

Rapid Response to Melamine in Dairy Products using Handheld NIR.



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Abstract

Near-infrared diffuse reflectance is uniquely suited to the analysis of both solids and pastes in the food industry. Near-infrared transmission is well suited to the analysis of liquids. The PHAZIR™ is well suited to rapid development of methods for solids, pastes and liquids for both qualitative and quantitative assessments of natural products. In the current context, qualitative assessment answers the question “Does this material resemble authentic materials?” and quantitative assessment answers “How much of ‘X’ does this material have?” Methods developed to answer one, or both, of these questions are a) easy to create, b) sensitive, c) easy to deploy and d) rapid in use. We present a method that was developed in approximately 6 hours that can positively detect less than 0.1% of melamine in a milk-based product. The method can be emailed and deployed at remote locations. Results from the analysis are available in 5 seconds of applying the instrument to the sample.

Introduction

This application note describes the rapid development of a method to detect melamine contamination in infant milk-based formulas. The development of this method was spurred by the unfortunate melamine contamination of milk products in China in September of 2008 and the contamination of pet food in the United States in April of 2007.

Near infrared spectrometers record the “color” of materials in the optical spectrum between 700 and 2500 nm. Portions of the spectrum are absorbed by exciting vibrations in the molecules in the material. In agricultural products, these absorptions arise from moisture, fat, protein and carbohydrates. Industrial chemicals, such as melamine, cyanuric acid and urea have dramatically different spectra and can be readily distinguished when mixed into natural products.

There are two approaches to contamination events: 1) generalized detection of unusual characteristics, and 2) specific detection of a single contaminant.¹ During the pet food contamination event companies implementing NIR technology were alerted to melamine contaminated batches of wheat gluten by their unusual spectra.² Companies relying on paper documentation, Kjeldahl method or the combustion

(Dumas) method were not able to detect contaminated wheat gluten. Companies using NIR were able to avoid recalls of most of their products. Once a threat has been identified, the same NIR instrument can be used for specific and more sensitive responses as shown here.

The following method was designed and implemented in a 6-hour period on September 22, 2008. The experiment has been repeated with different milk-based infant formulas. Similar results were achieved. A PHAZIR with an application built from the process can take spectra and display accurate results in 5 seconds.

Experimental

Materials

- PHAZIR™ 1624
- PhazirMG™
- Infant formula, 100 g
- Melamine monomer, 5 g
- Blade mill
- 2 dram borosilicate shell vials
- ±0.1 mg analytical balance

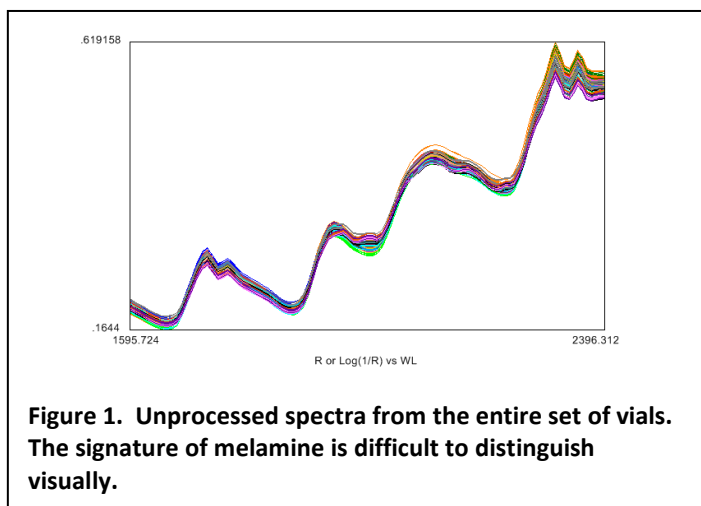
Procedure

A stock 10% w/w mixture was made of infant formula (45 g) and melamine (5 g) and homogenized using a blade mill. The blade mill was pulsed 50 times. Each 10 pulses the material was mixed within the mill by hand. Individual vials were made by adding an amount of stock and then adding unadulterated formula to achieve the desired ratio of ingredients (0, 0.5, 1, 2, 3, 4% w/w). The total weight of material was chosen so that the vials were only half full. Vial contents were homogenized by shaking and rolling the vials.

NIR spectra were taken at three distinct positions in triplicate through the side of each vial. Acquisition time for each spectrum was 4 seconds. The collected data were downloaded to a local PC via USB and analyzed using PhazirMG.

