CHEMOMETRICS AND VIBRATIONAL SPECTROSCOPY FOR THE DETECTION OF MELAMINE LEVELS IN MILK

Juan Antonio Fernández Pierna, Damien Vincke, Vincent Baeten, Clément Grelet, Frédéric Dehareng & Pierre Dardenne

Walloon Agricultural Research Centre (CRA-W), Valorisation of Agricultural Products Department
Chaussée de Namur, 24, B-5030 Gembloux (Belgium)
j.fernandez@cra.wallonie.be

Introduction

Since long the idea of a moving window along one dimension in numerical data has been used for different objectives. One of the first applications is the Savitzky–Golay filter that is applied to a set of digital data points for the purpose of smoothing the data, that is, to increase the signal-to-noise ratio without greatly distorting the signal. This technique is probably one of the most used as preprocessing tool in the area of vibrational spectroscopy. The idea of a moving window is also very popular in the area of evolving data (e.g. environmental data).

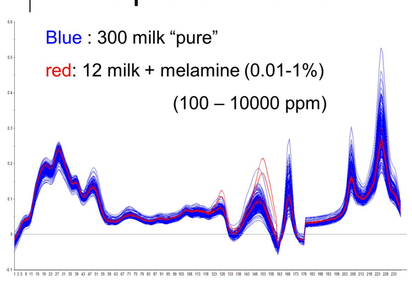
In this work, a moving window is selected along the wavelength axes in vibrational spectroscopic data (NIR, MIR, etc.). For each selected window in a calibration stage, a PCA analysis is performed by fixing the number of principal components. Spectral score residuals in the calibration set are extracted and used to build thresholds to be applied to the spectral score residuals of a prediction set. When a residual, at a certain wavenumber, falls out the defined thresholds, the sample could be suspected of being abnormal indicating the possible presence of unusual ingredients, and therefore allowing non-targeted analysis. A key point in all studies is to define the class 'normal' and 'abnormal' by fingerprint properties. In this work, this has been solved by the use of a local technique allowing, for each sample to be predicted, the selection of the most spectroscopically similar samples in the calibration set previous the application of the moving window PCA.

Workflow of LWPCA

1. Set up a "clean" set = **reference** set
2. For each unknown new spectrum**, Select k** closest spectra from the clean set based on correlation
3. Build a **PCA** model from the selected spectra for each window along the wavelength range
4. Compute the **residuals limits** of the PCA models
5. Apply the PCA models to **project** the unknown new spectrum
6. Compute the **residuals** of the projected spectrum
7. **Check if these residuals** are within the PCA residual limits

A case study

The study selected is based on milk contaminated with melamine. Melamine (2,4,6-triamino-1,3,5-triazine) is a chemical compound rich in nitrogen, which is illegally added to food/feed to artificially elevate the protein content values of products.



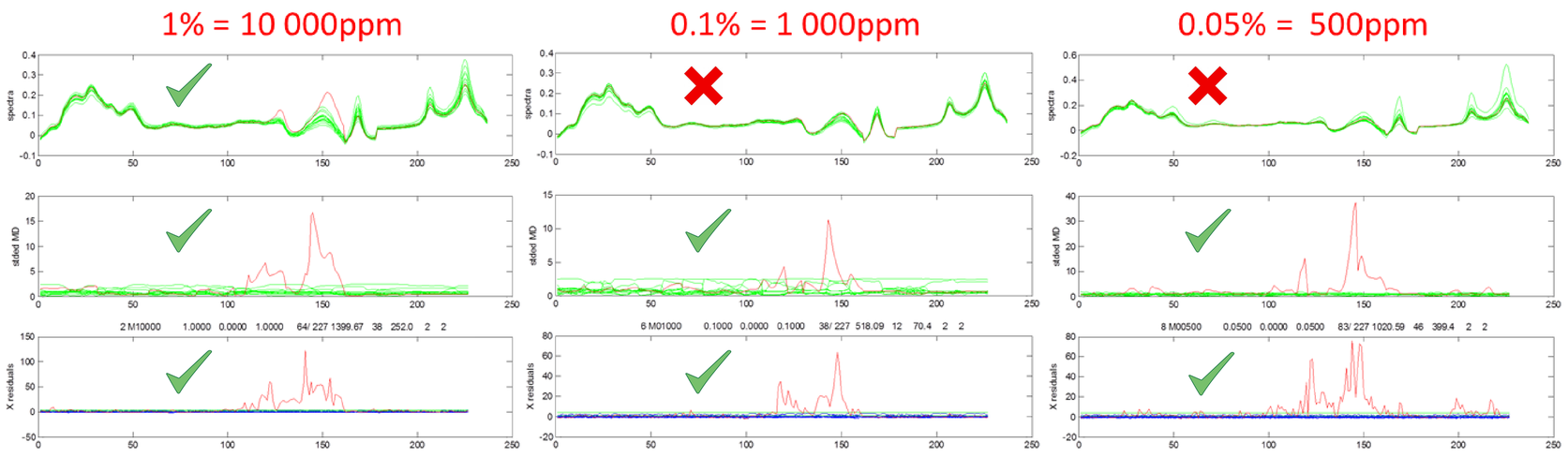
A data set consisting on 300 samples of UHT liquid milk was used as 'clean' data set. Moreover other 12 UHT liquid milk samples have been contaminated with melamine at different levels ranging from 0.01% to 1% (100 – 10000 ppm). All these samples have been measured using a Fourier transform mid-infrared (FT-MIR) spectrometer type FT 6000 (Foss, Hillerød, Denmark).

