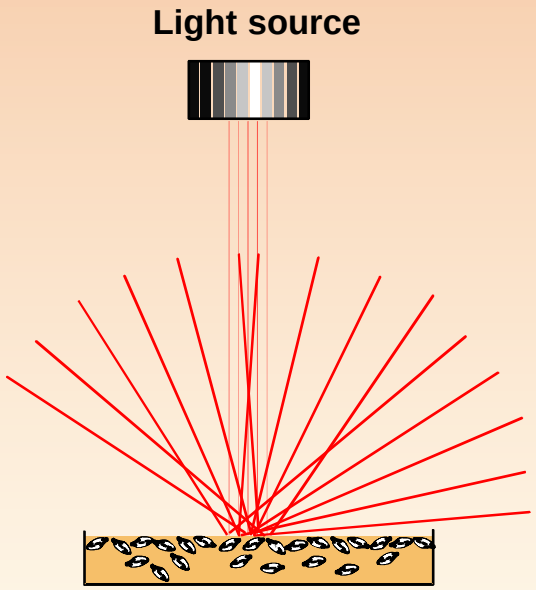
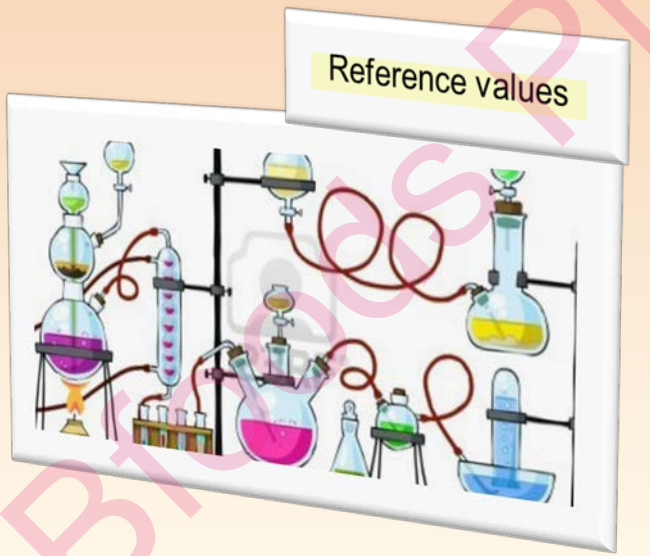
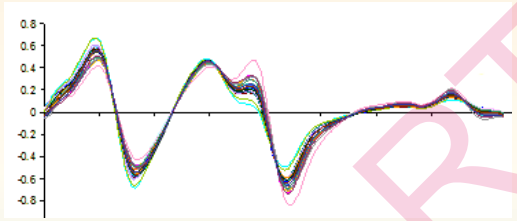
The Spectra, the Signal and the Noise

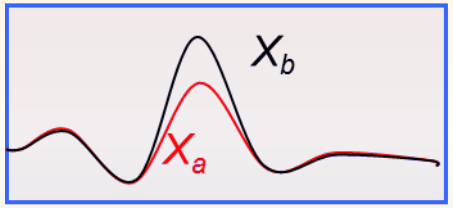
From spectra to calibration







Spectra



Patterns

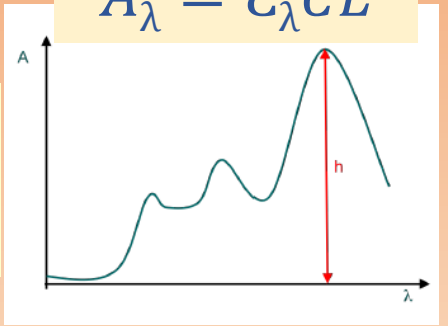
Calibration

results

Y_a , Y_b...

Limitations of the law

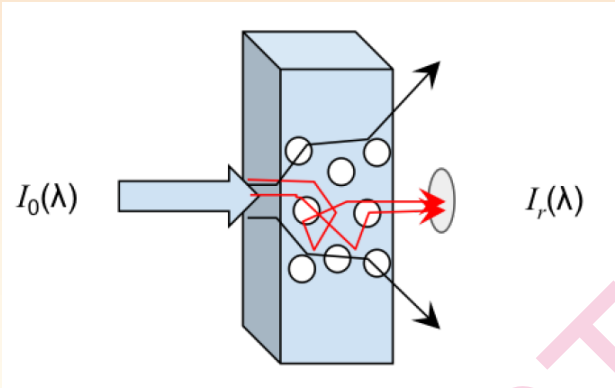
$$A_\lambda = \varepsilon_\lambda C L$$



Ideal conditions for near-infrared spectrometry (NIRS) correspond to a measurement of a transparent and low concentration solution where the concentration is directly connected to absorbance (Beer-lambert Law)

On raw products, such as flour, wood, soil, tubers….the law is no longer true due to many phenomena (scattering, instrumental noise, temperature, particle size…) that distorted the spectrum.

In the case of a real sample, the spectrum is disturbed by the scattering of photons and by the instrumental noise



Photon scattering:

- lengthens the average optical path length by a **factor k**
- leads a number of photons to escape the sensor, which adds a leakage term: **AL_λ**

The measurement noise is due to a set of random phenomena (parasitic light, electronic…) It translates into an additive term **AN_λ**

$$A_\lambda = k\varepsilon_\lambda LC + AL_\lambda + AN_\lambda$$

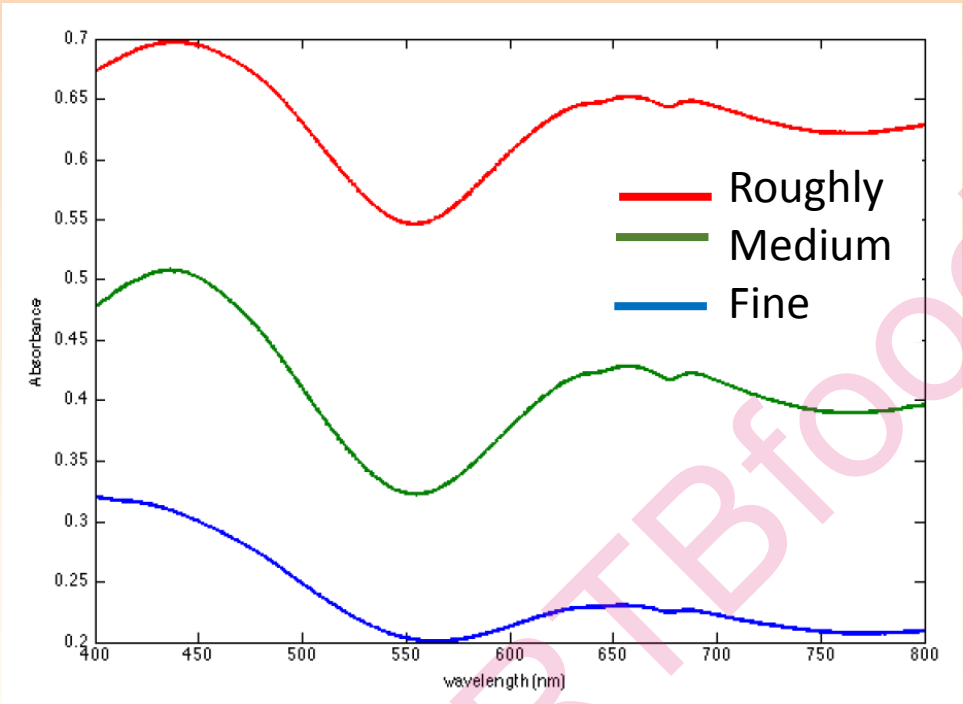
Finally, the measured absorbance is determined by a multiplicative term and 2 additive terms.

