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Milk authentication and discrimination via metal content clustering – A case of comparing milk from Malaysia and selected countries of the world

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ABSTRACT

Authenticity is an important issue nowadays as humans are concerned about the safety and quality of food they consume. In this regard, determining the geographical origin of milks using their elemental composition is of high importance. Therefore, we have studied the elemental composition of milk from various sources within a tropical region where there is no dramatic change in season. 24 essential and trace elements in 231 raw and factory cow milk samples were studied. Principal component analysis (PCA) and hierarchical cluster analysis (HCA) reveal that Malaysian milks are well separated from milk samples collected from selected countries based on their elemental compositions. However, it is noted that only 11 elements (Mg, Na, Ca, Ba, Cu, Fe, Zn, K, Se, Mo and Mn) are detected out of the 24 analyzed. Based on the observations from PCA. Between the detected elements, Ca, Na, Fe, Zn, Mn, K, Ba and Mg are observed to be the discriminating factors for the overall separation of Malaysian milk samples from milks of selected regions of the world. Toxic elements are not detected in any of the milk samples studied. NIST/Milk SRM 1849a-Infant/Adult nutritional formula, USDA was used to verify the accuracy of the methodology. Our study shows clear geographical origin clustering which map to the authenticity of milk and serve as a parameter for quality control of milk.

1. Introduction

Authenticity of food products has always been the attention of consumers and producers. Milk as one of the seven important and expensive food products is of concern (Moore, Spink, & Lipp, 2012) as it could be easily adulterated (de la Fuente & Juarez, 2005; Hrbek, Vaclavik, Elich, & Hajslova, 2014). Ascertaining the authenticity of milk is thus important, as it is a key source of nutrient in human health (Nagpal et al., 2012), providing the nutrients needed for a proper growth especially in bone mass formation. Milk in human diet also possibly plays an important role in preventing several chronic disorders such as obesity, diabetics, cancer and various cardiovascular diseases as suggested by several epidemiological studies (Pereira, 2014).

In milk, the amount of minerals is not constant and differs due to various aspects such as environmental condition, the animal's nutrition, stage of lactation and animal breed. The varying values reported for minerals in milk are mostly due to the above reasons and some could be from contamination due to milking and processing equipment or analytical errors (Caroli, Chessa, & Erhardt, 2009; Cashman, 2006; Kalač & Samková, 2010). The chemical form of trace elements and macronutrients present in milk is of importance since it might influence intestinal utilization and absorption (Cashman, 2002). Trace elements such as Zn, Mn, Co and Cr are of outmost importance for normal growth and metabolism (Joint et al., 2007; Stawarz, Formicki, & Massanyi, 2007). Metals are important in the physiological functions of animals and humans as they are essential cofactors of enzymes and thus any deficiencies may cause problems. The amount of metals in pure milk and dairy products is usually small but the content varies according to

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packing and manufacturing processes. There are metals such as Cd, Ni, Co and Cr, of which high levels of concentration might contaminate the environment and thus increase the possibility of these metals being transferred to milk and milk products, which often causes serious problems (Schuhmacher, Bosque, Domingo, & Corbella, 1991). Toxic metals and metalloids frequently enter the food chain from agricultural and industrial sources. Metal pollutants such as Cd and Pb which have toxic effects on human and animals enter the body of living beings via the food chain (Zheng et al., 2007). Toxicity of heavy metals on humans and animals is of concern because these metals have extensive industrial uses. The effect of some elements are cumulative, hence it is important to control their level in consumed foods. Consequently, it is of importance to measure and evaluate concentrations of essential and trace elements, including toxic metals in assessing the quality, authenticity and geographical origin of milk and dairy products during production and manufacturing (Feligini, Panelli, Sacchi, Ghitti, & Capelli, 2015; Khan et al., 2014; Osorio, Koidis, & Papademas, 2015; Rutkowska, Bialek, Adamska, & Zbikowska, 2015).

Different analytical methods together with chemometric tools have been used across the world to determine essential and trace elements in various food products (Barbosa et al., 2014; Borges, Gelinski, de Oliveira Souza, Barbosa Jr, & Batista, 2015; Reinholds, Bartkevics, Silvis, van Ruth, & Esslinger, 2015; Versari, Laurie, Ricci, Laghi, & Parpinello, 2014). Among the analytical methods used are inductively coupled plasma mass spectrometry (ICP-MS) (Batista et al., 2012; Chevallier, Chekri, Zinck, Guérin, & Noël, 2015; Kruzlicova, Fiket, & Kniewald, 2013; Ma et al., 2016) inductively coupled plasma optical emission spectrometry (ICP-OES) (Larrea-Marín, Pomares-Alfonso, Gómez-Juaristi, Sánchez-Muniz, & de la Rocha, 2010; Luis et al., 2015) as well as flame atomic absorption spectrometry (FAAS). For most cases, ICP-MS is used for analysis of elements in food (Chudzinska & Baralkiewicz, 2011; Tuzen, Sesli, & Soylak, 2007).

