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Development of two dielectric sensors coupled with computational techniques for detecting milk adulteration

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ABSTRACT

Milk adulteration is a challenging concern which leads to economic losses, quality deterioration of the end products in dairy industry, and consequently public health risks. The demands for reliable and fast methodologies have been already increased in dairy industry. Therefore, developing simple, rapid, and reliable instrumental methods is a necessity for detecting the milk adulterations. This research effort was aimed to combine the sensor technology with computational techniques for the milk adulteration detection. For this purpose, two dielectric sensors, parallel-plate (PPC) and cylindrical stub resonator (CS), were developed and evaluated to examine a number of prevalent milk adulterations (sodium bicarbonate, water, sugar, urea, and gelatin) with a range of variation. Dielectric power and amplitude were recorded versus frequency (swept within 0–150 MHz) for the PPC and CS sensors, respectively. The spectral data were then analyzed using some computational approaches consisted of SPLINE (moving cubic spline), NIPALS (principal component analysis), CLASS (classification and class modelling techniques), MRM (multivariate range modelling), TREE (classification trees), and PLS2 (correlation between blocks of variables)). Based on the results, the dielectric power spectra of the PPC sensor showed the frequency range of 15–60 MHz as the most sensitive band with respect to different adulterations and the amplitude-frequency response of the CS sensor revealed remarkable changes in the amplitude at the resonance frequencies. According to the data analysis, for PPC, two matrices were studied, with different range of the frequencies and it was proved that the data matrix with 145 variables has more discriminant information. Also, in the case of PPC data, classification tree showed the best result with 80% prediction ability for the milk samples while full classification accuracy was found for CS data. As a consequence, it was concluded that the adulterations in milk can be screened by both sensors coupled with computational techniques. Therefore, the methodologies presented here could be considered as a candidate for potential use in dairy industry.

1. Introduction

Milk, as the main and prevalent dairy product worldwide, has rapidly increasing consumption in community due to its high nutritional value and benefits to human safety leading to its high demands all over the world. Nonetheless, economic revenue has caused the fraudulent and adulterate motivations which threat the public health. It is worth mentioning milk fraud and milk adulteration are two different terms. Fraud in milk includes some illegal activities such as tampering, over run, theft, diversion, adulteration, mislabeling, and counterfeiting (Handford et al., 2016). Thus milk adulteration, as a subcategory of fraud, is the illegitimate adding foreign chemical compounds to milk for various aims such as increasing milk weight for sale by adding water, increasing milk shelf-life particularly in warm and hot seasons during transportation by adding detergent chemicals. Also, some chemicals can be added to enhance the cosmetic nature of milk like foamy appearance (Soomro et al., 2014). Therefore, dairies are facing a serious issue to characterize between authentic and adulterated milk samples because dairy industry has to confirm the raw milk quality supplied by farmers and ensure consumers for purchasing fresh milk from the market.

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Traditionally, screening milk adulteration is carried out by chemical assay methods and chromatographic techniques such as HPLC and GC–MS. These approaches suffer from many drawbacks because they are expensive, time-consuming and labor-intensive (Rebechi et al., 2016). Even human based methods like sensory evaluation have some disadvantages because much time and attempt should be spent to choose and train the expert panelists. Furthermore, besides subjectivity and low reproducibility of this method, human senses are prone to fatigue leading to response lag and impact on detection accuracy. Therefore these drawbacks limit the applications of above mentioned methods to rapid and cost-effective screen of milk adulteration.

One of the ways to detect milk adulteration is the fabrication and development of reliable diagnosing tools and techniques and nowadays, there is an increasing interest in developing simple, non-expensive, fast, and on line instruments for this goal. Such trend has therefore become of interest with application of non-destructive measurement tools such as electronic nose and tongue, electrical admittance measurement, biosensors, frequency conductance measurement, spectroscopy, image processing and ultrasound for milk adulteration evaluation. In this context, readers are referred to the following more recent studies about instrumental detection of milk adulteration (Finete et al., 2013; Abernethy and Higgs, 2013; Motta et al., 2014).

Santos et al. (2016) conducted an experimental procedure to quantify different milk adulteration types involving urea, hydrogen peroxide, synthetic urine and synthetic milk. For this purpose, they employed time domain nuclear magnetic resonance (D NMR) and multivariate techniques such as principal component analysis (PCA), soft independent modelling of class analogy (SIMCA), k nearest neighbors (kNN), and partial least squares regression (PLSR) to classify different levels of constitutes added to milk. They concluded that the technique could predict the adulteration levels and classification models with success rates larger than 90%. In another study, Lim et al. (2016) evaluated the melamine-milk powder mixture samples with different concentration levels within 0.02–0.1 g/ml range using NIR hyperspectral imaging system. They employed regression coefficient of partial least squares regression (PLSR) for developing models to melamine particles detection. Although the method showed an effective tool to milk adulteration detection, this type of imaging system is expensive.

