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Detection of adulteration of goat milk powder with bovine milk powder by front-face and time resolved fluorescence

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ABSTRACT

The increasing importance of goat milk renews the need to examine the authenticity of goat milk powder and to identify frauds with cow milk powder. The use of front-face and time-resolved fluorescence techniques to identify biochemical composition and structure changes could assist milk powder frauds analysis. This study aimed to use fluorescence spectra and lifetimes to differentiate frauds of goat milk powder with cow milk powder. We analyzed the fluorescence spectra by partial least squares and found a good prediction result. Employing analysis of variance, we observed different fluorescence lifetimes for goat milk powder with cow's milk powder in six categories. In addition, we use linear regression to create a model to predict the amount of cow's milk in each the samples using the mean intensity lifetime. These results indicate that front face and time-resolved fluorescence can assist on the analysis of powder milk and its composition.

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1. Introduction

Milk is an important source of nutrients and dry milk comprises most of the international dairy commodity tradable volumes (Karoui & Blecker, 2011). Milk powder has prolonged shelf life, is easy to store and transport, and does not need to be refrigerated due to its low moisture content (Ceballos et al., 2009; Karoui & Blecker, 2011; Liang, 2000). Cow's milk are produced in large volumes, has low market prices and cheaper production, however cow milk allergy is very common, particularly among children (Haenlein, 2004; Selvaggi, Laudadio, Dario, & Tufarelli, 2014). Goat milk is similar to cow milk in composition, but it lacks beta-carotene and agglutinin, has smaller fat globules and different casein types, which makes it more easily digested (Costa et al., 2014; Haenlein, 2001, 2004; Park et al., 1994). Because its composition and less allergenic properties, goat milk is being considered an excellent raw material for industrialized food for infants, the elderly, and people with particular medical needs (Jenness, 1980; Montilla & Calvo, 1997; Park et al., 1994). Several reviews are currently available on the composition of goat milk with respect to that of cow milk (García, Rovira, Boutoial, & López, 2014; Haenlein, 2004; Selvaggi et al., 2014).

The growing interest in goat milk propels the need to investigate the authenticity of goat milk powder and possible contaminations or frauds with cow milk powder. The studies on rapidly, lower cost, and nondestructive detection methods for composition/adulterants is becoming essential for food safety and public health. Spectroscopic techniques have deserved special attention (Baum, Hansen, Nørgaard, Sørensen, & Mikkelsen, 2016; Mendes et al., 2016; Rocha, Paiva, Anjos, Furtado, & Bell, 2015; Varriale et al., 2015) as an alternative method for laborious and time-consuming or costly tests such as capillary electrophoresis and isoelectric focusing of γ-casein (Song, Xue, & Han, 2011). The potential of fluorescence for identifying chemical components indicates that spectroscopic fluorescence-based techniques can identify possible contaminations or frauds in milk (Di, Yong, Jiahui, & Shuijuan, 2009; Forcato, Carmine, Echeverría, Pécora, & Kivatinitz, 2005; Guan, Liu, Ye, & Yang, 2005; Kulmyrzaev, Levieux, & Dufour, 2005; Morales, Romero, & Jiménez-Pérez, 1996; Moros, Garrigues, & de la Guardia, 2007; Wu, He, Feng, & Sun, 2008).

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Milk contain several fluorophores, including tryptophan residues, vitamin A, flavins and advance Maillard reaction products. Fluorescence techniques have been used in dairy research to detect structural changes in dairy products and front-face fluorescence spectroscopy can investigate fluorescence properties of turbid or opaque samples (E. Dufour & Riaublanc, 1997).

Time resolved fluorescence offers some advantages for the characterization of food products when compared with steady-state spectroscopy, because it measures the time dependence (lifetimes) of the fluorescence instead of its emission intensity. Lifetimes are determined from the fluorescence intensity decay and do not depend on excitation, duration of light exposure and method of measurement. More important, photo bleaching does not alter the fluorescence lifetime, and it is independent of the fluorescence intensity and largely independent of fluorophore concentrations (Berezin & Achilefu, 2011; Marcu, 2012).

Milk powders has three fluorescence lifetimes at 315/468 nm excitation/emission (Brandao, Anjos, et al., 2017, Brandao, de Carvalho dos Anjos, et al., 2017). The cow milk powders present an increase on the third lifetime at 315/468 nm excitation/emission when compared to goat milk. The interaction of vitamin A with lipids, fat globule membrane and protein can differs for cow and goat milk powders causing this distinction on the third fluorescence lifetime (Brandao, Anjos, et al., 2017, Brandao, de Carvalho dos Anjos, et al., 2017).

In this study, we investigate the potential of static fluorescence and time resolved fluorescence methods as an alternative for rapid screening quantification of frauds in goat milk powders with cow's milk powders.

