonable data transfer is possible already with only 3 samples in a transfer set. The decrease of RMSEP with the growth of number of transfer samples is not dramatic. The samples in transfer sets were chosen to be uniformly distributed along the analyte concentration axis.

3.1.2. Simulated instruments I3 and I4

In case of more complex data structure with interference from other components the conversion of the spectral shape is still possible (Fig. 3b). Responses of both **I3** and **I4** contain overlapping signals from three other species besides analyte. Since the interference is different for two instruments (it is higher for **I4** and smaller for **I3**, **I3** is a “better” instrument for target analyte), it takes more samples in a transfer set to capture the variance structure and the rank of the data. 3 samples are absolutely not enough for data conversion – RMSEP with converted data is one order of magnitude higher than original). The rank is captured with 5 transfer samples, but even with 7 transfer samples RMSEP obtained for the converted data from **I4** (Table 1) is still higher than original RMSEP from **I3** (0.15 a.u.). Further increase of the transfer set will not substantially improve the results due to the complex data. As above, transfer sets were chosen to be uniformly distributed along the analyte concentration axis. Obviously, in case of transfer between two instruments with substantially different interference the choice of a transfer set is a more complicated task, which requires dedicated studies.

3.2. Performance of the suggested transfer procedure with real data

3.2.1. EDX – UV-Vis data

29 aqueous solutions containing copper, nickel and cobalt in concentrations 200–1000 ppm were analyzed with EDX and UV-Vis spectrometers (Fig. 2). PLS regression models were constructed for each of the three metals using EDX measurements in the samples #10–29 and were optimized using full cross-validation. PLS models were based on 2 latent variables for copper and nickel, while cobalt

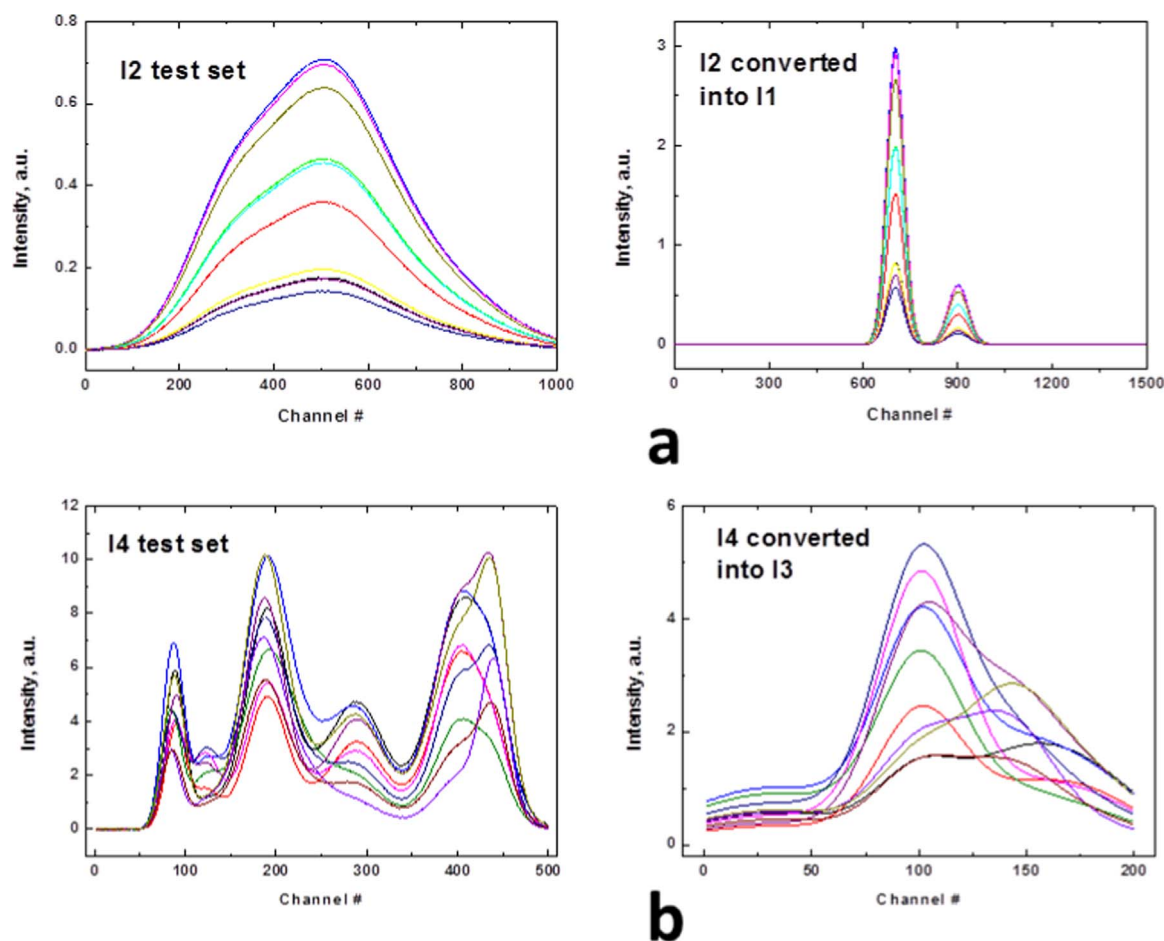


Fig. 3. Results of instrument response conversion: a) from **I2** into **I1** format; b) from **I4** to **I3** format.

