Determination of Heavy Metals (Pb, Cd) and some Trace Elements in Milk and Milk Products Collected from Najran Region in K.S.A.

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Abstract: Milk and milk products are a very important human nutrient since their consumption has increased in recent years. Good quality measurements are essential to control and maintain milkand its products and processes quality, both in manufacturing trade and in research. The presence of toxic elements in milk and its products may create significant health problems for people. The aim of this paper was to determine the content of toxic and trace elements in different milk and milk products samples, sold in major supermarkets chains in Najran..Inductively coupled plasma atomic emission spectrometry (ICP-AES) was used for the quantitative determination of elements in this matrix .Analysis were performed after the chemical mineralization of the samples with nitrogen acid.
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Keywords: Milk, Milk products, ICP-AES, heavy and trace elements.

1. Introduction:

Milk is an excellent source of most essential minerals for human. It contains mostly calcium, phosphorus and constitutes the most important source of bio available calcium in our diet **(ICAR,1981)** .Milk and dairy products are part of a healthy diet .So ,it is necessary that milk should be obtained from healthy animals as well as collected and stored in satisfactory healthy conditions free from environmental contamination .That is to be all containers applied for packaging milk at milking ,at the collection or to store must be made of stainless steel, aluminum or iron foliated in perfect finishing and seamless.

Milk and milk products are the most diversified of the natural foodstuffs in terms of composition contain more than twenty different trace elements most of them are essential and very important such as copper, zinc, manganese and iron **(Pennington *et al.,* 1995)**.These metals are co-factors in many enzymes and play an important role in many physiological function and lack of these metals cause disturbances and pathological conditions **(Schuhmacher*et al.,* 1991)**.

Ingestion of contaminated feeding stuffs and water was considered the main sources of metal residues in secreted milk where they pass into the milk **(Antonion*et al.,* 1989; Rossipal*et al.,* 2000 and Frodello*et al.,* 2002)**. The amount of metals in contaminated milk is admittedly minute, but their contents may be significantly altered through manufacturing and packaging process where metal contamination may occur at several stages during dairy processing e.g. from factory door, plant equipment's, catering operations, ceramic, enameled utensils, metal containers and water used in dairy production**(Reilly,1991).**

The presence of heavy metals as cadmium and lead even in low concentrations, leads to metabolic disorders with extremely serious consequences and causing serious problems as it causes many health problems such as weakness, heart failure , cancer and also affects the kidneys **(McCally,2002 and Licata *et al.,* 2004).** The hazards of metals to humans from consumption of contaminated foods depend on the relative levels of the metal and its speciation **(Robert, 1996).**

For carrying out these determinations through using different techniques; flame atomic absorption spectrometry **(Kondyli*et al.,* 2007; Pohl and Prusisz, 2007),** capillary zone electrophoresis **(Suarez-Luque*et al.*,2007),** inductively coupled argon plasma emission spectroscopy **(Park, 2000)**, different pulse anodic stripping voltammetry technique **(Tripathi*et al.*,1999)**, inductively coupled plasma optical emission spectrometry **(ira and Maihara, 2007)** ,flow injection spectrometric methods **(Nogueira*et al.,* 1998),** atomic fluorescence spectrometry **(Cava *et al.*,2004)**, atomic absorption spectrometer **(Abolfazl*et al.*,2012)** and stripping potentiometer **(Munoz and Palmero, 2004).**

Owing to serious health risks, the levels of heavy metals (Cd, Pb) and trace elements (Cu, Zn, Fe, Ni, Co and Cr) were determined in canned milk and milk products of different types spread in Najran markets.

2. Material and Methods:

2.1 Reagents and solutions:

All reagents used were of analytical reagent grad (Merck). Deionized water was used for the preparation of all solution.

The working standard solutions were prepared by diluting the stock solutions (1000 mg/l) in 10% hydrochloric acid. All working standard solutions were stored in polypropylene bottles.

The nitric acid (65%) and hydrogen peroxide solutions used were of ultrapure grade, purchased from Merck.

All glassware was initially washed with detergent and water, and then the glassware was rinsed several times with deionized water and dried.

2.2 Sample preparation:

Milk and milk products from different producers were the samples analyzed in this study and they purchased in local markets in the Najran city in KSA.

A know volume of milk and its products (5 gram) was evaporated to near dryness, wet- ashed (Crosby ,1977) and taken up in 50 ml of 0.1N HCL.

