Calibration transfer—a question of your needs

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Introduction

The prospect of saving expenses by applying the near infrared (NIR) technique has lead to a steady growth of this method in the area of industrial quality control. Nevertheless, many users turned their back on this technique, as a result of unfulfilled expectations. The reason for this can be found mainly in the development of methods for the quantitative data evaluation, which is often based on a time-consuming and expensive reference analysis. The costs for the development of only a few chemometric models can easily amount to the order of the price of the NIR spectrometer itself, but this is usually accepted. This is critical, especially for process applications. Here a "pay back of investment" should be reached within a period of less than one year.

The second, but more important cause, is the fact that such models ideally, should be valid over an unlimited period of time (unchanged analyte) and that they should not be changed by instrumental reasons like aging effects or exchange of optical components, which would require a continuous re-calibration. The extreme would be the transfer of an existing model from the initial spectrometer (master—used to generate the calibration) to an independent spectrometer (slave), a requirement found especially for the in-line process control.

Many NIR instrument vendors are trying to take such problems into account by a software-aided fit of the slope and/or offset of the calibration model. In this case, a repetitive measurement of the calibration samples performed on the slave spectrometer is required. This, in fact, corresponds to a new calibration with all related costs. In the case of high precision FT-NIR spectrometers with a wavenumber accuracy of better than 0.1 cm^{-1} , the calibration data transfer between comparably equipped systems proves successful without the need of further adapting the model.

Experimental

This study will show the successful transfer of calibration data from one central measuring instrument ("master") onto a second instrument ("slave"). To make sure the experiments were made under praxis-oriented conditions two spectrometers of different ages were used. Moreover the measurements were made by different operators at different times, using different probes and detector elements:

Spectrometer No. 1 ("master"): age: three years, detector: InAs (peltier-cooled)

■ Spectrometer No. 2 ("slave"): age: brand new, detector: InGaAs (peltier-cooled)

Identical instruments of the Vector 22/N-F (Bruker Optik GmbH, Karlsruhe, Germany, see Figure 1) and identical mounted fibre optic probes N236-P (optical path length: 1 mm, Bruker Optik GmbH, Karlsruhe, Germany) were used. These experiments were made in air-conditioned rooms at 20°C with



Figure 1. Process NIR spectrometer VECTOR 22/N-F (Bruker Optik GmbH, Karlsruhe, Germany.

chemicals delivered by Merck KGaA (Darmstadt; Germany). Methods were developed by using a PLS1 algorithm (software OPUS/QUANT 2.0, Bruker Optik GmbH, Karlsruhe, Germany).

Results and discussions

In the past, extreme efforts have been made in order to guarantee a successful transfer of calibration data from one central NIR spectrometer to several additional units.¹ First, we tried to create some kind of standard to which all analytical methods were adapted mathematically. In this context, the bias and slope correction were established in modern analytical NIR software as

well as chemometric algorithms like, for example, "piecewise direct standardisation".¹

Unfortunately, a calibration in the near infrared range usually uses statistical-mathematical methods and, therefore, such corrections ,generally, require a correspondingly large amount of sample measurements. This leads to a correspondingly high consumption of time and money. Another possibility is to adapt all measurements to spectra of certified standards. According to these standards, the raw data of each instrument will be corrected and standardised. This sounds quite practical but requires the use of instruments which work reproducible for a long period of time.

A promising way, generally, to solve the problems described is to use modern FT-NIR spectrometers with mirror optics. Besides general advantages of the FT-technology, these systems are distinguished by high throughputs of light and excellent technical specifications (spectral range: 12.500 arrai 4.000 arrai when using fibre artic

12,500 cm⁻¹–4,000 cm⁻¹ when using fibre optic probes, optical resolution: 2 cm^{-1} ; reproducibility: 0.01 cm⁻¹, accuracy: 0.1 cm⁻¹ for the VECTOR 22/N-F used in this study).

In particular, the so-called "cube corner" design was excellently qualified as mirror elements in interferometers in the past. Such mirrors are characteristical for reflecting a beam of light parallel to its starting point, independent from the incoming angle (see Figure 2). This is the reason why FT instruments can be aligned permanently using such mirrors, i.e. these systems cannot be deadjusted after a certain time even by punching or by vibrations. Using cube corner mirrors in combination with the advantages of the FT-NIR technology² allows high, precise alignment of all spectrometers from the company's side (see Figure 3). The spectra measured with these NIR photometers should, therefore, be relatively independent of the corresponding instrument-a manipulation of this data after the measurement is not necessary.