modelling required 3 latent variables. These comparatively simple models (in terms of LVs) are due to the comparatively simple data set where there is no strong overlapping of the spectral bands. Following the DS procedure UV–Vis data for the samples #1–9 (test set) were converted into EDX format using different transfer sets selected from the mixtures #10–29. The EDX spectral shape and intensities were in a good agreement with that observed for converted UV–Vis data. Concentrations of Cu, Ni and Co were predicted using converted UV–Vis data by PLS models constructed with EDX data. RMSEP values were calculated and compared to assess the performance of the conversion procedure.

Three samples (namely # 12, 13 and 23) were chosen as a transfer set, since they cover high, low and middle concentrations of all three metals. Fig. 4a shows original EDX data and converted UV–Vis data using this transfer set. Table 2 illustrates the results of transfer. For comparison purposes the RMSEP values obtained in the test set with original EDX data and original UV–Vis data (based on calibration with samples #10–29) are shown. Table 2 also provides the results from transfer set based on samples (# 14, 15, 17) which are uniformly distributed in the concentration space – all these samples are close to the center of the concentration cube. UV–Vis model based on samples # 12, 13 and 23 demonstrates the advantages of model transfer in comparison with calibration based on a small number of samples.

The conversion of the data between different analytical instruments using DS procedure allows for maintaining reasonable precision in concentration assessment with transferred data. When transfer samples are not uniformly covering the concentration space (e.g. samples 14, 15, 17) the transferred data will not allow for application of the initial regression model. The choice of transfer set will be further studied in more details with marzipan data set.

3.2.2. Marzipan dataset

Original spectra from Infracore 1255 and Infracore II are shown in Fig. 1S in Supplementary material. Fig. 4b shows the results of data conversion from Infracore II format into Infracore 1255 for two samples which are different in sugar and moisture content. In all further discussion in this section this type of conversion (converted Infracore II data will be used with PLS model derived for Infracore 1255 data) will be considered. Reasonable match between the signals of two different instruments can be observed.

In order to explore the influence of transfer set we performed the following study. First, the acceptability criteria for transfer quality were introduced. Transfer sets allowing for $\leq 25\%$ relative increase in RMSEP (in transferred data) compared to original precision were arbitrarily considered as “acceptable”, those with 25–50% increase were considered as “intermediate”, and those $> 50\%$ were considered as “inacceptable”. In terms of sugar content, where original model had RMSEP of 2.8% mass. sugar, these are the sets with $\leq 3.5\%$, 3.5 – 4.2% and $> 4.2\%$ RMSEPs correspondingly. Fig. 2S (Supplementary) shows concentration plot of marzipan samples where axes denote moisture content and sugar content. Arbitrary we can divide all samples in four groups (marked with red circles). In order to form representative transfer set it seems logical to guess that this set should cover the whole concentration range; it should contain samples from all different groups; the number of the samples should be at least equal to the number of the groups.

The following choice patterns will be considered: 1) transfer set contains 4 samples, each of them represents one group from concentration plot; 2) randomized choice. Each pattern was checked with 48 different transfer sets. RMSEP values were calculated for each transfer set obtained with a particular set. Table 3 shows the distribution of

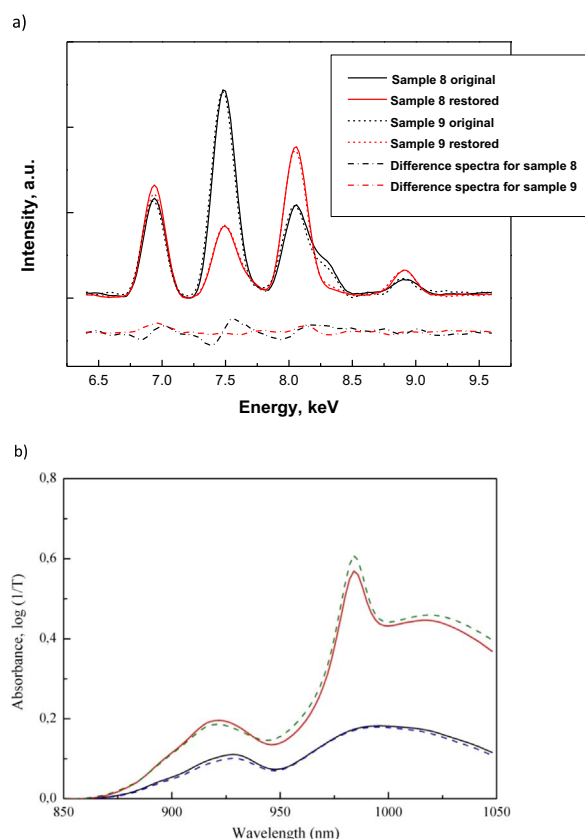


Fig. 4. Results of data conversion a) Original EDX data and converted UV–Vis data for two samples. b) solid lines – original Infracore 1255 data, dash lines – converted Infracore II data.

