

A White Paper from FOSS

Standardization of FT-IR instruments

Using FOSS patented standardization procedure it is possible to reduce the need of Slope and Intercept adjustment and further increase the precision and lifetime of FTIR analyzer

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FOSS standardization

FOSS has a unique patented Standardization concept. This standardization concept is applied on all FOSS Fourier Transformed (FT) Infrared (IR) analysers and enables all instruments of the same type to give the exact same results if measuring the exact same sample. This is possible because all instruments produce the exact same spectrum of the same sample. Using standardized instruments, it is possible to transfer calibration models from one instrument to another and thereby use global calibration models on all instruments – even on instruments that were not originally present when the models were developed. What is more, the FOSS standardization procedure is able to correct for all differences between instruments optics and compensates for instrument drift over time.

Cuvette wear

Most of the cuvettes from the FOSS FTIR analysers are made of Calcium Fluoride (CaF_2), a unique material with excellent transmittance of IR light. However, CaF_2 is slightly dissolvable in water causing the cuvette to wear off over time. This wear will increase the distance between the glasses of the cuvette resulting in a slightly “larger” cuvette with an increased light path length. The amount of sample in the light path way increases as the cuvette becomes larger. This results in a higher intensity of the spectra since the intensity and the light path length is directly proportional to the concentrations according to Lambert-Beers’s law (Figure 1).

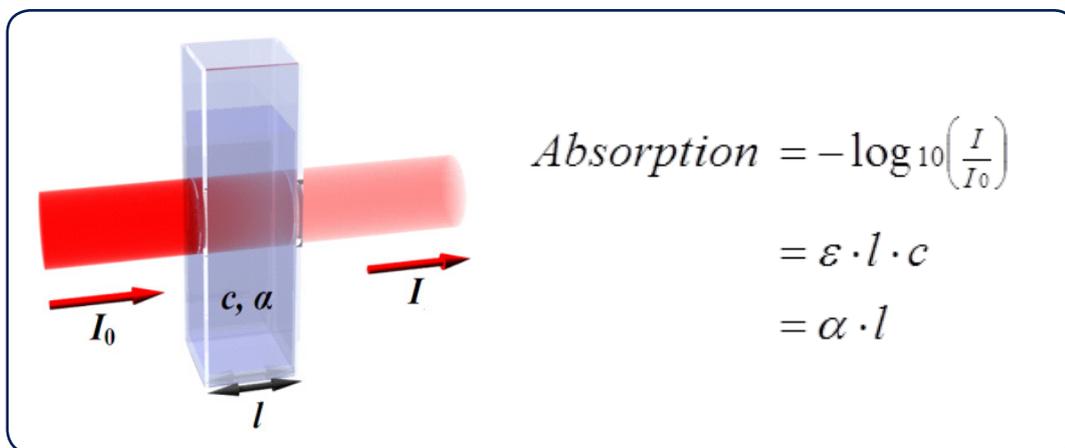


Figure 1, The incoming light intensity ' I_0 ' through a cuvette with a path length of ' l ', with a concentration of ' c ', a molecular extinction coefficient ϵ and an absorption coefficient ' α '. The outgoing light intensity is ' I '.

Lack of standardization will have an undesired impact on results of the analyser therefore compensating for cuvette wear is the primarily aim for the standardization function. The standardization function also removes variations in frequency (wavenumber / wavelength) misalignments. Misalignment of the wavelength axis can be caused by variations of the intensity of the IR source and laser, as well as the sensitivity of the IR detector and the position of the optical element.

Slope/intercept (S/I) adjustment can also correct for difference in light intensity but does not compensate for wavelength misalignment. Furthermore, S/I correction is laborious and costly as it requires several reference samples to be analyzed and the correction has to be done for every component. The standardization procedure removes the instrument-to-instrument variation and thus facilitates transfer of calibration models from one instrument to another. In this way, it is possible to get the same prediction on two instruments with the same prediction model.