A corresponding study for the calibration data transfer has been worked out in order to show the suitability of such a permanently aligned FT-NIR



Figure 2. Influence of the tilt of the mirror at a classical Michelson interferometer (above) and a Rocksolid interferometer (below) with cube corner design (Bruker Optik). A tilt of the mirror at the Michelson interferometer leads to a corresponding dealignment of the system. For the Rocksolid[™] interferometer the reflected light ray will be transmitted parallel to the direction of the source (independent from the angle of the incoming light). This interferometer is permanently aligned.



Figure 3. Alignment of an NIR spectrometer by means of the rotational fine structure of water steam. The alignment of the wave number range is made by means of the water vapour band at 7306.74 cm⁻¹. A precise alignment is only possible if the fine structure of the gaseous water has been measured with a correspondingly high spectral resolution. In order to demonstrate this the water vapour bands were measured with a spectral resolution of 2 cm⁻¹ as well as with a spectral resolution of 2 cm⁻¹ enables the exact display of the rotational bands at 7306.74 cm⁻¹.

spectrometer for tough development of methods. First, mixtures of acetone, styrene and vinyl acetate in a range from 0 to 100 volume percent were measured with spectrometer No. 1 (the "master") to carry out the experiments. With the spectra received, a PLS calibration was made. The quality of the resulting analytical model was estimated via cross-validation (see Table 1, column 2). The optimisation of the methods was intentionally carried out with non-manipulated raw data. Hence, it is guaranteed that negative influences, after the method transfer to the second instrument, will directly cause an increase in the error of the analysis.

After cross-validation the method has been transferred to the second instrument (the "slave"). Once again, the already examined mixtures of acetone, styrene and vinyl acetone were measured and the non-manipulated raw data were analysed. The resulting values will be shown in Table 1 (column 3) v. the values of the method validation on the "master" instrument. Generally, it can be seen that the transfer to the second instrument causes no significant increase of the errors of analysis. The errors in cross-validation and the errors of the analysis of the independent test data set, generally, are between 0.1 and 0.5%.

The same result is found by creating the cali-

bration on instrument No. 2, transferring the resulting method to instrument No. 1 and, once again, testing an independent test data set (see third and fourth column of Table 1). Nor, in this case, does the transfer of the method to another instrument lead to noticeable influences on the accuracy of the analysis.

This is an excellent result which assumes that a general transfer of calibration models for more component mixtures should be possible for a wide concentration range. This, of course, leads to the

Table 1. Root mean squared error of analysis for the calibration data transfer of the system acetone/styrene/vinyl acetate for a concentration range between 0 to 100 volume percent (PLS1 calibration with the following settings: acetone: rank 6, no data preprocessing, spectral range 6,100–5450 cm⁻¹; styrene: rank 4, no data preprocessing, spectral range: 12500–6100 cm⁻¹; vinyl acetate: rank 5, no data preprocessing, spectral range: 6100–4600 cm⁻¹.

Component	root mean squared error of analysis (master) in- strument No. 1	root mean squared error of analysis (slave) in- strument No.2	root mean squared error of analysis (master) in- strument No.2	root mean squared error of analysis (slave) in- strument No. 1
acetone	0.17%	0.14%	0.09%	0.22%
styrene	0.32%	0.50%	0.30%	0.31%
vinyl acetate	0.54%	0.30%	0.37%	0.33%

Table 2. Root mean squared error of analysis for the calibration data transfer of the system ethanol/isopropanol for a concentration range between 0 to 5 percent volume for isopropanol (PLS1 calibration with the following settings: rank 3, no data preprocessing, spectral range: 6100–5450 cm⁻¹.

Component	root mean squared error			
	of analysis (master)	of analysis (slave)	of analysis (master)	of analysis (slave)
	instrument No. 1	instrument N'.2	instrument No.2	instrument No. 1
iso-propanol	0.058%	0.055%	0.054%	0.060%

question if this is also true for a correspondingly limited concentration range with only slight errors of the analysis. For this test pure ethanol was added to 0 to 5% volume of isopropanol. Once again, the above mentioned experimental procedure was carried out. Table 2 summarises the results for the analysis of the isopropanol. Here also the transfer of calibration data to another instrument will not lead to a significantly statistical increase in the errors of prediction. A transfer of the non-manipulated raw data was also easily possible.

References

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