

Development of a Rapid Method for the Untargeted Detection of Contaminants in Milk Using Vibrational Spectroscopy and Chemometrics: the Example of Melamine

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Introduction

In this study, a procedure is proposed for the characterization of agro-food products using vibrational spectroscopy. New crises of adulteration/contamination with illegal ingredients other than known ones continue to occur from time to time. By relying only on targeted analysis methods, adulteration could get out of control and analysis. In contrast to targeted analysis, which uses information from known possible unusual ingredients, an untargeted experiment registers all information within a certain correlation/similarity, including data from new products. Untargeted analysis will mean alerts can be given more rapidly and fraud detected more easily. Until now, untargeted analysis has been associated mainly with direct analysis techniques, such as mass spectrometric-based metabolomics or isotope-assisted methods. Only a few studies have linked untargeted analysis with vibrational spectroscopic methods.

In this work, vibrational spectroscopic techniques combined with new concepts in multivariate analysis is used for characterizing liquid UHT milk samples spiked with varying levels of melamine. Melamine has been illegally added to food/feed to artificially elevate the protein content value of products. Strict regulations have been enforced throughout the world and many papers have been published. Here, a new tool, Local Window Principal Component Analysis (LWPCA) based on a moving window associated to the use of a local technique allowing for each sample to be predicted, the selection of the most spectroscopically similar samples, is proposed as untargeted analysis of samples.



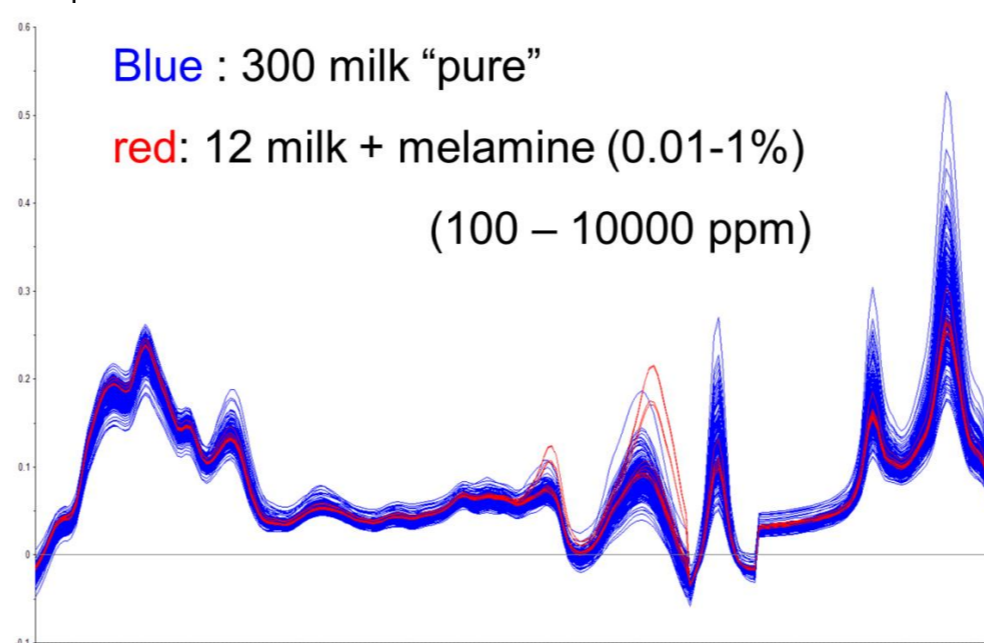
Workflow of the LWPCA method

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

Chemometrics and Intelligent Laboratory Systems
Volume 152, 15 March 2016, Pages 157-162
Use of a multivariate moving window PCA for the untargeted detection of contaminants in agro-food products, as exemplified by the detection of melamine levels in milk using vibrational spectroscopy