The spectra, the signal and the noise

A very visual example:

A glass of green color, crushed in different particle sizes, shows that the more the glass is crushed the more it appears as white.

The color as captured by the camera is directly related to the absorbance measured by a spectrometer.



Absorbance spectra of same glass at different particles sizes

The absorbance spectra measured for the three glasses are therefore different, whereas their dyes concentrations and therefore their chemistry are identical.

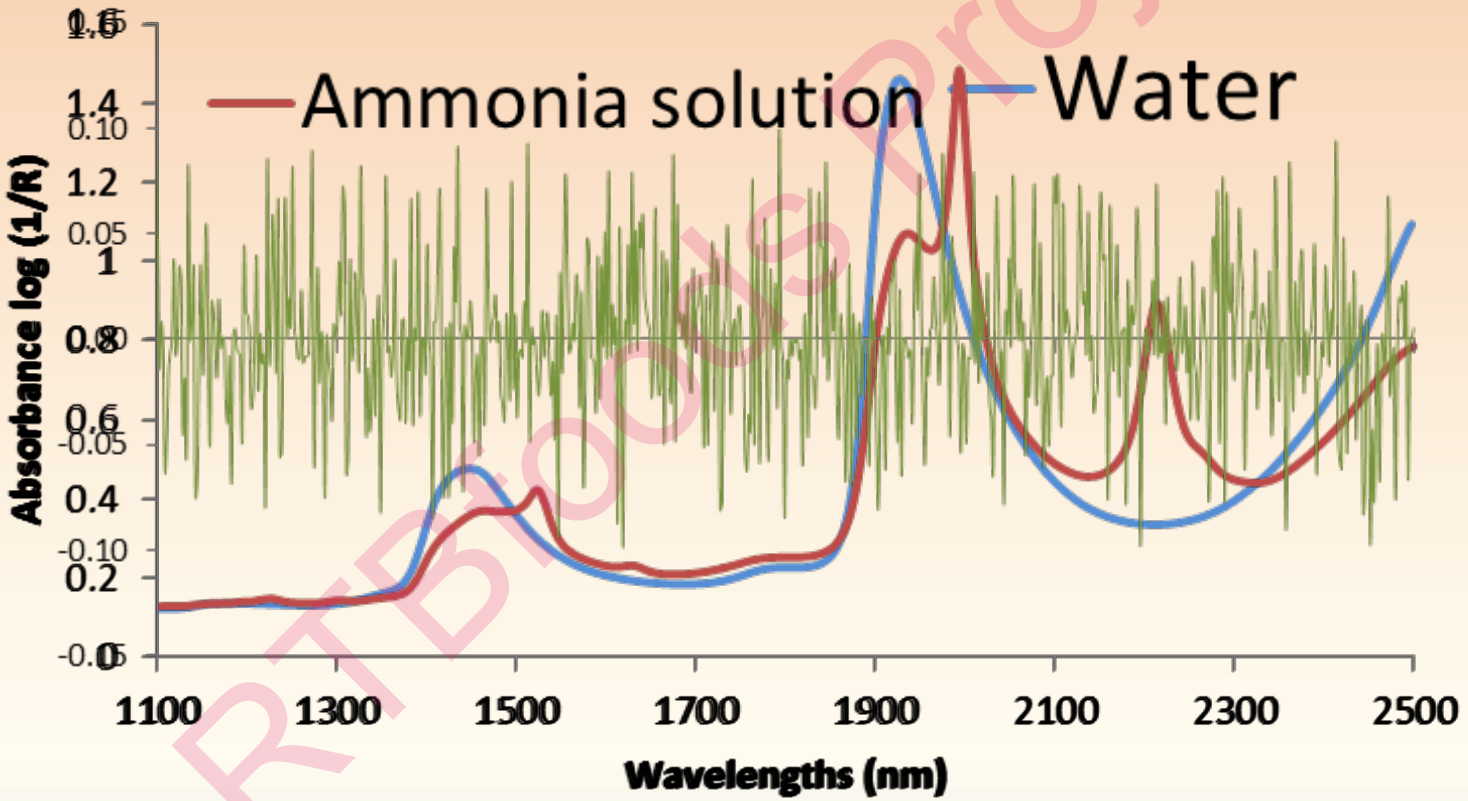
CheMOOCs, 2016
Jean-Michel Roger IRSTEA, Montpellier, France
Martin Ecarnot INRA, Montpellier, France

Spectrum = Chemistry + Physique + Noise

At the beginning…was the noise

Then interaction light/matter: absorbance + scattering

Then came complexity : multi absorptions



The spectra, the signal and the noise

The spectra, the signal and the noise

Spectrum = Chemistry + Physique + Noise

Auto correlation of spectral information (Collinearity)

Scattering of the light (changes in abs and baseline offsets)

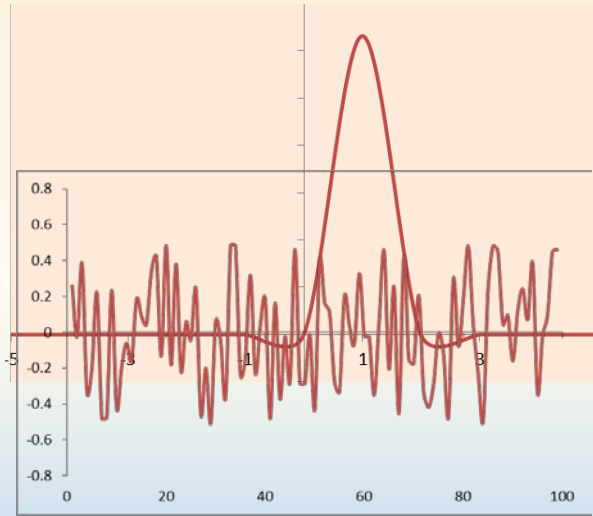
Noise : ratio signal/noise. Sensibility repeatability

We need to clean the signal before calibration

$$A_\lambda = k\varepsilon_\lambda LC + AL_\lambda + AN_\lambda$$

Reduction of the noise: reduce AN(λ)