Results & Discussion

The method of preparation allows good control of homogeneity through the blending process. The success of the method is primarily dependent on the ability to homogenize the sample and precise knowledge of



Conclusions

A rapid to implement method for the detection of melamine in milk-based products is shown. The method can be applied to other protein powders, and other agricultural products, that may be subject to adulteration. The PHAZIR can be used as a rapid response tool for contamination events.

In routine use, the same spectrum used to determine adulteration can be used to obtain information about moisture, protein, fat and carbohydrate content. The results are displayed to the user and can be logged for later analysis.

¹ H. Martens, T. Næs, *Multivariate Calibration*, Wiley Interscience, Chichester, 1991.

² Personal communication, June 2007.

³ D.M. Haaland and E.V. Thomas, *Analytical Chemistry*, 60, 1202 (1988).

⁴ B.J. Barnes M.S. Dhanoa and S.J. Lister, *Applied Spectroscopy*, 43, 772 (1989).

composition. Errors in either step cause confusion in the analysis steps. This is common to any analytical method.

Raw spectra, shown in Figure 1, were imported into PhazirMG and analyzed using PLS1 regression.³ A broad combination of preprocessing functions⁴ was evaluated using the built-in macro function. The best results are summarized in Table 1. The corresponding regression is shown in Figure 2 and the regression vector in Figure 3. The features seen are readily traceable to melamine features.

Table 1. Results from optimization.

Preprocessing	Parameters
Wavelength range	1960 - 2209 nm
Standard Normal Variate (SNV)	
Savitzky Golay (SG)	2 nd der., 7-point, 2 nd degree
PLS1 Regression	
2 factors	
Rotation by concentration	
SEP cross-validated = 0.07% w/w (700 ppm)	

Repeating the process with different brands and types of infant formula produces very similar results. Milk products primarily differ by moisture, carbohydrate, protein and fat content. Melamine is distinct from these components. The preprocessing steps chosen remove variation in the spectra due to powder packing, particle size and emphasize the features of melamine.

Cross validation provides a check for model robustness by taking out a small subset of the full calibration, building a model on the remaining spectra and predicting the concentration on the subset. The errors of the rotations are accumulated and reported as a standard error of prediction (SEP). SEP is used in the same way as standard deviations to estimate limits of detection.

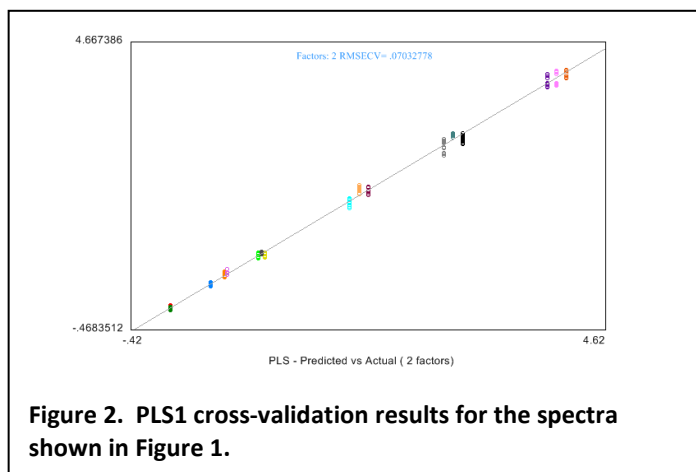


Figure 2. PLS1 cross-validation results for the spectra shown in Figure 1.

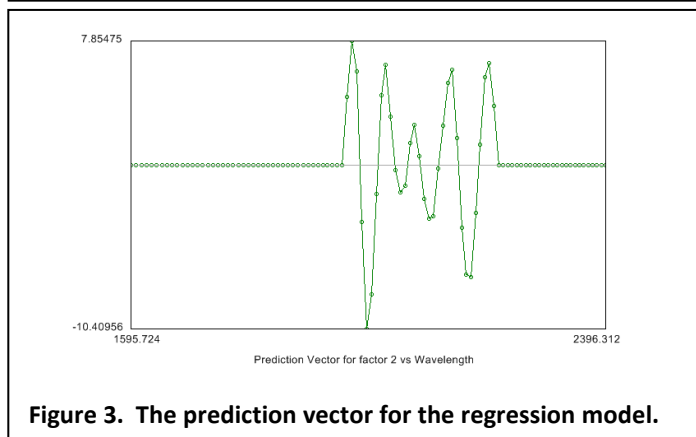


Figure 3. The prediction vector for the regression model.