Standardization procedure

In order to standardise an instrument, a standardization liquid (equaliser) has to be analysed. The spectrum of the equaliser is then compared to a 'Gold equaliser spectrum' which is stored on every FTIR analyser. From the difference between the Gold equalizer spectrum and the equalizer spectrum of the present instrument, the standardization correction parameters A, B and α and β are calculated. The A and B coefficients correct for wear, whereas α and β adjust the wavelength axis. These four parameters are applied then to all spectral results. This reduces the need for slope and intercept correction of calibration models as all instruments predict identically. Details on the mathematics can be found under 'Calculation of standardization parameters'.

Monitoring instrument drift

The correction parameters from the standardization procedure can be monitored to assure optimal performance. Of the four correction parameters, the A-value which corrects for wear of the cuvette is the most important parameter as it has biggest impact on the results. The 'A' value is a slope correction factor which adjusts the spectra to a standardized cuvette path length. For a new cuvette, the A-value is 0.85-1.15 depending on the type of the instrument. Over time, as the cuvette wears off, the A-value decreases. When it reaches 80 % of its original size, it is recommended by FOSS to change the cuvette, as the compensation with the standardization process will not be sufficient any longer. This is because the instrument noise stays the same when increasing the path length but the signal-to-noise ratio will decrease. How fast the A-values decrease, i.e. the rate of the wear, depends on the number of intakes (samples and zero settings). Therefore, the standardization frequency has to be determined for each instrument, as it differs from one instrument to another.

Standardization frequency

The optimal standardization frequency can be calculated based on the A-values which have been followed for a longer period. The A-values can be found in the instrument standardization log which is calculated after each standardization. The standardization log can be exported to e.g. Excel and the number of intakes can be plotted against the A-values. From this plot, the required frequency of standardization can be determined. In Figure 2, the cuvette wear, expressed as decreasing A-values, is plotted against the number of days.

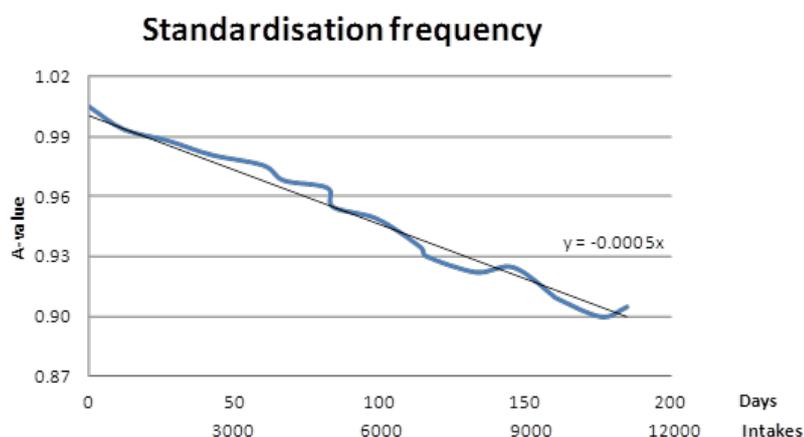


Figure 2, The A-value plotted against number of days and number of intakes. The rate of A-value decrease (cuvette wear) is approximately 0.0005 per day.

FOSS recommends that the A-value maximum should change 0.01 between each standardization. An A-value change of 0.01 corresponds to approximately 1% relative change in prediction results. In Figure 2, A-values are plotted against a time period of approximately 200 days which corresponds to 120000 intakes. In this plot, the rate of A-value decrease is 0.0005 per day (the slope of the trend line in Figure 2) which is 60 intakes. This would give allowance of 20 days (0.01/0.0005) or 1200 intakes between each standardization. The calculation of standardization frequency can be based on fewer A-values than the 120000 intakes (shown in the example) however, the more data for the calculation, the more precise estimation of the rate of the cuvette wear.

Cuvette lifetime

The lifetime of the cuvette is different from instrument to instrument and depends on the type of product analysed. Crystal compounds, acidity level and flow volume through the cuvette will increase the wear of the cuvette. The time between cuvette replacements can be followed in the standardization log. In Figure 3, the decrease in A-value is plotted over a period of 1½ year. When the A-value falls to maximum 75% of the original A-value of a new cuvette, the cuvette need to be changed. The cuvette lifetime in this example is approximately 6 months.