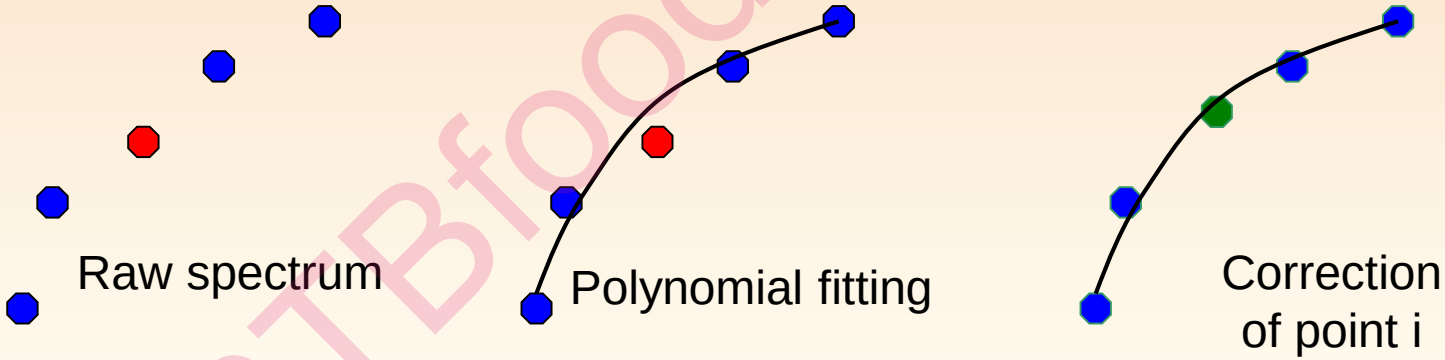
- Available tools to limit the effects of noise
  - **smoothing**
  - **normalisation / centering spectra**
  - **Derivation**



Smoothing spectra (Savitzky-Golay)

- The signal is "smoothed", usually by a polynomial function, based on a few neighboring dots ("window")

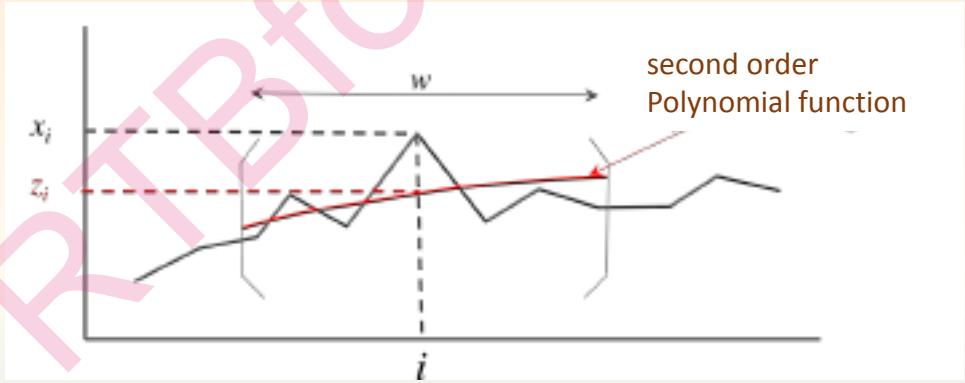
$$Abs_{ij} = a + bx_i^2 + b'x_i + \varepsilon$$



The central ordinate of the window is replaced by the central ordinate of the polynomial

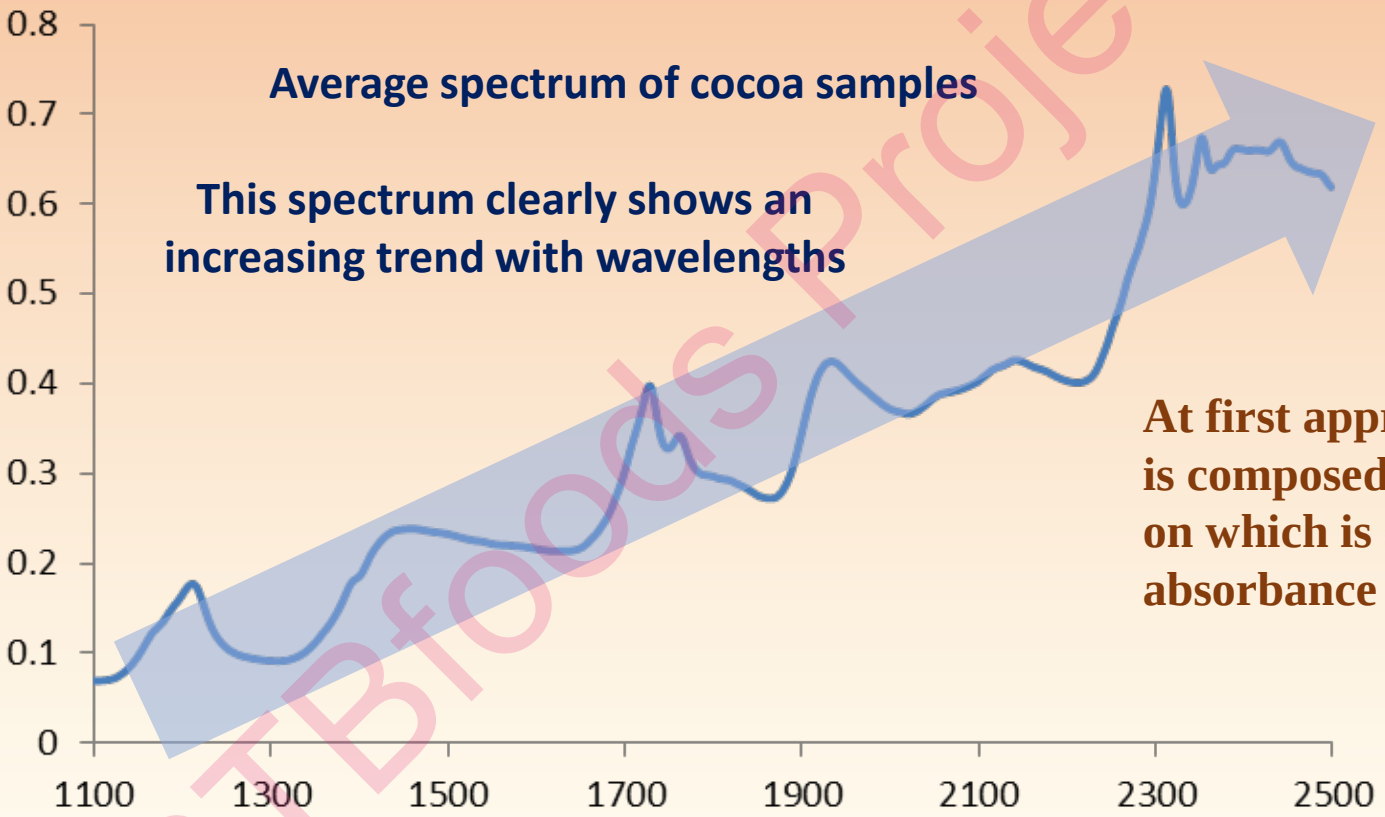
Smoothing spectra

- Smoothing is then made on the following point by the same procedure with a "window" shifted from one point
- Allows you to choose the width of the window
  - **1 = no smooth – risk of artefacts**
  - **4 or 5 = medium smooth**
  - **10 to 20 = very strong smooth– risk of loosing information**



