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Melamine detection in milk using vibrational spectroscopy and chemometrics analysis: A review

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ABSTRACT

Major advances in the field of chemometrics combined with the use of vibrational spectroscopy have proven essential for the identification and quantification of food contaminants. These techniques, which have guided the work of regulatory agencies overlooking the food industry, can be readily applied to monitor food processing, quality control, and quality assurance. These processes can ensure product authenticity with respect to variety, geographical origin, and presence or absence of contaminants. Food analysis by vibrational spectroscopy provides overall chemical composition of the tested food sample; therefore, it is widely considered to be a highly reliable and empirical fingerprints of that samples. In 2008, melamine adulteration of milk powder in China resulted in devastatingly adverse effects for both consumers and the overall Chinese economy at large. As a result, regulatory agencies have markedly increased their interest in using fast, reliable, and accurate methods for identifying food contaminants. In this article, we provide a detailed overview of the uses of vibrational spectroscopy methods and chemometrics for the detection and quantification of melamine in dairy products.

1. Introduction

Dairy products are essential components of a healthy diet for all age groups, owing to their high nutritional value (Hilding-ohlsson, Fauerbach, Sacco, Bonetto, & Cortón, 2012; Savindo et al., 2010). Protein content in milk is important for the production of many products with significant impact on their sensory and rheological characteristics, and has thus been used as a metric of quality by many industries. Since compounds rich in nitrogen can mimic a high protein concentration, standard methods cannot distinguish between nitrogen from protein and non-protein sources, leading to widespread use of such compounds to adulterate milk-based products (Haughey, Graham, Cancouët, & Elliott, 2013; Mauer, Chernyshova, Hiatt, Dering, & Davis, 2009; Moore, DeVries, Lipp, Griffiths, & Abernethy, 2010; Santos, Pereira-Filho, & Rodriguez-Saona, 2013a; Yang et al., 2009).

In 2008, melamine, an organic compound that is 66.6% nitrogen by mass, was used to adulterate protein levels in milk produced locally in China (Finete, Gouvêa, Marques, & Netto, 2013; Miao et al., 2009; Yan, Zhou, Zhu, & Chen, 2009). The adulterated products resulted in illness in 294,000 individuals, hospitalization of 50,000, and death of six children (Fig. 1). The ingestion of melamine at levels above the safety limit can induce renal failure and death in infants. The resulting crisis, which scared local consumers, prompted many countries to recall Chinese products in a precautionary effort. To prevent further contamination, the melamine limit in food was established.

The Chinese Government and United States (US) Food and Drug Administration (FDA) have determined that 1 mg/kg is the maximum limit allowed in infant formula and 2.5 mg/kg for other foods (Lin, 2009; Liu, Lin, & Li, 2010; Mauer et al., 2009). Since product authentication and food quality are of prime importance for ensuring the health of consumers, monitoring of food products by reliable methods is an essential goal.

Gas chromatography (GC), liquid chromatography–triple-quadrupole tandem mass spectrometry, high-performance liquid chromatography (HPLC), thin-layer chromatography, and capillary electrophoresis have been used to detect residues of melamine (Chi, Liu, Guan, Zhang, & Han, 2010; Desmarchelier, Cuadra, Delatour, & Mottier, 2009; Garcia et al., 2012; Koh et al., 2011; Mauer et al., 2009; Wen et al., 2010).

Abbreviations: AOAC, Association of Official Analytical Chemists; AWT, Adaptive wavelet transform; ANN, Artificial neural networks; 2DCS, Two-dimensional correlation spectroscopy; FDA, Food and Drug Administration; FT, Fourier transform; GC, Gas chromatography; HPLC, High performance liquid chromatography; IR, Infrared spectroscopy; LC/MS/MS, Liquid chromatography coupled with mass spectroscopy; LS-SVM, Least squares-support vector machine; LOD, Limit of detection; LQ, Limit of quantification; LOD, Limit of detection; LQ, Limit of quantification; MIR, Mid infrared spectroscopy; NIR, Near infrared spectroscopy; N-PLS, Multi-way partial least squares; NPLS-DA, Multi-way partial least squares discriminant analysis; OPLS, Orthogonal projections to latent structures; PCA, Principal components analysis; PLS, Partial least square; PLS-DA, Partial least square discriminant analysis; Poly-PLS, Polynomial partial least square; RDP, Relative deviation of prediction; RSD, Relative standard deviation; RMSEC, Root mean square error of calibration; RMSECV, Root mean square of cross-validation; RMSEP, Root mean standard error of prediction; SERS, Surface-enhanced Raman spectroscopy; SIMCA, Soft independent modeling of class analogy; SORS, Spatially offset Raman spectroscopy; SVM, Support vector machine; SVR, Support vector regression; USA, United States of America.

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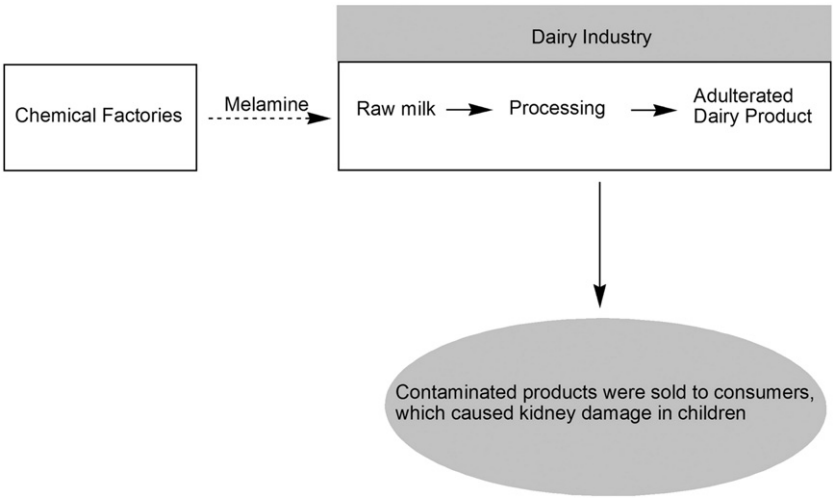

Fig. 1. Melamine fraud in China's dairy products.