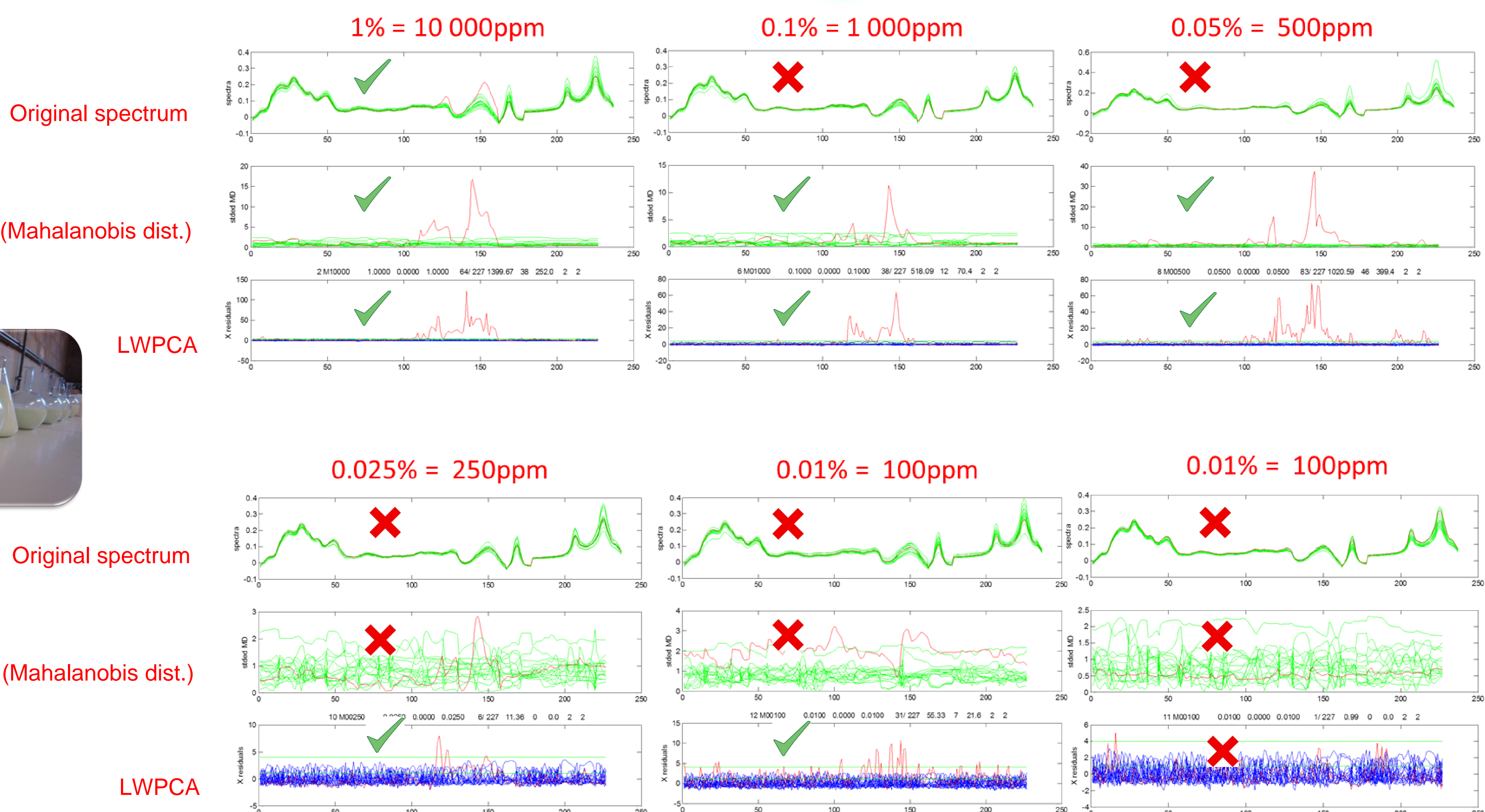
The case study: melamine in milk

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



Conclusions

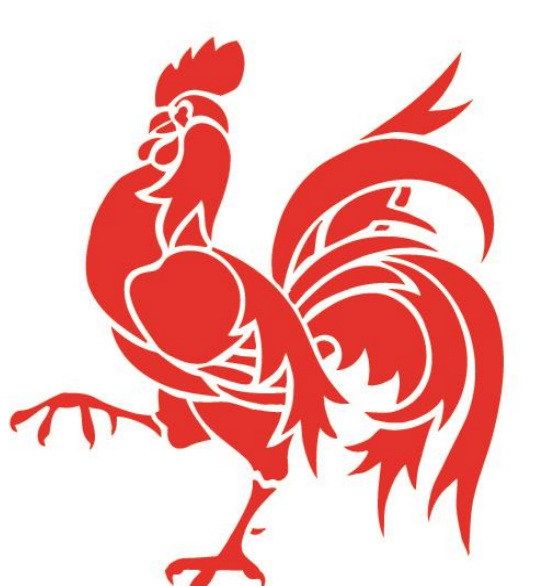
These results show that no clear conclusion can be obtained when looking directly at the spectra. GH values detect abnormalities at levels higher than 500 ppm. LWPCA allows detecting contamination at levels up to 100 ppm; however at those levels the detection of melamine in milk becomes unstable, which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



This work was performed in the framework of the European Union's Seventh Framework Programme for research, technological development and demonstration under grant agreement no 613688 FOODINTEGRITY project. The authors are grateful to Frédéric Dehareng and Clément Grelet from the Agricultural Product Technology Unit of the CRAW from supplying the data.



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