Reduction of baseline shifts: reduce AL(λ)
De-trend

The spectra, the signal and the noise



Average spectrum of cocoa samples

This spectrum clearly shows an increasing trend with wavelengths

Increase of scattering with wavelengths

Increase of molecular coefficient of absorption (ε_λ)

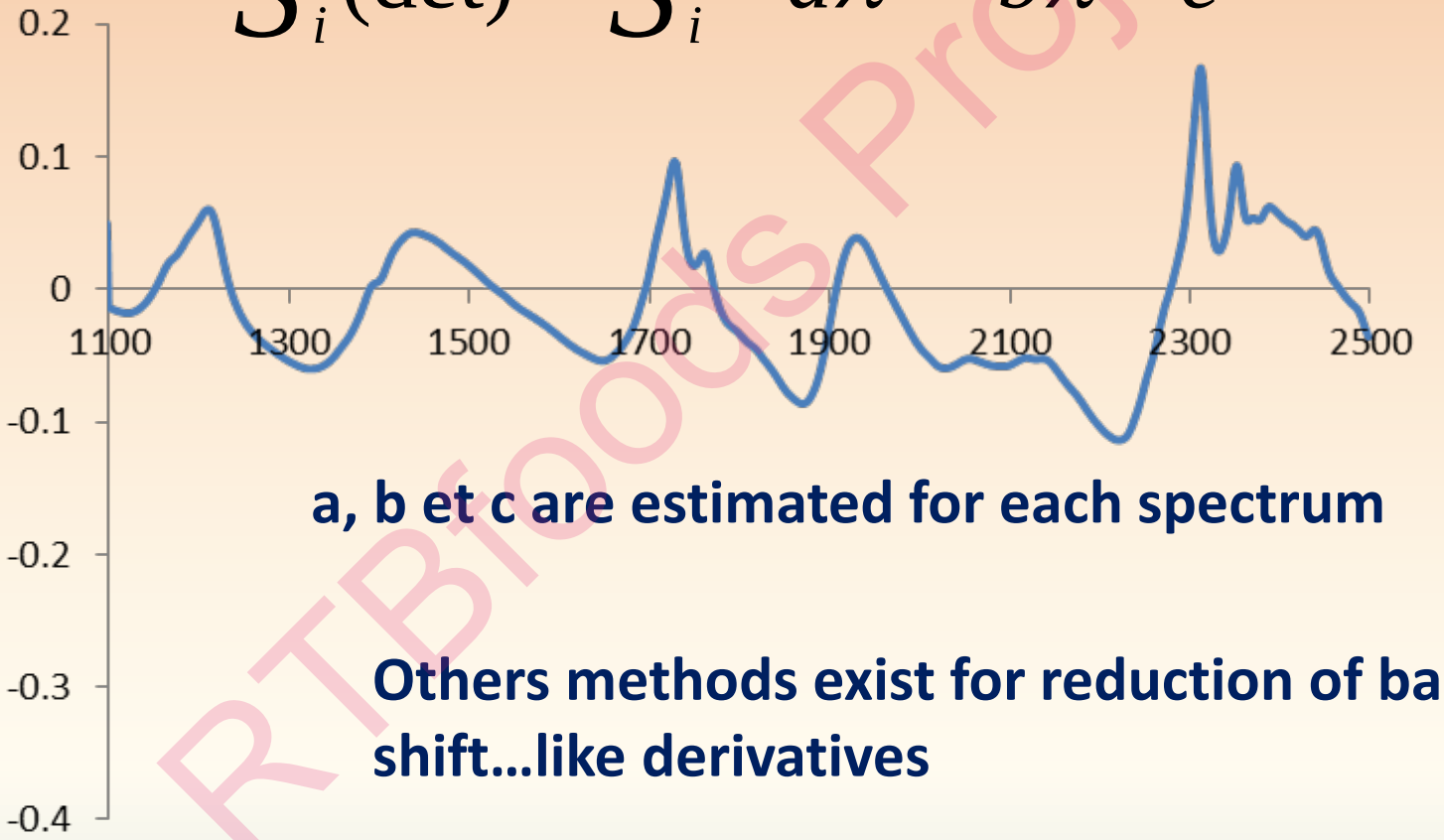
At first approach, this spectrum is composed of a baseline Al(λ) on which is superimposed an absorbance spectrum

The most common method of reducing baselines is Detrend

Detrend consists in removing from the spectrum its global tendency, modeled by a polynomial.

This polynomial can be of different degrees

$$S_i(\text{det}) = S_i - a\lambda^2 - b\lambda - c$$



a, b et c are estimated for each spectrum

Others methods exist for reduction of baseline shift…like derivatives

Derivatives

The spectra, the signal and the noise

Reduction of baseline shifts: reduce AL(λ)

- Isolation and amplification of the spectral differences
- Peak separation/Enhance Spectral Features
- Eliminate Slope and correction of baseline shifts and linear drift
- But ...
- Parallel increase of noise and decrease of the ratio s/n