These methods exhibit high sensitivity, but for the most part are labor intensive, costly, and require harmful reagents.

The need for a reliable and high-throughput screening method for melamine content has prompted the use of spectroscopic methods in conjunction with chemometrics analysis (Haughey et al., 2013; Hilding-ohlsson et al., 2012; Liu, Wen, Dong, Lai, & Zhao, 2013; Yang, Liu, & Kexin, 2013). Vibrational spectroscopy techniques are rapid, non-destructive, and capable of detecting contaminants in food with good accuracy and precision. Many authors have used infrared and Raman spectroscopy to determine the authenticity of oil, gluten, butter, chicken feed, carbohydrate powders, juices, honey, coffee, milk, vinegar and wheat (Balabin & Smirnov, 2011; Borin, Ferrão, Mello, Maretto, & Poppi, 2006; Downey, Briandet, Wilson, & Kemsley, 1997; Shao & He, 2009; Lin et al., 2008; Mauer et al., 2009; Ozen, Weiss, & Mauer, 2003; Rohman & Man, 2010; Uysal, Boyaci, Genis, & Tamer, 2013; Wu, Feng, & He, 2008).

Chemometrics is an interdisciplinary field that involves multivariate statistical analysis, mathematical modeling, and information technology. A major attribute of chemometrics is its ability to reduce the complexity of large data sets, thereby allowing for a more comprehensive understanding of their implications (Fig. 2) (Aprea et al., 2012; Cruz et al., 2013; Santos, Pereira-Filho, & Rodriguez-Saona, 2013b; Savori, Rasmussen, Mikkelsen, & Engelsen, 2013; Yucel & Sultanoglu, 2013; Zielinski et al., 2014).

The main chemometric methods used to detect melamine levels in adulterated milk are based on either unsupervised pattern recognition analysis, such as principal component analysis (PCA) or supervised classifications, namely partial least square-discriminant analysis (PLS-DA) and soft independent modeling by class analogy (SIMCA) (Gemperline, 2010; Otto, 2007; Vandeginste et al., 1998). Multivariate calibration methods based on partial least square (PLS), support vector machines (SVM), and artificial neural network (ANN) have also been used to predict melamine content in adulterated samples. In addition, univariate linear regression has been used.

Authentication of dairy product enables regulatory agencies to guarantee food quality, and in turn, preserve consumer health and prevent worldwide scandal. According to these considerations, the objective of this study is to review recent efforts using vibrational spectroscopy methods and chemometric analysis to detect and quantify melamine in dairy products.

2. Melamine in milk

Milk protein, a precursor of several bioactive peptides, with antimicrobial activity, is a source of essential amino acids, calcium, zinc, copper, and phosphate ions. In addition, milk protein, facilitates the absorption of many nutrients (Claeys et al., 2013; Ebringer, Ferencík, & Krajocovic, 2008; Haug, Hostmark, & Harstad, 2007). However, milk is

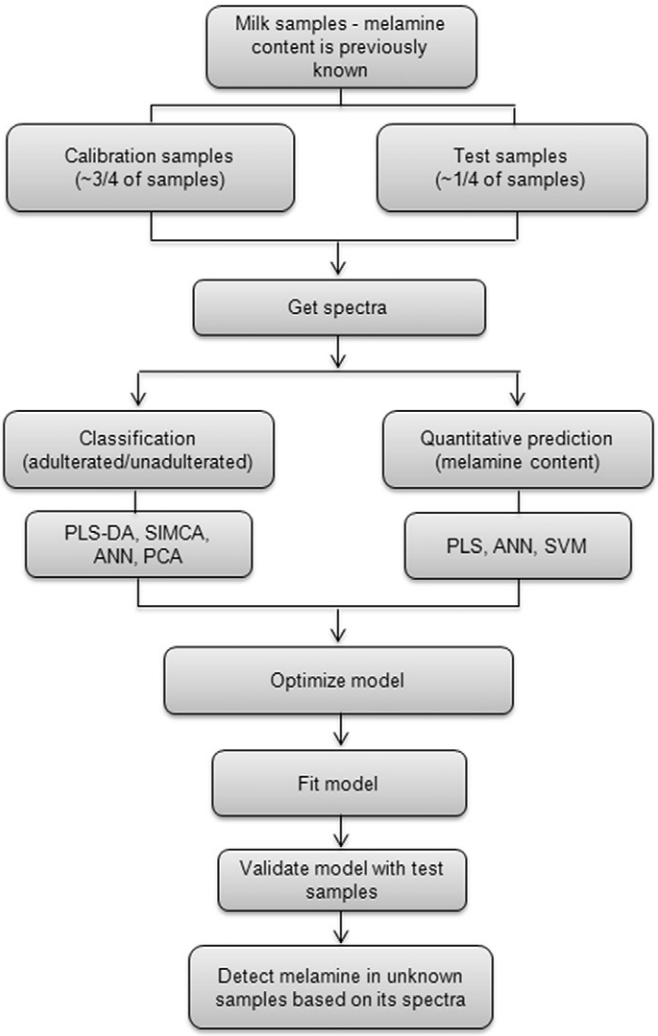

Fig. 2. Chemometrics methods for melamine detection or quantification.