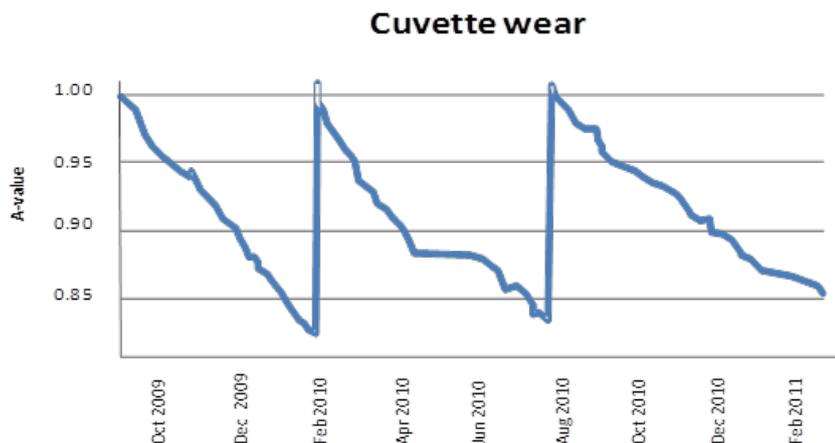


Figure 3, A-values plotted against the time period from October 2009 to February 2011. In this period, two changes of cuvette have been made.

Overcompensation

It is important not to make 'Slope/ Intercept' adjustments to compensate for cuvette wear. Rather perform a standardization which will correct the real cause of the drift in the instrument predictions. If the instrument has drifted and you make Slope/Intercept adjustment to compensate for this wear, the predictions will show a jump once the standardization is carried out. If this occurs, the slope and intercept must be reset back to Slope = 1 and Intercept = 0.

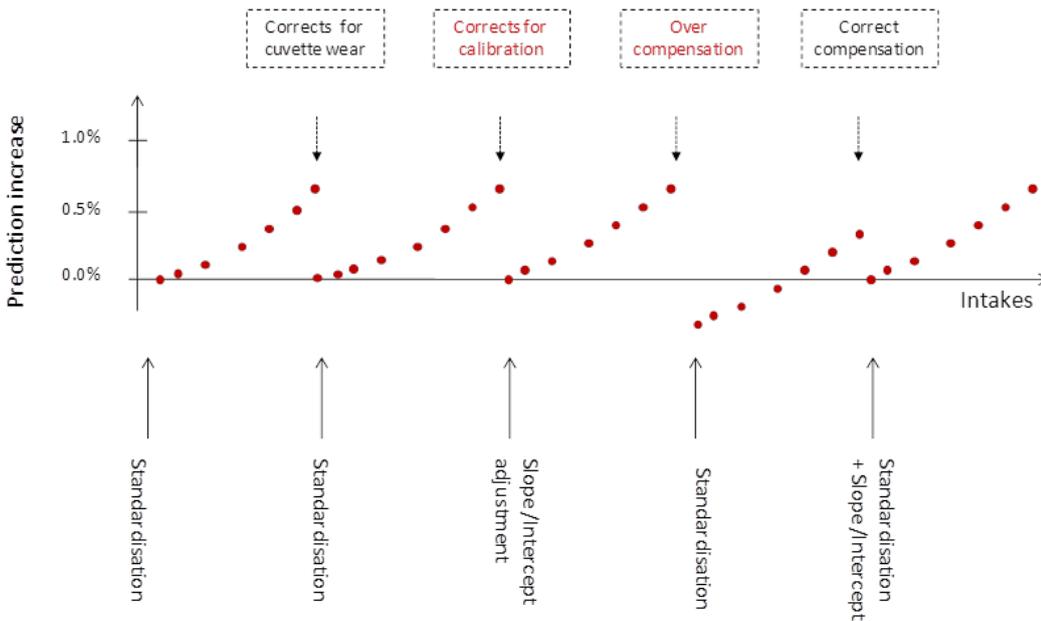


Figure 4, The impact of standardization and Slope/ Intercept adjustment on the instrument predictions. Slope Intercept compensation of drift will be reflected as a jump in prediction after standardization.

