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Quantitative analysis of melamine in milk powders using near-infrared hyperspectral imaging and band ratio

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ABSTRACT

Since 2008, the detection of the adulterant melamine (2,4,6-triamino-1,3,5-triazine) in food products has become the subject of research due to several food safety scares. Near-infrared (NIR) hyperspectral imaging offers great potential for food safety and quality research because it combines the features of vibrational spectroscopy and digital imaging. In this study, NIR hyperspectral imaging was investigated for quantitative evaluation of melamine particles in nonfat and whole milk powders. Melamine was mixed into milk powders in a concentration range of 0.02–1.00% (w/w). A NIR hyperspectral imaging system was used to acquire images (938–1654 nm) of melamine powder, whole milk powder, nonfat milk powder, and mixtures of melamine and each of the milk powders. Two optimal bands (1447 nm and 1466 nm) were selected by a linear correlation algorithm with pure milk and pure melamine. Band ratio ($B_{1447/1466}$) images coupled with a single threshold were used to create resultant images to visualize identification and distribution of the melamine adulterant particles in milk powders. The identification results were verified by spectral feature comparison between separated mean spectra of melamine pixels and milk pixels. Linear correlations (r) were found between the number of pixels identified as containing melamine and melamine concentration in nonfat milk and whole milk powders, which were 0.980 and 0.970 or higher, respectively. The study demonstrated that the combination of NIR hyperspectral imaging and simple band ratioing was promising for rapid quantitative analysis of melamine in milk powders.
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1. Introduction

Recent recalls involving infant food and milk products contaminated with melamine (2,4,6-triamino-1,3,5-triazine) have aroused widespread food safety concerns. Melamine is a nitrogen-rich chemical substance (66% nitrogen by weight) that is commonly used as an industrial chemical in the production of melamine formaldehyde resins for manufacturing laminates, coatings, commercial filters, glues or adhesives (Jawaid et al., 2013). Melamine is sometimes illegally added to food products such as milk, infant formula, frozen yogurt, pet food, biscuits, candy, and coffee drinks to increase apparent protein content (Chan et al., 2008; WHO, 2011). Although melamine has low toxicity, its consumption may lead to kidney stones, eventual renal failure, and ultimately death (Brown et al., 2007; Tsai et al., 2010). In 2004, an outbreak of food adulteration with melamine led to renal failure in dogs and cats in Asia (Brown et al., 2007). In 2007, US scientists confirmed that pet food adulteration with melamine caused the illnesses and death of thousands of cats and dogs (Puschner et al., 2007). In 2008, consumption of melamine-contaminated infant formula and related dairy products in China caused more than 51,900 infants and young children to suffer from kidney illness, including six child deaths (Sun et al., 2010). The European Union (EU) set a maximum residue limit for melamine in dairy products and high-protein foods at 2.5 mg/kg, and the US Food and Drug Administration (FDA) set it as 0.25 mg/kg in milk and dairy products (Filazi et al., 2012). The Ministry of Health of China updated the dairy standards in 2010 and

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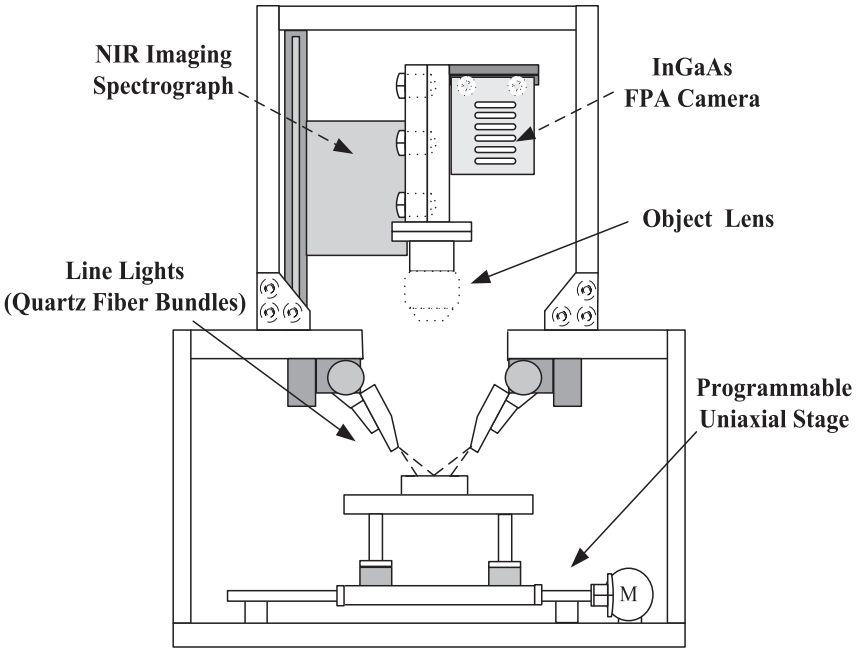

Fig. 1. Schematic of the NIR hyperspectral imaging system for acquiring reflectance images of powder samples.

stressed that addition of melamine to dairy products is prohibited (Guo et al., 2011).