The derivatives are coupled with other mathematical treatments reducing noise

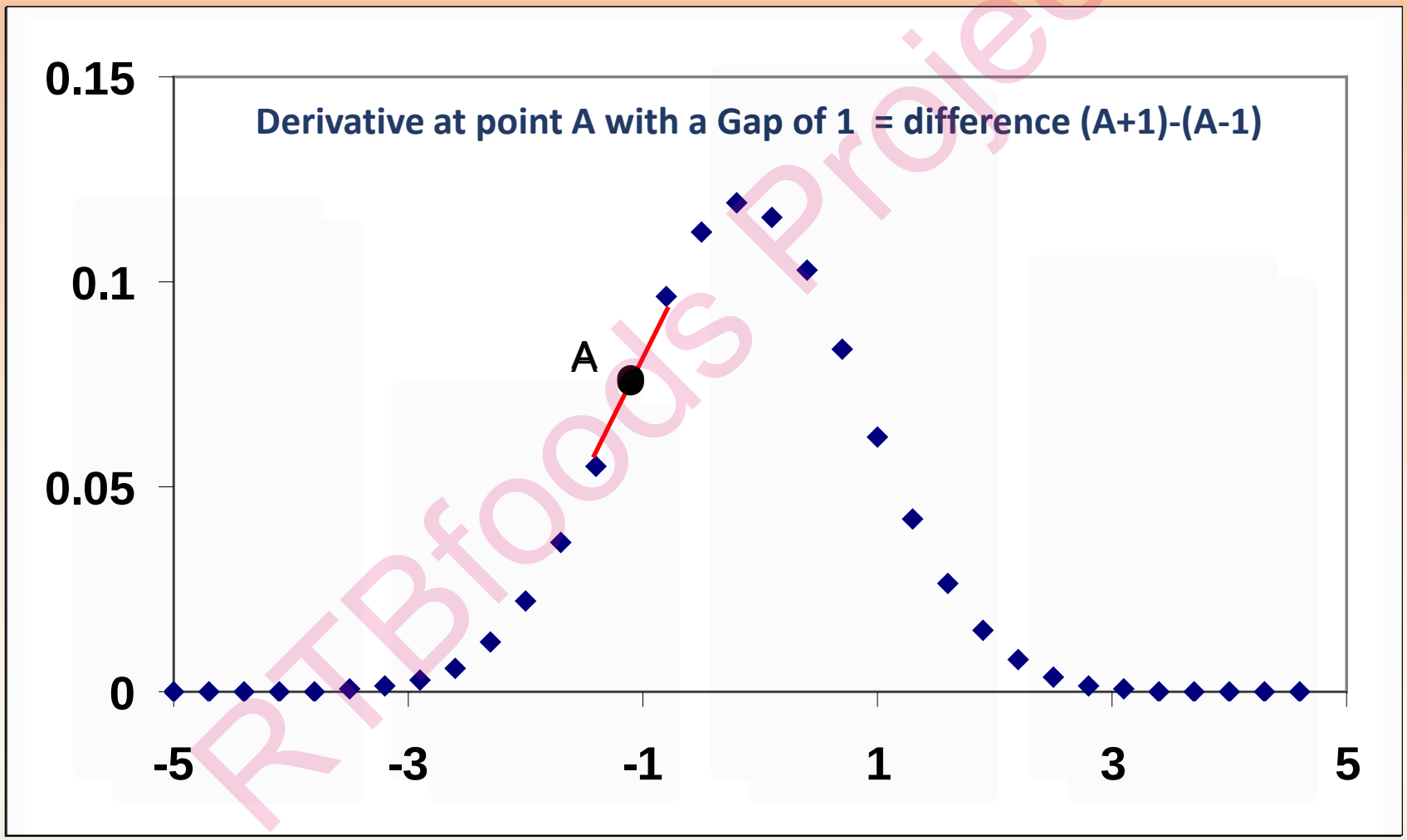
The derivatives are done with specific algorithms which derivative and smooth in the same time

Derivatives – Advantages and disadvantages

- Advantages
  - Removes effects of pathlength differences caused by differences in grinding
  - Can help spectral interpretation in some cases.
- Disadvantages
  - Makes spectra much more complicated
  - Can make spectral interpretation more difficult in some cases.
  - Requires optimisation of spectral segment and gap sizes.

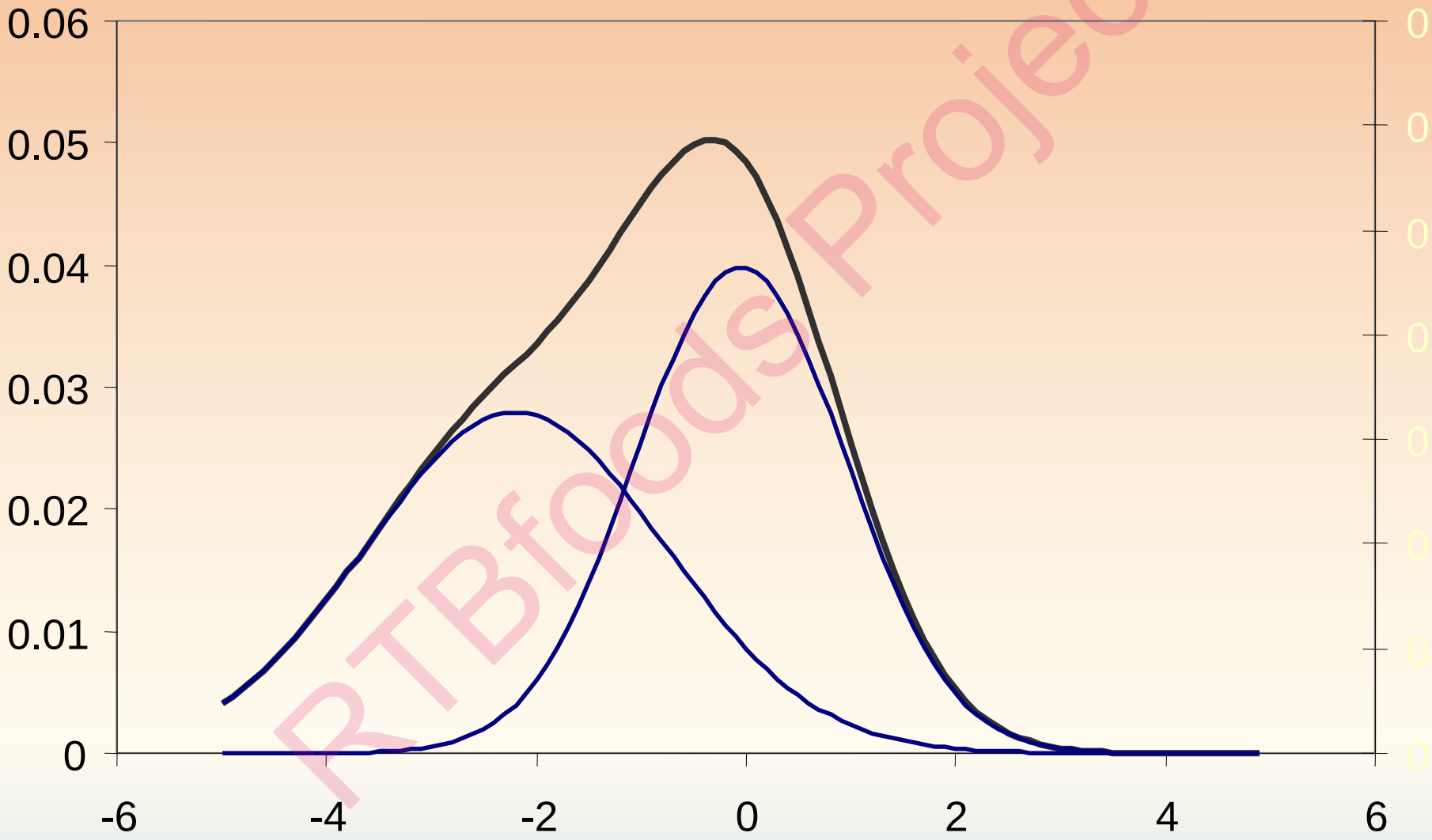
The spectra, the signal and the noise

Karl Norris derivative: consists to do the difference in absorbance between points according to Gap.