To the best of our knowledge, no information has been reported on essential and trace elements in raw cow milks in Malaysia as a representative of a tropical region compared to other regions in the world. This work is thus an attempt to study the differences and similarities of the concentrations of these elements in the tropical region of Malaysia and other selected areas of the world. Moreover, in recent year's detection of fraud and determination of authenticity of milk as raw material for all dairy products is of concern especially in confirming the traceability and labeling of the product. This is important to prevent consumers from toxic and harmful elements in milk such as residue of pesticides, antimicrobials, fertilizers, mycotoxins, heavy metals and other contaminants as a requirement for developed countries (Jooste, Anelich, & Motarjemi, 2014).

In this work, we used an environmentally friendly method in the microwave digestion process where very small volumes of nitric acid and hydrogen peroxide are used. The recoveries using this method are comparable to other methods, which use much higher volumes of nitric acid and hydrogen peroxide (Khan et al., 2014; Potortì, Di Bella, Lo Turco, Rando, & Dugo, 2013; Rahimi, 2013; Rey-Crespo, Miranda, & Lopez-Alonso, 2013).

2. Material and methods

2.1. Sampling

From Peninsular Malaysia a total of 52 raw cow milk samples were collected from farms in the northern region (Perlis, Kedah and Terengganu, Ipoh and Pinang) and the southern region of (Johor, Melaka, Selangor, and Pahang) as shown in Fig. 1a and b. The raw cow milk samples were collected early in the morning before milking time in three sampling periods of Nov–Dec, July–Aug and May–June. The milk samples were directly poured into polypropylene bottles, labeled properly and transferred to the lab in an icebox. Samples delivered to the lab were kept in a −20 °C freezer.

Seven raw cow milk samples were also collected from farms in the northern and southern regions of Iran. Factory milk samples consisted of, Malaysian (5 samples), New Zealand (1 sample) and Australian (1 sample) which were purchased from supermarkets in Malaysia. Factory milk samples from other regions of the world were also collected from supermarkets in Turkey (3 samples), Iran (3 samples), Azerbaijan (1 sample), Belgium (1 sample), Canada (1 sample) and U.S.A. (2 samples) upon any travel to those regions. Each of the samples was triplicated and analyzed. Fig. 1a shows the sampling sites of either raw or factory cow milk from the selected regions of the world using the JMP®, Version < *Pro 12.0.01* > SAS Institute Inc., Cary, NC, U.S.A, 2015 software and Fig. 1b shows the raw cow milk collection stations in Malaysia.

2.2. Sample preparation

Initially, the milk samples were freeze dried using Christ Freeze Dryer model ALPHA 1-2 LO Plus Germany. Prior to analyses, the samples were digested using Microwave-assisted digestion (MAD) device, CEM Mars-Xpress (CEM Corporation, Matthews, NC, USA). For this 0.10 g of freeze dried milk samples was weighed and poured in the microwave vessels then 2.0 mL of ultra-pure 60% nitric acid Merck Germany and 1.0 mL of ultra-pure 31% hydrogen peroxide Merck Germany were added and left for 10 min to stabilize the reaction. The program used for digestion was as follows first, the power was set to 300 W for 2 min, then, the power was raised to 600 W for 10 min, and finally, the power was set to 300 W for 5 min. After the digestion period, the content of vessels was transferred to polypropylene volumetric flask and diluted with ultrapure water which was prepared using water deionizer with a resistivity of more than 18 MΩ cm from PURELAB® UHQ II system (ELGA®, UK) was utilized to produce deionized water.

2.3. Sample analysis

ICP-MS 7500ce Agilent with an octopole reaction system (ORS) was employed in this research. An Octopole reaction system comprises of an octopole ion guide inside a pressurized reaction cell and can be operated in both collision and reaction mode for the removal of polyatomic spectral interferences that can reduce the polyatomic ion effects by chemical reaction. Argon gas used for the whole experiment was of spectral purity of (99.999%). Each day prior to the beginning of the experiment the instrument was tuned with 1 ppb Agilent tuning solution used for ICP-MS 7500cs of Li, Co, Y, Ce, Tl in 2% HNO3 and 0.5% HCL to cover the entire mass range and obtain high sensitivity. The setting of the instrument is reported in Table 1.

All calibration standards were made from the Agilent multi element environmental calibration standard consisting of 1000 mg L^{-1} (Ca, Fe, K, Mg, Na) and 10 mg L^{-1} (Ag, Al, As, Ba, Be, Cd, Co, Cr, Cu, Mn, Zn, Mo, Ni, Pb, Sb, Se, Th, Tl, U, V) in 5% HNO_3. All the standards were diluted using ultra-pure water and used for determining the concentration of elements in the digested milk samples.

For the liner calibration plot, five different calibration standards, which are 50, 100, 300, 1000, 5000 ng/mL, were used for Ca, Fe, K, Mg, Na, and 0.5, 1, 3, 10 and 50 ng/mL were used for the rest of the elements. In the calibration plots, the correlation coefficient varied from 0.998 to 1.000 depending on the element that shows good linearity in the range of the concentrations made. To overcome the polyatomic interferences, different isotopes of the required