Various methods for the detection of melamine in foods for human consumption and animal feeds have been reported in recent years, including high performance liquid chromatography (HPLC) (Ehling et al., 2007; Muñiz-Valencia et al., 2008; Chao et al., 2011), mass spectrometry (MS) (GB/T 22388-2008; Filigenzi et al., 2008), enzyme-linked immunosorbent assay (ELISA) (Garber, 2008; Yin et al., 2010), capillary electrophoresis (CE) (Chen and Yan, 2009), chemiluminescence (CL) (Wang et al., 2009), and molecularly imprinted polymer film (MIP) (Pietrzyk et al., 2009). For these chromatographic approaches, sample pretreatment is relatively time-demanding and labor-intensive.

Near-infrared (NIR) and Raman spectroscopy have been applied to melamine detection in milk (Mauer et al., 2009; Balabin and Smirnov, 2011; Liu et al., 2009) because of high penetrability, nondestructive behavior, and ease of pretreatment. However, spectroscopic assessments with relatively small point-source measurements do not provide the spatial information of melamine particles. NIR hyperspectral imaging technology combines the features of imaging and spectroscopy to simultaneously acquire both spatial and spectral data, which is valuable for investigating the location where the components being studied are distributed and for monitoring of particular banned chemicals (Huang et al., 2014). Several studies in recent years have investigated the imaging of melamine in feed materials and milk powders (Fernández Pierna et al., 2014; Huang et al., 2014; Fu et al., 2014). Although these studies provided detection results for melamine particles in which imaging allowed for the visualization of the distribution of melamine particles within images of milk powder mixture samples prepared with various melamine concentrations, there was no exploration of the relationship between melamine concentration and the number of pixels identified as containing melamine. To establish efficient imaging systems, essential spectral wavelengths are first sought through a variety of strategies, such as Principal Component Analysis, (Linear) Discriminant Analysis, Decision Boundary, Projection Pursuit, and kernel methods (Landgrebe, 2002). These algorithms treat the raw pixel spectra as input vectors in high dimensional spaces and rely upon linear or nonlinear mapping to a feature space by optimizing certain criterion. Band ratio, the ratio of spectral values at two different bands, offers the potential of substantially reducing processing time during classification (Kim et al., 2007). Therefore, the objective of this study was to develop band ratio methodology for the detection and quantitative prediction of melamine-adulterated milk powders using NIR hyperspectral imaging.

2. Materials and methods

2.1. Sample preparation

Nonfat milk powder (Organic Valley, La Farge, WI, USA) and whole milk powder (Hoosier Hill Farm, Fort Wayne, Indiana, USA) were purchased from a local supermarket. Melamine was obtained from Sigma-Aldrich Company (St. Louis, MO, USA) with 99% purity. The ranges in particle size of milk powder and melamine were 5–39 μm and 7–39 μm, respectively. For each of the two milk types, ten milk–melamine mixtures were prepared with melamine concentrations (w/w) of 0.02%, 0.04%, 0.06%, 0.08%, 0.10%, 0.20%, 0.40%, 0.60%, 0.80% and 1.00%. Twenty-five grams of dry powder mixture were placed in a plastic vessel (89 mm diameter × 102 mm height) and mixed with an acoustic mixer (Resodyn Acoustic Mixers, Model LabRAM, Butte, MT, USA). The intensity, frequency and mixing time were set as 100%, 61.9 Hz and 10 min, respectively, to enhance the uniform distribution of the melamine particles within the dry milk. Next, each milk–melamine mixture was put in a custom-designed aluminum plate (15 mm height, 50 mm width, 50 mm length) with one square well (2 mm depth, 30 mm width, 30 mm length) which was spray painted in flat black. The well was slightly overfilled by milk–melamine mixture powder using a spoon, without compressing the dry powder, and then leveled across the top using a card to smooth the sample surface and remove excess powder. A well contained approximately 1.0 g of sample mixture. A total of four replicates (sets) for each mixture were prepared. Likewise, three preparations each of whole milk powder and nonfat milk powder, and two preparations of pure melamine were imaged.