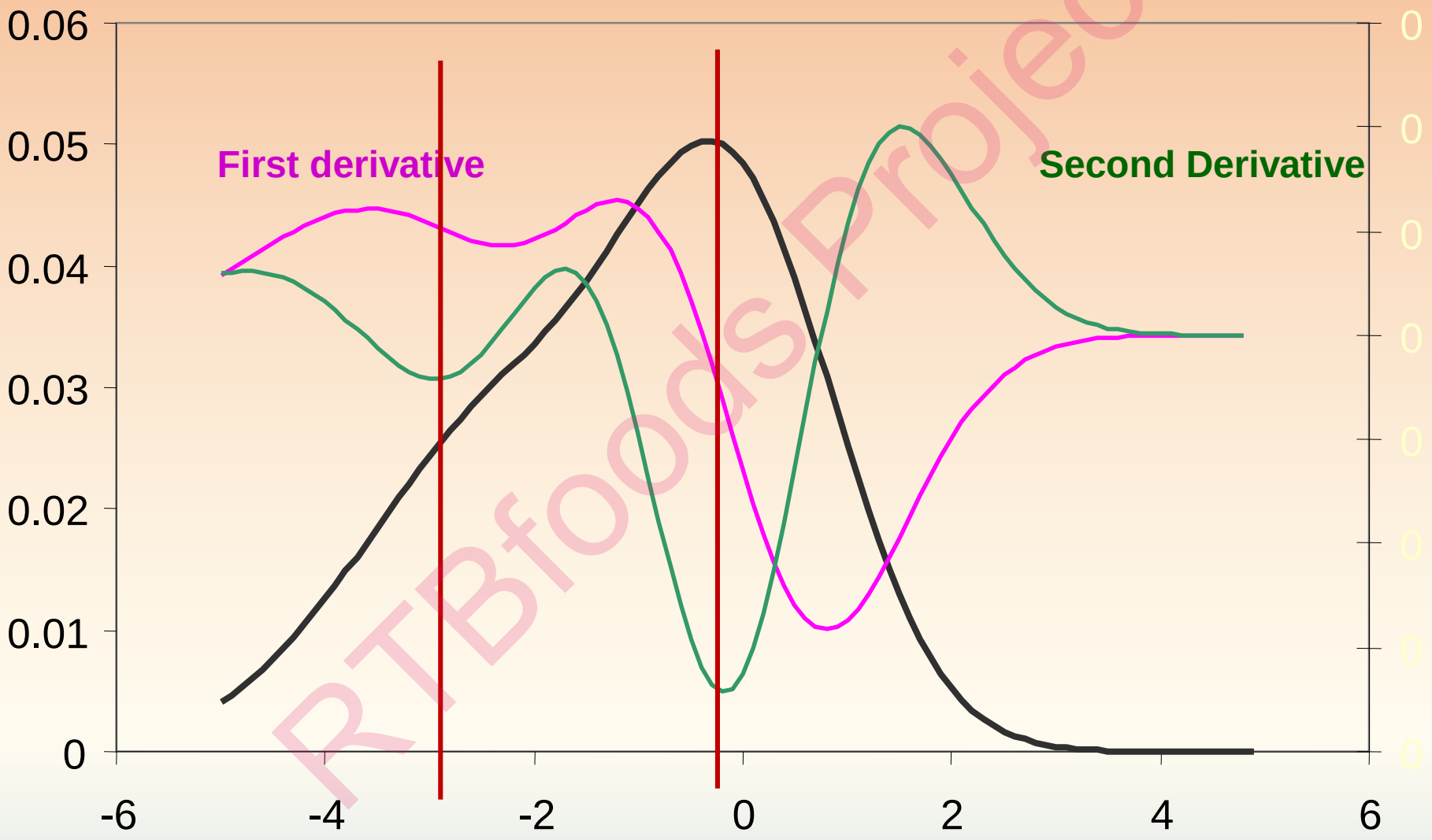
The spectra, the signal and the noise

Spectra of the sum of 2 Peaks



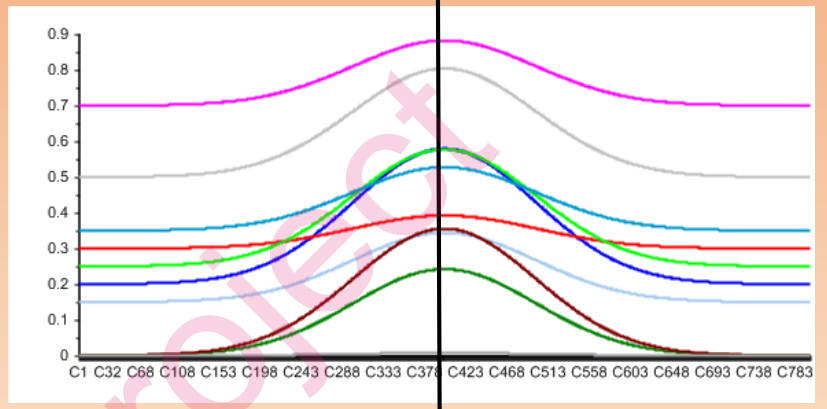
The spectra, the signal and the noise

Spectra of the sum of 2 Peaks



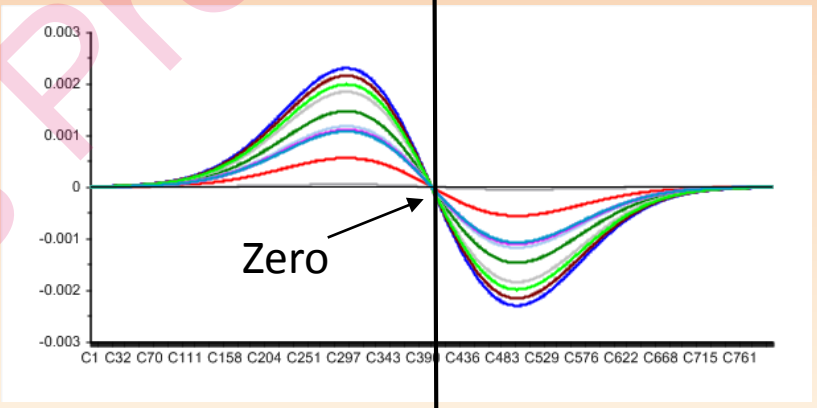
The spectra, the signal and the noise

Gaussian curves of various offsets and intensities



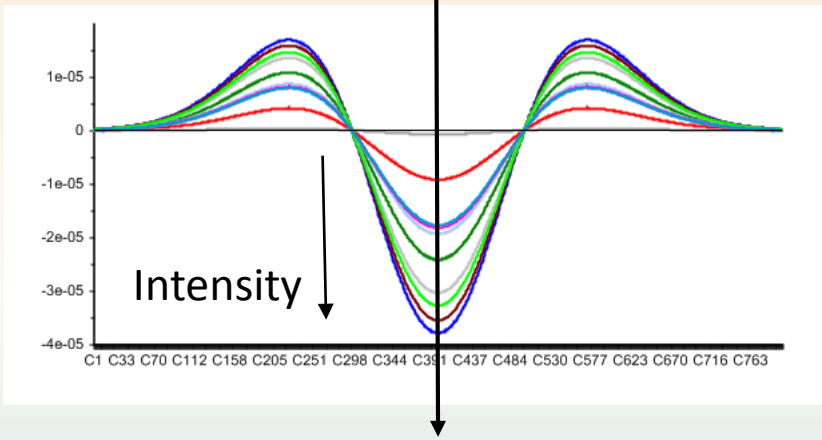
First derivative of Gaussian curves

- The baseline offset has been removed under derivatization
- The peak maxima in the raw data has now become a zero point in the derivative.

