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Investigation of macro, micro and toxic element concentrations of milk and fermented milks products by using an inductively coupled plasma optical emission spectrometer, to improve food safety in Turkey

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ABSTRACT

In this study, the quantification of macro, micro and toxic elements in milk and its products was carried out using inductively coupled plasma optical emission spectrometry (ICP-OES) after using sample preparation procedures (wet digestion, dry digestion, and microwave digestion). Samples were collected from farms and markets in Edirne, Turkey. Ca, Mg, Na, K, Cu, Fe, Mn, Zn, Al, and Ba concentrations in the farm milk and its products ranged from 823 to 1499, 109–476, 218–1498, 905–1694, 0.094–0.26, 2.0–3.7, 0.014–0.105, 1.2–5.2, 0.192–0.35 and 0.075–0.191 mg kg^{-1} respectively. The results in commercial milk and milk based products (minimum-maximum in mg·kg^{-1}) were: Ca 791–1518, Mg 107–518, Na 221–1594, K 901–1692, Cu 0.068–0.23, Fe 2.2–4, Mn 0.019–0.087, Zn 2–5, Al 0.124–0.40 and 0.080–0.197. Macro, micro and toxic element contents of the commercial milk and its products in this study generally were higher than that of the natural samples. However, a tolerable daily diet of these elements by the Trakya region is well below the Turkish Food Codex (TFC) levels of macro, micro and toxic elements.

1. Introduction

Milk, yoghourt, and other dairy products are largely consumed worldwide and economically important in many countries all over the world. The high nutrient density of the milk-based products supplies about 10% total energy and 15–25% dietary protein and fat intake [1]. It is common knowledge, that milk and dairy products are great sources of nutrients include proteins, vitamins (A, B6, B12, thiamine, riboflavin, niacin, folic acid, and pantothenic acid) and minerals (calcium, potassium, zinc, selenium, phosphorus, and magnesium) [2]. Milk proteins and minerals help in the growth of babies and children and reduce blood pressure. A large body of scientific research showed that the consumption of the milk and fermented dairy products to help improve immune function in the body, can reduce the risk of many diseases such as GI system diseases, cardiovascular system diseases, musculoskeletal diseases, urogenital system diseases, dermatology, immune system diseases, allergy, nervous system diseases, cognitive system diseases, weight control, obesity, aging, nutrigenomics of fermented dairy foods, dental health [3]. In addition, they have a strength bones, reduce risks of certain types of cancer, improve intestinal health, prevent the formation of kidney stones, enhance nutrient absorption and regulate body weight.

Minerals and vitamins are necessary for human life and play important roles in metabolic functions such as maintenance of pH, and bone health, osmotic pressure, nerve conductance, muscle contraction, energy production, and in almost all other aspects of life growth [1]. National Dairy Council provided mineral contents such as calcium, phosphorous, magnesium, iron, zinc, iodine, copper, manganese, selenium, chloride, potassium, and sodium levels in milk [4]. The most important mineral in milk and milk products is calcium. Institute of Medicine of the National Academics of Science indicates for calcium that 800 mg day^{-1} for 3–8 years old, 1300 mg day^{-1} for 9–17 years old, and 1200 mg day^{-1} for people over 50 years [5].

The composition of milk and dairy products is influenced by several factors such as animal, which taken, breeding, processing methods of the milk, the fermentation procedure of the dairy product, environmental factors, fortification processes, and storage. Fermentation and storage can effect both the macro-nutrient composition and micronutrient content in milk-based products [1].

Fermented dairy products produced by participating specific groups of microorganisms in milk-based products. As a result of the fermentation process, pH of the milk component's decrease, some milk proteins coagulated, and milk products undergo more nutritious and healthier

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[6,7,8]. Fermented dairy foods play a fundamental role in human nutrition. They are good sources of macro-nutrients (carbohydrates, fats, and proteins) and micronutrients (calcium, phosphorous, magnesium, and zinc) [9]. That's why the determination of macro-nutrients and micronutrients in these samples is often required in order to determine the quality of milk-based products [10].

The contamination in fermented milk product depends on several factors. They might come from physical contamination (metals, and/or glass pieces, wooden pieces, plastics and other physical materials introduced during the consumption of fermented milk products) or by chemical contamination from the natural toxic, metal ions, veterinary drug residues, residual detergents, pesticides, some food additives using in production of fermented milk products [11]. Trace levels of metals like copper, cadmium, and mercury is most likely found in traditional yoghourt [12]. Milk and fermented milk products contain more than twenty different elements. Elements like Cu, Zn, Mn, and Fe are an example of essential ones, and they are very significant for the normal metabolism, growth, and development. [12,13]. On the other hand, elements such as Pb, Cr, Hg, and Cd are very important because of their toxicity and metabolic roles [14,15]. Some elements are co-factors of many enzymes and play an important role in several physiological functions of humans and animals. Deficiency of these essential element causes disturbances and physiological conditions [12,16,17].

Atomic spectrometric techniques like flame and graphite furnace atomic absorption spectrometry (FAAS and GFAAS), high-resolution continuum source of atomic absorption spectrometry (HR-CS-AAS), as well as inductively coupled plasma emission and mass spectrometry (ICP-OES and ICP-MS) can be used element determinations in milk and milk-based products [9,10,12,14,18,19,20–24]. The determination of elements in milk and milk-based products is particularly difficult to perform directly because of their complex matrix; therefore, sample preparation is an important step in the whole analytical procedure. Different ~~detection~~ sample preparation processes have been used to date for this purpose, such as dry ashing, wet digestion, and microwave digestion [25].