Figure 4 shows how prediction will climb over time as a consequence of wear of the cuvette. At first, the instrument is standardised and the predictions are unaffected. As a consequence of wear, the instrument predictions will slowly rise as the number of intakes increases. A Slope/Intercept adjustment can compensate for this drift too, but if the instrument then is standardised, this will be reflected as a negative jump in prediction. The way to remove this overcompensation is to set the slope and intercept to 1 and 0 respectively. The correct procedure for securing optimal instrument performance is to:

- calculate the required standardization frequency as explained in the previous section,
- do the standardization with the required frequency and, if necessary,
- perform Slope/ Intercept adjustment of all the prediction models (preferably once a month).

Calculation of standardization parameters

The patented FOSS standardization procedure (Pat. No. 9,933,792) is a mathematical adjustment, where the spectra collected on any instrument (slave) are adjusted to match the Master spectrum (also called 'Gold spectrum'). Here, we introduce a mathematical model which adjusts the spectral differences between the Master and slave instrument.

Before an instrument can be standardized, it has to be zero-set in order to remove environmental influence on the optical and electronic system. The zero setting removes the internal instrument variation, whereas the standardization removes the instrument-to-instrument variation.

The Master spectrum and the slave spectrum of the standardization liquid (equalizer) are compared in order to obtain standardization parameters for the correction. This standardization liquid (equalizer) is optimal for this purpose since it has two well defined absorption peaks, which are easily identified as two local maxima in the spectrum.

Wavelength misalignment

A difference in wavelength of the two lasers in the interferometers will result in a shift of the wavelength axis which can affect the result of the instrument. Figure 5A (left) show a big difference in x-axis alignment and intensity between the spectra of an identical sample measured on both the Master and the slave instrument.

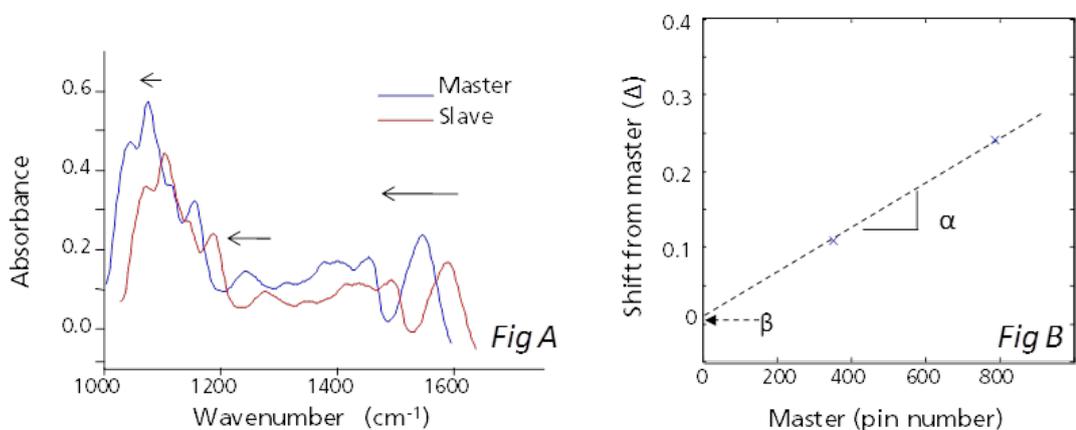


Figure 5, A) Master spectrum and slave spectrum display a shift in the wavelength and intensity axis. B) The slope of 'α' and an intercept of 'β' of straight line drawn through the two absorption peaks of the Master and the slave and origo (0,0)

The two well defined absorption peaks of the standardization liquid are used for the adjustment of the wavelength axis. The peak positions of these local maxima are identified for the slave spectrum, whereas the position of the maxima of the Master spectrum is known and therefore fixed on the wavelength axis from the beginning of the process. The positions of the two maxima of the Master and the slave are plotted against each other (Figure 5B).