Detergent materials are also used to reduce milk microbial load especially in warm transportation conditions. The study by Kumar et al. (2016) dealt with the detection of aniodic detergent in milk using unmodified gold nanoparticles. They suggested the fabricated sensor does not need expensive instrumentation and is simple to use in dairy. However, their method was merely specific for detergent detection not for a variety of adulteration types.

In recent years, special attention has been paid to computerized methods in milk adulteration research. Since distinguishing among adulterated samples needs to consider many variables, so the instruments should be coupled with such computational approaches so called chemometrics to achieve high classification accuracy. Such techniques combined with rich-data instrumental systems are used to qualitatively classify unknown samples with similar attributes as well as to quantitatively determine the adulteration levels in samples (Moore et al., 2012).

Mendes et al. (2016) employed orthogonal partial least square (OPLD) and multiple layer regression (MLP) for analyzing the data gained by fatty acid (FA) profile method on adulterated milk samples. However, the method proposed by the authors is time consuming.

Measuring dielectric properties has been shown promising results for milk evaluation (Nunes et al., 2006; Guo et al., 2010) because such properties (dielectric constant, dielectric loss factor, loss tangent) mainly depend on the physicochemical changes in the food sample (Naderi-Boldaji et al., 2015; Mireei et al., 2016). The dielectric studies on milk are more dedicated to detection of milk freshness or compositions (e.g. fat content) and less to adulteration detection.

This study was thus aimed at the development and application of two different types of dielectric sensors for detection of some prevalent adulterations in milk. The measurement systems have been coupled with advanced chemometrics to screen the type and also the level of milk adulterations. This is the first study to develop and examine the dielectric sensors as a simple, cheap and non-destructive method to milk authentication. The low cost of the sensors is one of the major advantages of this method because it does not require any particular costly measuring system. Considering above novelty statements and to knowledge of the authors, the available literature lacks reports on the title of this study. Therefore the research idea in this paper to screen the type and the level of adulterant substances using dielectric sensors combined with computational techniques is quite original and novel.

2. Materials and methods

2.1. Instruments and measuring principles

2.1.1. Parallel-plate dielectric sensor

A parallel-plate capacitor (PPC) was constructed with dimensions of $50 * 50$ mm and 25 mm gap between the plates. The selected dimensions were based on a series of trial and errors which resulted in a more sensitive performance of the sensor with respect to the adulteration levels of milk. Larger dimensions (either larger area of plates or the gap between the plates) of the sensor showed poor sensitivity most likely because of insufficient power of the function generator to provide an effective penetration of electrical field through the milk in particular at higher frequencies. The plates were cut from 0.2 mm thick aluminum sheet and vertically installed on Plexiglas plates glued on a base plate. The total volume of the space between the plates was 62.5 cm^3. BNC (Bayonet Neill–Concelman) connectors were installed on the backside of the capacitor plates for connections to the function generator and spectrum analyzer. The capacitor was connected to a sweeper function generator with a frequency range of 0–150 MHz (Owon, AG 4151, Hong Kong) and a spectrum analyzer (GWInstek, GSP-827, Taiwan) through 75 Ω coaxial cables (Fig. 1a). Sinusoidal voltage was supplied by the generator at the frequencies of 0.03, 0.04, 0.05, 0.06, 0.1, 0.5, 1, 1.5, 2, 2.5, …, 150 MHz and the dielectric power was recorded by "EagleShot", the interfaced software of the spectrum analyzer. This measurement principle was termed dielectric power spectroscopy by Naderi-Boldaji et al. (2015) where a similar principle was applied for the non-destructive measurement of sugar concentration in sugarcane. This measurement technique suggests a simple and low cost instrumentation by a combination of a function generator and a spectrum analyzer (Mireei et al., 2016) while the independent measurement of dielectric constant and loss factor needs expensive equipment such as a network analyzer. The power of a capacitor can be calculated as (Mireei et al., 2016):

$$P = (8.85 \times 10^{-12})\pi\varepsilon_r V^2 f \frac{A}{D} \quad (1)$$

where P is the power (W), ε_r the complex dielectric permittivity, V the excitation voltage, f the excitation frequency and D the distance between the plates.

The relative permittivity of a biological material is a complex physical quantity whose real part, ε' indicates the fraction of energy stored in the material when subjected to an external elec-