The objectives of this study were: (1) to determination of the various major (Ca, K, Mg, Na), minor (Cu, Fe, Mn, Zn) and toxic (Al, Ba, Cd, Ni) elements in the raw cow milk and milk-based products (yoghourt, ayran, kefir), (2) to investigate the major, minor and toxic composition in commercial cow's milk and milk-based products, (3) to compare the mineral contents of raw and commercial cow' milk and dairy products, and (4) to evaluate the accuracy and precision of digestion procedures (microwave, dry, wet) and ICP-OES technique in cow milk and milk-based product samples.

2. Experimental

2.1. Instrumentation

The dry ashing was done using the Daihan Scientific muffle furnace (model FPX-12, Korea). Microwave MarsXpress closed vessel sample preparation system (CEM, Matthews, NC, and the USA) was used for decomposition of the samples and reference materials. An inductively coupled plasma optical emission spectrometry (ICP-OES), Varian Vista-MPX (Varian Inc., Victoria, Australia) was used to measure macro, micro, and heavy metal contents. The instrumental operating parameters were as follow: 1.3 kW of Rf power, 1.0 L min^{-1} of nebulizer gas flow, 15 L min^{-1} of plasma-Ar flow and 1.5 L min^{-1} of auxiliary gas flow. Wavelengths used for the elements were: aluminum (Al), 396.152 nm; barium (Ba), 455.403 nm; calcium (Ca), 317.933 nm; cadmium (Cd), 214.439 nm; copper (Cu), 327.395 nm; iron (Fe), 238.204 nm; potassium (K), 766.491 nm; magnesium (Mg), 279.553 nm; manganese (Mn), 257.610 nm; sodium (Na), 589.592 nm; nickel (Ni), 231.604 nm; zinc (Zn), 213.857 nm.

2.2. Reagents and standards

All chemicals were of analytical-grade. The high-quality deionized water (18 MΩ cm^{-1} resistivity) was obtained by using an ELGA Elgastat Maxima system. Hydrochloric acid (37% w/w), hydrogen peroxide (35% w/w), perchloric acid (70–72% w/w) (Merck, Darmstadt, Germany) and nitric acid (65% w/w) (Sigma-Aldrich, Steinheim, Germany) were also used for digestion and diluting the samples. Standard stock solutions containing 1000 mg L^{-1} of Ca, Mg, Na, K and 100 mg L^{-1} of multi-element calibration standard (Al, B, Ba, Be, Bi, Ca, Cd, Co, Cr, Cu, Fe, Ga, K, Li, Mg, Mn, Na, Ni, Pb, Se, Sr, Te, Tl, Zn) were supplied from the Merck (Darmstadt, Germany). The stock solution and working standards were diluted in HNO_3 (in 0.5%). For the linear calibration plot five different calibration standards, which are 75, 100, 150, 200, 300 mg L^{-1} were used for Ca, K, Mg, 25, 40 50, 75, 100 mg L^{-1} for used for Na and 0.04, 0.10, 0.30, 0.60 and 1.25 mg L^{-1} were used for the rest of the elements. Good linearity was obtained ($r^2 > 0.98–0.99$) for all elements within specified concentration ranges. The accuracy and precision of the study were determined using certified reference material (CRM): National Research Centre for Certified Reference Materials (China) milk powder NCS ZC73015.

2.3. Collection and pre-treatment sample

Sample collection is very important in the experiment. Therefore, sample collection section consisted of two groups: natural samples and commercial collecting samples.

2.3.1. Commercial sample collection

Commercial cow's milk and fermented cow's milk product such as yoghourt, ayran, and kefir samples used for the experiments were collected randomly from local markets in the city of Edirne, Turkey. The number of samples depended on the number of brands available in the market. It consisted ten dairy yoghourt, ayran, milk and nine kefir. In each category, the samples belonged with different brands, purchased in triplicate. The brand name of the commercial yogurts was labeled cy1, cy2, cy3, cy4 etc. The commercial kefir, ayran and milk samples analyzed were similarly labeled such as ck1, ca1, and cm1 respectively. Commercial samples were kept in their original packages. All samples were stored at −18 °C in deep freeze prior to analysis.

2.3.2. Natural sample collection

Cow's milk was collected at different times from a small farm in Edirne. They were labeled hm1, hm2, etc. Samples have been stored in polyethylene containers. Collected milk samples were used for manufacturing of the following fermented dairy product such as yoghourt, ayran, and kefir.

Natural yoghourt product manufacturing: Milk was about heated 80–85 °C for 30 min or 95 °C for 10 min. The important point for the manufacturing of the yoghourt was the milk temperature. Therefore, milk was cooled to 42–45 °C. This temperature was the ideal growth in temperature in the starter culture. A small amount of existing yoghourt with live bacteria was added to lukewarm milk by using a wooden spoon and stirred gently to distribute. After inoculation, milk was poured into a glass container which was covered with clothes and kept warm for approximately 4–5 h. When the fermentation was finished, the yoghourt was stored at +4 °C until analyzed. The preparations of natural (homemade) yogurts analyzed were carried out triplicate and labeled such as ny1, ny2, ny3, etc.

Natural ayran product manufacturing: Natural ayran samples were made in the laboratory using traditional methods for domestic production. Yoghourt samples (natural) and water was mixed at 1.8:1 (w/v) and then blending of ayran samples was performed by using a shaker. Ten batches of ayran were performed from the same yoghourt. Home-prepared ayran samples were kept at 4 °C until analysis and labeled such as ha1, ha2, ha3, etc.

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