Table 2.

RMSEP values (ppm) in prediction of metal content in test set after data conversion from UV–Vis into EDX format.

	Cu	Ni	Co
Original EDX data, PLS calibration based on samples # 10–29	28	19	19
UV–Vis data converted into EDX, transfer set based on 3 uniformly spread samples (# 12, 13, 23)	19	33	27
UV–Vis data converted into EDX, transfer set based on 3 near central samples (# 14, 15, 17)	252	362	235
UV–Vis native data with calibration based on samples # 12, 13, 23	32	129	289
UV–Vis native data with calibration based on samples # 10–29	15	28	21

transfer sets chosen according to the specified criteria over three quality groups and average RMSEP values.

Both types of choice allows for relatively small average errors compared to original 2.8% sugar mass. However, in case of choice based on the concentration plot the percentage of “acceptable” transfer sets is much higher (75 against 46%), while in case of randomized choice 25% of sets are found to be “inacceptable”.

Addition of extra samples to transfer sets does not lower significantly the resulted average RMSEP values, but it just lowers the scatter between RMSEP values obtained in transferred data with various transfer sets.

Table 3.

Choice of transfer sets in two different ways.

	Average RMSEP, sugar % mass.	% “acceptable”	% “intermediate”	% “inacceptable”
4 samples according to randomized selection	3.9	46	29	25
4 samples represents the groups from concentration plot	3.3	75	25	0

Decrease of the number of transfer samples from four to three samples from different groups on the concentration plot leads to substantial increase in average RMSEP values (up to 4.5% mass sugar) with 45% of sets yielding “inacceptable” decrease of precision.

Another possible option is the choice of transfer set according to PCA score plot derived from spectral matrix of the samples, but in this case the number of “inacceptable” sets obtained with the procedure described above for four samples was around 20% with average RMSEP of 4.2% mass. sugar. This is easily understood taking into account the variance structure of the spectral matrix which is not always directly associated with target concentrations.

3.3. Future work and perspectives

Obviously, there are certain limitations on the instruments that can be subjected to the inter-instrumental transfer. Instruments having very different interference from sample matrix are likely to be poorly compatible in terms of data conversion. Thus, the suggested procedure is definitely not universal and has to be applied with a great care.

Further dedicated research is needed to address several important issues. First, an effect of the choice of transfer set must be further carefully studied using already suggested methods (e.g. [18,19]) or developing a new one especially for this procedure. Another question regarding a transfer set is whether it can be modelled using some standard reagent solutions without using real samples. It can be very important for variety of real samples which are rare, expensive or hard to standardize, like e.g. wine samples. Besides direct standardization another mathematical procedures can be developed for data conversion between different instruments. These issues must be carefully addressed before the suggested data conversion method can be adopted in everyday analytical practice.

Once the inter-instrument transfer procedure will be explored in details and well established it will open up a number of very attractive opportunities. For instance, global multivariate calibration model constructed with a very large number of samples for one particular instrument may become available for application with numerous other instruments based on other detection principles. This may be especially beneficial for transferring models between older and newer versions of the same analytical device where different analytical resolution and selectivity can be attained, or for transferring reliable calibrations models from full-scale spectrometers to optical sensors employing limited number of LEDs [20]. Since it is the data itself which are being converted, the idea can also be applied for transfer of classification (qualitative) chemometric models.

The first practical application of the suggested transfer procedure was already reported in [21], where DS was applied for transformation of potentiometric data into voltammetric format, and vice versa. It was possible to quantify tartaric acid in the grape musts using the data obtained from potentiometric system with the regression model developed for voltammetric system. Only 20% decrease in precision was observed for the converted potentiometric data compared to initial voltammetric model.

4. Conclusion

Direct standardization method is suitable for conversion of analytical response between two different analytical methods. The suggested approach was tested with both simulated and real data and showed

reasonably good performance. PLS regression models constructed for EDX analysis of copper, nickel and cobalt in complex aqueous mixtures were successfully applied for quantification of the same elements from UV–Vis spectra of corresponding solutions. PLS models for sugar quantification in marzipan derived for NIR measurements in a certain wavelength range were successfully applied with insignificant loss in precision for the data obtained by another NIR instrument operating in another wavelength range. In all studied cases the number of transfer samples is rather small. Taking into account the results obtained with marzipan dataset, it can be hypothesized that in most of the real cases calibration transfer through data conversion will require fewer samples than constructing new regression model. The choice of samples for transfer set is particularly important and the study shows that uniform distribution of transfer samples over target analyte concentration space is desirable.

In our opinion further development of the suggested approach will allow for construction of global calibration models not in the framework of a particular analytical method, but in the framework of a particular analytical object, and this global model can be applied to data from various analytical methods available in different laboratories.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.talanta.2017.04.039.

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