

When to use chemometric near infrared transfer steps

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Introduction

Good analytical practice is to calibrate every item used for an analysis. Calibration of glassware, balances, instruments, standards, even reagents, is usually basic to a successful analysis. In chemometric near infrared (NIR) spectroscopy, however, the aim is to eliminate these calibrations for routine operation. This is accomplished by performing an initial calibration on a data set derived from a large number of samples representative of the whole, including expected ranges of impurities. When done properly, the resulting calibration algorithm (the model) can be used for routine analyses without further calibration. This is the principle of doing it right the first time.

However, the above process demands the spectrometer used for the routine analyses will never change its characteristics, or if the original calibration is transferred to a different spectrometer, the second spectrometer is identical in its characteristics. These conditions are difficult if not impossible to meet. Spectrometer responses will change due to drift, breakdowns and replacement of parts. Further, any spectrometer system to which the calibration is transferred will have different response characteristics.

Transfer of calibrations from one spectrometer to another is accomplished with software transfer programs. These programs work by comparing spectra taken on both spectrometers and deriving adjustment factors. These factors are used to adjust spectra from the “parent” spectrometer to convert them so they match spectra taken on the “child” spectrometer. This procedure, when done properly, minimizes most or all of the differences in spectrometer conditions.

The transfer problem is not always easy or straightforward. Much attention has been focused on this process.¹⁻⁸ The efforts, though, have been directed towards improving mathematical treatments. Questions remain about which spectrum should be the reference.

There are two approaches to deciding which spectrum should be the reference and which spectra should be transferred. The transfer can be forward, i.e. transferring the original calibration spectra to the time of use or to another spectrometer. The alternative is backward, transferring spectra of unknowns back to the original calibration time or of the spectra obtained on another spectrometer to the original calibration set.

Which is better, forward or backward transfer? In general, the transfer should be backward. However, the transfer should be forward if (i) the routine analysis demands a very rapid calculation of results, (ii) transfer of the calibration spectra to another spectrometer is not required and (iii) very slow spectrometer drift is not critical.

There are a number of reasons for backward instead of forward transfers. Calibration spectra are not altered, thereby avoiding the possibility of introducing noise into the calibration set. The effects of spectrometer drift with time are minimized (the alternative is to periodically transfer the calibration set forward in time even if using the same spectrometer). Additionally, several

spectrometers could be “slaved” to the original one in a network, such as a web of spectrometers working in a plant, with each spectrometer performing one or more analyses.

There are several disadvantages of backward transfers. It must be done every time an analysis is performed. The spectra of the transfer standard taken when the routine analyses are done must be identified so the computer can identify which spectra to use for the transfer comparison. The transfer standard must be stable. Finding a transfer standard that has a spectrum roughly equivalent to spectra of the samples is not always easy. There is an increase in analysis time due to the scanning of the transfer standard. Extra time is spent in performing the transfer calculation (usually several seconds). Finally, for automatic and in-line analyses, because the transfer standard must be scanned periodically, there must be a way to change from scanning samples to scanning the transfer standard. This usually means extra plumbing and computer programming.

Thus, there are three choices to be made; backward transfer, forward transfer or no transfer. Regardless of what choice is made, spectra of a transfer standard should be obtained at the same time calibration spectra are recorded. This allows the option of using a transfer at a later stage.

The choice of using a transfer standard can usually be made in the initial stages of developing a model. This is done by testing the calibration algorithms with and without a transfer step applied to validation samples. Only if the use of a transfer step degrades the performance of the calibration algorithm, or if the disadvantages listed above are important, should the use of a backwards transfer step be excluded.

Example

The following data illustrate the advantage of a backward transfer. A product is routinely analyzed for 21 constituents with chemometric NIR in the author’s laboratory. A control sample is also analyzed. Results taken four months apart were compared. Calculations were made with

Table 1. Analytical values for two constituents, comparing results with and without inclusion of a transfer step. The values are compared with original values, obtained four months earlier.

	Original value	With a transfer step	Without a transfer step
Constituent 1			
Average	8.440	8.453	8.602
Standard dev.	0.010	0.004	0.02
No. of samples	7	5	5
Null hypothesis		−0.01–0.2	0.14–0.18
Constituent 2			
Average	64.32	67.15	45.97
Standard dev.	2.0	2.2	1.8
No. of samples	7	5	5
Null hypothesis		−0.2–6	16–20

and without a backward transfer. Comparisons for the most precise and least precise analyses are shown in Table 1. The statistical test shown in the last row is the difference between averages for the initial set and the set being tested, plus and minus the student t times the standard deviation. The value of t is for a 95% confidence level. If the range does not include zero there is a significant difference between the two averages.

The comparison of values clearly shows the use of a backward transfer is advantageous. The null hypothesis range includes zero when a transfer step was used. When a transfer step was not used, the null hypothesis test failed. Other analyses done in this laboratory also show the same advantages. Further, out of the last ten methods here, only one has not shown improved results when a transfer step was included.

Conclusion

In conclusion, use of a backward transfer is preferred over that of a forward one. A good practice is to use a transfer step even if one does not initially seem beneficial. This is because the backward transfer could help avoid future problems. Moreover, a backward transfer will tend to preserve the pristine nature of the calibration set, which is always a valuable point.

References

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