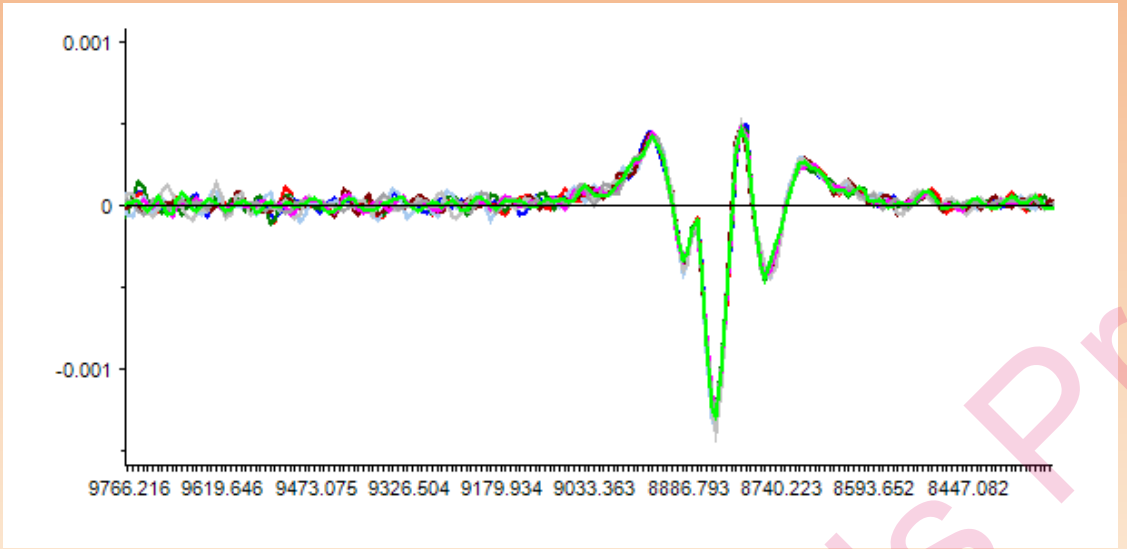


Second derivative of Gaussian curves

the intensities of the original curves can be seen in the second derivatives in order of intensity. Useful property, when performing quantitative analyses.

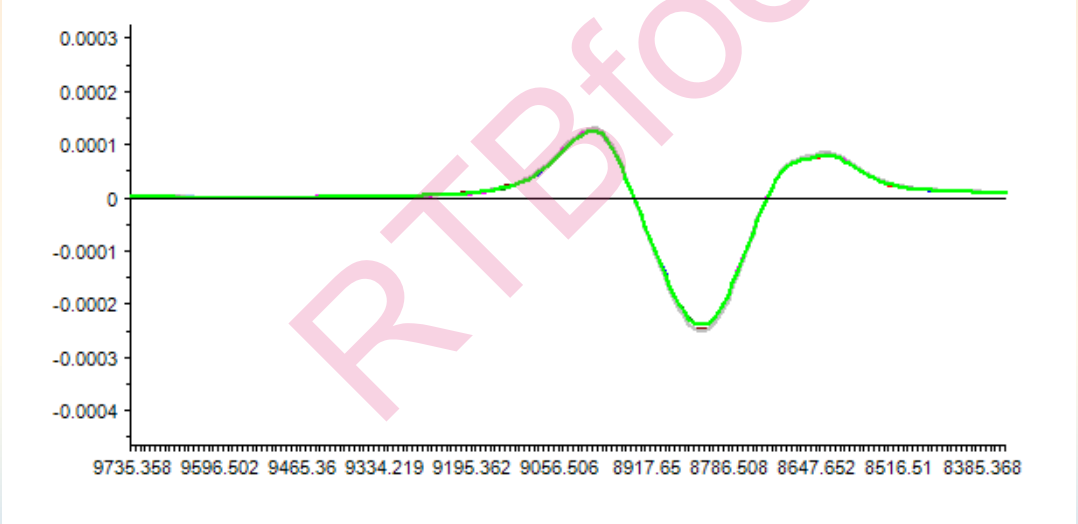


Derivative data with a segment size set too small



Noisy features remain in the spectra when the segment size is too small

Derivative data with a segment size set too large



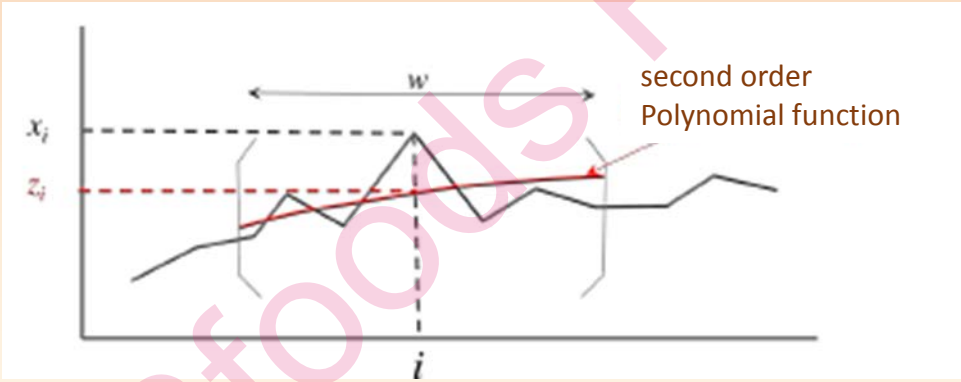
Some relevant information has been smoothed out.

Associated to derivative smoothing

The spectra, the signal and the noise

Savitzky-Golay Smoothing

The Savitzky-Golay algorithm fits a polynomial to each successive curve segment, thus replacing the original values with more regular variations. Note that a first-order polynomial is equivalent to a moving average



You can choose the length of the segment

small 4 data points
large 20 data points

Standard Normal Variate (SNV)