2. Material and methods

2.1. Sample preparation

We acquired three batches of goat milk powder and cow milk powder products in local markets from the same fabricant. We performed adulterations of the goat milk powder with cow milk powder by creating samples with a fixed amount of bovine milk powder. The percentage of bovine milk on the samples were 0%, 1%, 3%, 5%, 8%, 10%, 15%, 20%, 25%, 30%, 50% and 100%. For each adulteration and each batch, we made triplicate samples with 130 mg approximately, totalizing 114 samples. The samples were hard-pressed on a hydraulic press using 3 tons for 1 s, creating a disc with 1 cm of diameter. We used a circular holder for solid samples provided by Edinburgh Instruments to fix the pressed discs for measurement. We performed all measurements directly after the preparation of the samples and in room temperature (~20 °C).

2.2. Fluorescence spectroscopy

The front-face fluorescence emissions were measured with excitation at 315 nm wavelength acquired from 340 to 600 nm with 1 nm intervals. The excitation source was an Edinburgh nF900 ultrafast nanosecond flashlamp filled with hydrogen gas. The acquisitions were performed with the Edinburgh FL920 spectrometer with a blue sensitive photomultiplier to detect the emitted photons. We define the dwell time to 0.1s and each emission was the sum of three repetitions.

2.3. Time resolved fluorescence spectroscopy

We recorded the fluorescence intensity decay using the time-correlated single photon counting (TCSPC) method. The excitation source was an Edinburgh nF900 ultrafast nanosecond flashlamp filled with hydrogen gas. The acquisitions were performed with the Edinburgh FL920 spectrometer with a blue sensitive photomultiplier to detect the emitted photons. The full width at half maximum (FWHM) of the instrument response function was typically 3 ns and time resolution was 0.098 ns per channel. The experiments present no significant background and a software provided by Edinburgh Instruments was employed for analysis of the individual decays, which were fitted to multi-exponential curves. The fluorescence intensity as a function of time can be described by: $I(t) = \sum_i \beta_i \exp[-t/\tau_i]$, where β_i are the pre-exponential factors and τ_i are the lifetimes.

Samples were excited at 315 nm and the fluorescence intensity decay registered at 468 nm. The decay profile intensity was fitted to a one, two, three and four exponential decay using deconvolution with the instrument response function via the software F900 provided by Edinburgh. We analyzed the quality of the fit by evaluating the residuals distribution and the statistical parameter reduced-χ^2 (reduced chi squared). The best fitting occurred for three exponentials decays, which average reduced-χ^2 value was 1.22 and we obtained a uniform residual distribution. The software provides the values for the three lifetimes and the normalized pre-exponential factors β_{n1}, β_{n2} and β_{n3} (which sum equals to 1).

2.4. Data processing

We performed partial least squares (PLS) regression using SIMPLS algorithm on the normalized emission spectra to study the combinations of variables and comparison of the spectral patterns for cow and goat milk samples and the mixed samples. We performed all PLS calculations on MATLAB® software using 78 samples to construct and calibrate a valid model and 36 samples with different adulterations (3 chosen randomly from each adulteration % group) to validate.

The differences in the decay values τ_1, τ_2 and τ_3 between different adulterations were analyzed by one-way analysis of variance (ANOVA) using Fisher's LSD and Tukey methods. We divided all samples in 6 groups: 100% Cow, More than 30% Cow (50%), 20%–30% Cow (25% and 30%), 10%–20% Cow (10%, 15%, and 20%), Less than 10% Cow (8%, 5%, 3%, and 1%), and 100% Goat, corresponding to percentage of bovine milk on each sample.

From the results of the fit of experimental decays we calculated the mean intensity lifetime, using the definition (Sillen & Engelborghs, 1998). Mean intensity lifetime: $\langle\overline{\tau_I}\rangle = \sum_i \beta_{ni}\tau_i^2 / \sum_i \beta_{ni}\tau_i$.

We used Minitab 16 Statistical® software to perform two general regression using the mean intensity lifetime with aspect to the percentage of cow milk present on the samples and the τ_3 lifetime with aspect to the percentage of cow milk present on the samples.

3. Results

Front-face fluorescence intensity is lower for cow milk powder when compared to goat milk powder for excitation sources at 315 nm wavelength (Brandao, Anjos, et al., 2017, Brandao, de Carvalho dos Anjos, et al., 2017). To analyze the fluorescence spectra of cow, goat and hybrid milk powder samples we employed partial least square (PLS) regression.

The use of PLS regression on the spectral data resulted in 8 components, which explained more than 99% of the total variation for the excitation wavelength 315 nm. The estimated mean squared prediction error was of 0.002 for predictors and 1.99 for response. Fig. 1 shows the results calculated by the PLS model (*fitted*) versus the real value measured (*observed*) during the experiment of the cow's milk percentage on the samples.

Fig. 2 shows the calculated residuals (the difference between the fitted value and the observed value of the cow's milk percentage)

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