Results

Original spectrum

GH (Mahalanobis dist.)

LWPCA



Original spectrum

GH (Mahalanobis dist.)

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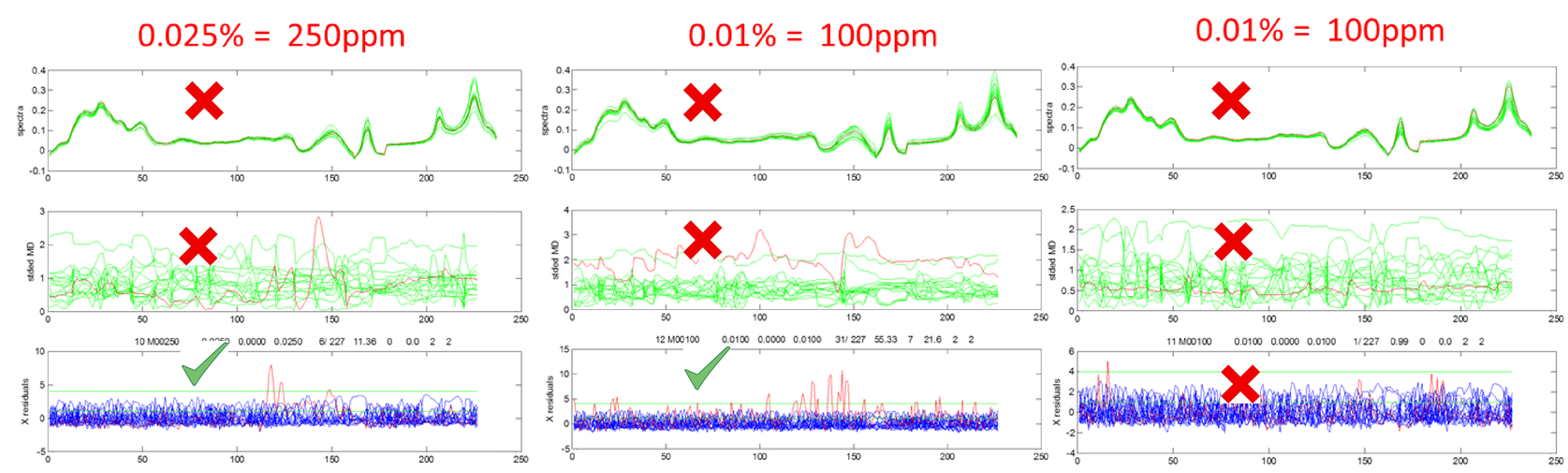

Conclusions

These results show that no clear conclusion can be obtained when looking directly at the spectra. GH values detect abnormalities at levels higher than 500 ppm. LWPCA allows detecting contamination at levels up to 100 ppm; however at those levels the detection of melamine in milk becomes unstable, which is an indication that the technique has probably reached its limit of detection.

In this work a local moving window PCA method has been proposed for the characterization of an important agronomical product and the detection of possible contaminants using vibrational spectroscopy. The application shown here shows the possibilities of this method for the detection of abnormal spectra in the samples. In the example presented here, liquid UHT samples have been contaminated with melamine, making it thus a targeted study. However the method should be used as a method for detection of abnormalities (real contamination or fraud) in the data and a previous step for further analyses. Moreover, as there is a local selection of the most spectroscopically similar samples, the spectral library can be multi-products, which can also drive to the development of unique predictions… but this is another story.

Acknowledgments

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Walloon Agricultural Research Centre