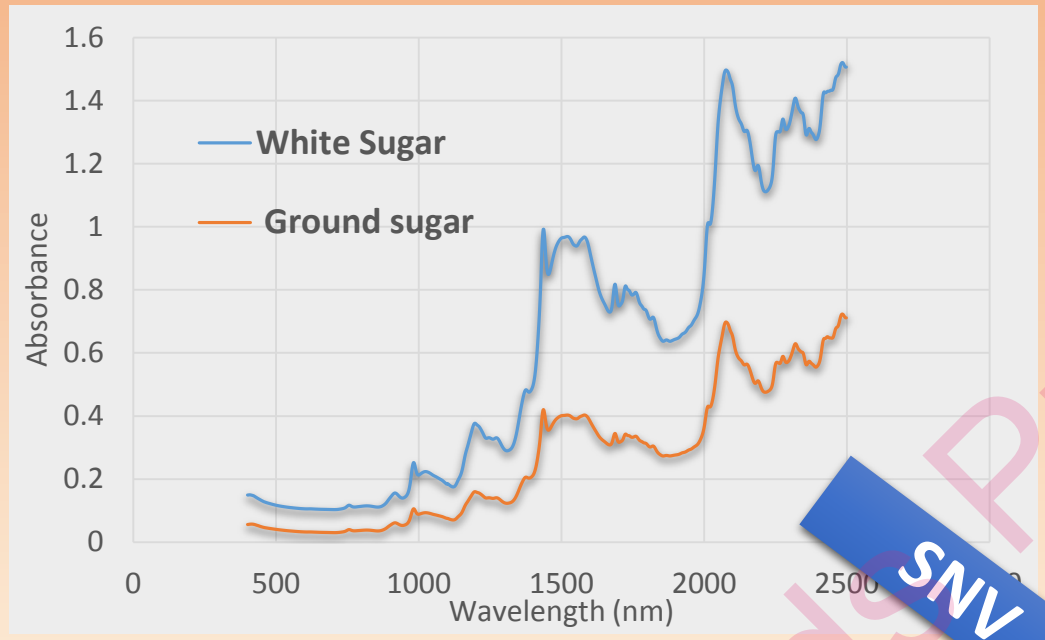
Correction of both addictive and multiplicative effects

- Centering of the spectrum (Remove mean to each value, Xc)
- Reduction (division by the standard deviation of each value, Xcr)

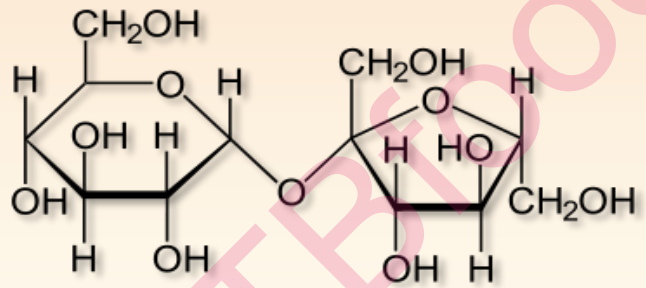
$$S_i(SNV) = \frac{x_i - \bar{x}_i}{SD.}$$

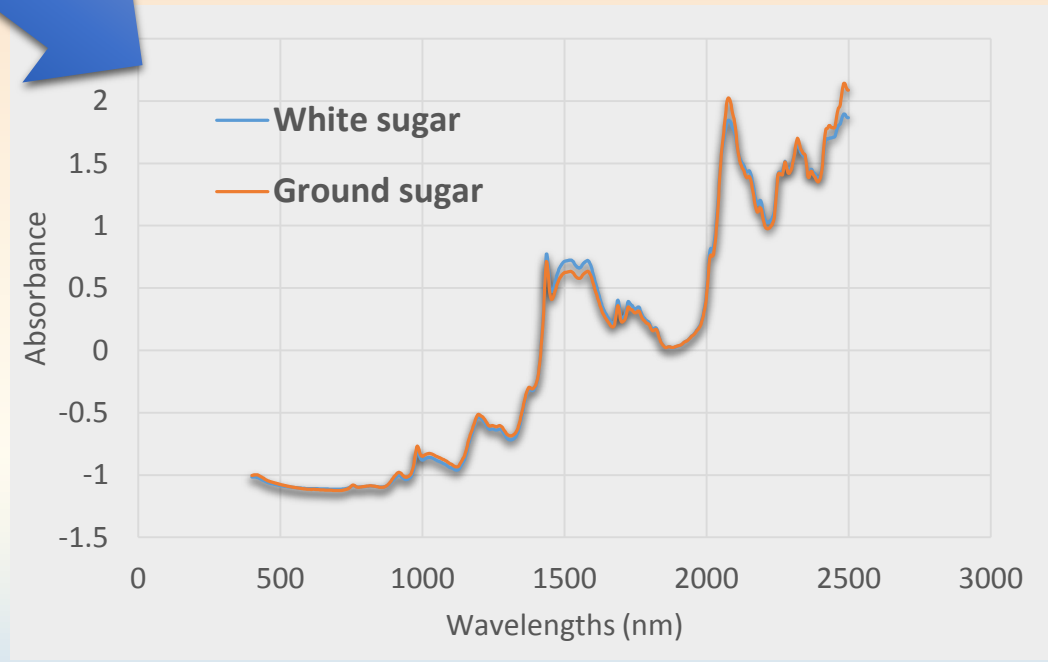
- The calculation is done for each spectrum
- SNV is usually associated with detrend

The spectra, the signal and the noise



SNV





Multiplicative Scatter Correction (MSC)

Correction of both addictive and multiplicative effects

The MSC identifies additive and multiplicative effects of a spectrum x, compared to a reference spectrum x_{ref}

MSC assumes that the spectrum x is of the form $$X = a + bx_{ref} + e_{ref}$$ Only the residual e_{ref} contains information !

MSC assumes that the reference spectrum xref is known. The underlying idea of the MSC is that each measured spectrum is composed of a baseline **(a)**, a multiple of (**b**) model spectrum x_{ref}, and a residual (**e_{ref}**) differentiating it from this global trend.

The corrected spectra is $$Xmsc = \frac{x_{ref} - \hat{a}}{\hat{b}}$$ $\hat{a}, \hat{b}$ are estimated by linear regression

The average spectrum of the spectral matrix is usually taken as reference spectrum (x_{ref}).

The spectra, the signal and the noise

Multiplicative Scatter Correction (MSC)

- The calculation is done for each spectrum BUT the average spectrum depends on the calibration base
- One sample will have a different correction depending on the base in which it is calculated!
- For fairly homogeneous bases (and fairly constant spectra), MSC and SNV treatments achieve equivalent corrections

Other methods used for reduction of the multiplicative effect: decrease k

$$A_\lambda = k\varepsilon_\lambda LC + AL_\lambda + AN_\lambda$$

The logarithmic transformation:

One of the properties of the logarithm function is that it checks: log (ab) = log (a) + log (b). Thus it transforms a multiplicative effect (kx) into an additive effect (log (k) 1 + log (x)).

This transformation requires that x is strictly positive everywhere. For example, log can not be applied after derivate. This transformation is particularly suited to intensity spectra or in reflection, since it is the "natural" transformation of the Beer-Lambert law.

Signal normalization: consists in dividing the whole spectrum by a statistic sensitive to the multiplicative effect.

In theory, we can choose different dividends: the maximum, the sum, the average, the norm, the standard deviation, ...

In practice, it is better to avoid dividing by a "single" value, such as the maximum, which can be subject to error or artefacts

It is better to use a statistic that "integrates" a large part of the signal and which will therefore less noisy.

The spectrum standard is used by the SNV-Standard Normal Variate method.

Illustration of pretreatments

In blue white Sugar

In red white Sugar ground

The spectra, the signal and the noise