Figure 5B illustrates the best straight line drawn through the three points; 1) the x-axis the peak position of the spectrum and the y-axis, 2) the difference between the peak position of the spectrum and that of the slave spectrum and 3) origo (0.0). This line has the slope of α and an intercept of β and these two parameters are applied on the spectra, and thereby correcting the wavelength misalignment (Figure 6A). This misalignment is mainly reflected in the α-values and is an expression of the frequency of the laser.

Intensity drift

When the spectrum has been corrected on the wavenumber (x) axis it also needs to be corrected in the intensity direction (y). Similarly, the absorbance intensity is mathematically adjusted to fit the intensity of the Master spectrum (Figure 6A).

The intensity drift of the spectrometer may be described as different intensities measured at the same wavelength for the same sample in two similar instruments. A difference in cuvette thickness, caused by wear of the cuvette, changes the amount of light absorbed which result in a shift in the intensity axis (Figure 6A). The equalizer spectrum of the

Master instrument and the slave instrument are plotted against each other resulting in a straight line with a slope of A and an intercept of B (Figure 6B)

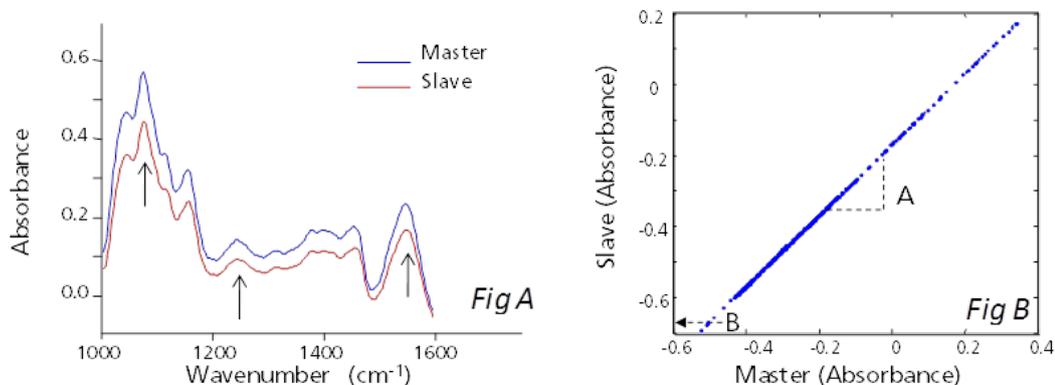


Figure 6, A) Master spectrum and the slave spectrum show a shift only in the intensity axis. B) the slope of 'A' and an intercept of 'B' of the straight line drawn through the three points constituted by Master spectrum on the x-axis and the slave spectrum on the y-axis.

The A and B values together with α and β are applied on the future spectra and the spectra of the instruments have now been standardised (Figure 7).

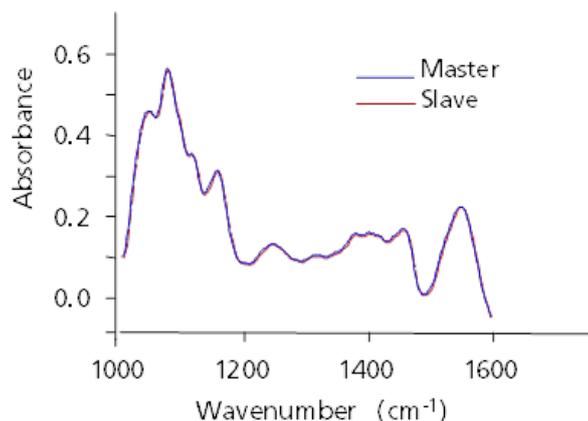


Figure 7, The Master spectrum and the slave spectrum are almost identical after applying the standardization parameter on the slave spectrum.

With this standardization process, all instruments may be standardized as often as needed. As a result, global calibration models can be developed and can be implemented on all instruments with only very small adjustments required.

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