2.3 Sample analysis:

A Spectroflame P (Spectro Company, Germany) ICP-AES instrument was used. After scanning a blank, a standard solution and a sample solution in the programmed wavelength range, the background correction wavelengths were selected manually at appropriate background positions for each analytic peak. Instrument configuration and general experimental conditions are summarized in (Table 1). For each sample three determinations were performed and average results were reported. Detection limits of the elements studied in milk and its products samples (Table 2) were determined from the standard addition curves of each element in different samples. It was based on the usual definition as the concentration of analyte yielding a signal equivalent to three times the standard deviation of the blank signal. The detection limits of the method are good and permit the determination of the elements in milk and its products at background concentrations

3. Results:

The sampling data (Tables 3.4) were analyzed for pb, cd, cr, cu, zn, Ni, Coand Fe .The results of the mineral analysis of milk and milk products samples are given in (Tables 5.6). The pb content level in canned milk and milk products depends on the method used to seal the cans. Contrary to this is the use of welded or lacquered cans with low lead content (Dobrzanski***et al.,*** 2005).Lead is toxic to the blood, nervous, urinary, gastric and genital systems (Fox, 1987 andZraly ***et al.,*** 2007). Furthermore, it is also implicated in causing carcinogenesis (Enb,2009).The concentrations oflead in milk samples (Evaporated and powder) were ranged from(0.01 to 0.02 mg/kg) within permissible range. But in milk products were ranged from (0.01 to 0.2 mg/kg).The highest pb concentrations were detected in canned cream (Green-Farm andAl-Tag cream) followed by canned cheese. Labneh samples were containing lead in permissible limit (WHO/FAO 1996).

In all milk and its products samples were contain cadmium in amount less than authorized limit 0.01mg/kg by (WHO/FAO 1996),except in Luna evaporated milk, concentration of cadmium was higher (0.03 mg/ kg). Regular absorption of cd causes damage to the proximal renal tubules and calcium, phosphorous, glucose, amino acid and small peptides are lost in the urine. Once cd accumulates in tissues it cannot be removed safely by chelation therapy without causing kidney damage (Fox,1987).Cadmium affects calcium metabolism and skeletal changes resulting from calcium loss and ends in a decrease bone mineral density (Nordberg,2004).

In fact, Cu and Zn have numerous functions in the human body and they are essential elements for human health. Cu serves as antioxidant and helps the body to remove free radicals and prevent cell structure damage and Zn function as a cofactor for many enzymes of the body. The highest concentration of Cu in all cheese samples ranged from (0.56 to 1.78 mg/ kg) followed by powdered milk samples (0.16 to 0.42 mg/kg) and Labneh samples (0.17 to 0.38 mg/kg). Evaporated milk and cream samples showed smallest values ranged from (0.11 to 0.22 mg/kg). Iron is vital components of blood hemoglobin required for oxygen transportation, enzyme systems and is necessary for red blood cell formation, function and brain function (WHO/FAO, 1996). Iron contents in Nido powdered milk showed highest level (1.13 mg/ kg) comparison to all analyzed samples. The trace minerals contents (Co, Ni and Cr) of the commercial samples under analysis generally were lower than the contents of essential elements (Cu, Zn and Fe).

Table 1. ICP-AES operating conditions

Operating condition	
RF frequency	27.12 Hz
Power RF	2.5 Kw
Outer gas flow rate	Ar 17 L/min
Carrier gas flow rate	Ar 1L/min
Intermediate gas flow rate	Ar 1L/min
Observation height	18mm above work coil
Plasma's temperature	8000-9000K

Table 2. Detection limits for ICP-AES method

Element	Detection limit (ng/g)	Element	Detection limit (ng/g)
Cd	0.63	Fe	0.5
Co	0.92	Pb	7.03
Cr	1.87	Zn	4.0
Cu	0.90	Ni	1.03

Table 3 Milk samples

Samples	Production date	Expire date	Production country
Evaporated milk			
Almarai	11-6-2012	12-6-2013	Almarai Company K.S.A.
Al-Taie	6-1-2012	7-1-2013	Al-NafeaTradingCo.Holland.
Rainbow	20-5-2012	21-5-2013	Holland.
Bonney	26-5-2012	25-5-2013	Germany.
Luna	8-6-2012	8-5-2013	National Food Industries L.T.D Jeddah K.S.A.
Powdered milk			
Luna	16-6-2012	29-11-2013	National Food Industries L.T.D Jeddah K.S.A.
Rainbow	10-11-2011	22-4-2013	Friesland CompanyHolland.
Nido(Nestle)	20-5-2012	19-11-2013	Nestla Company-U.A.E
Velor(Goody)	22-3-2012	28-9-2013	Newzeeland (Malaysia)
Anchor	23-4-2012	7-10-2013	Newzeeland K.S.A.
Evaporated milk			
Almarai	11-6-2012	12-6-2013	Almarai Company K.S.A
Al-Taie	6-1-2012	7-1-2013	Al-NafeaTradingCo. Holland.
Rainbow	20-5-2012	21-5-2013	Hollanda.
Bonney	26-5-2012	25-5-2013	Germany.
Luna	8-6-2012	8-5-2013	National Food Industries L.T.D Jeddah K.S.A.
Powdered milk			
Luna	16-6-2012	29-11-2013	National Food Industries L.T.D Jeddah K.S.A.
Rainbow	10-11-2011	22-4-2013	Friesland CompanyHolland.
Nido(Nestle)	20-5-2012	19-11-2013	Nestla Company-U.A.E.
Velor(Goody)	22-3-2012	28-9-2013	Newzeeland (Malaysia)
Anchor	23-4-2012	7-10-2013	Newzeeland K.S.A.

Table 4 Milk products

Samples	Production date	Expire date	Production country
Cream			
Almarai	27-8-2012	25-2-2014	AlmaraiCompany K.S.A.
Al-Tag	8-5-2012	10-11-2013	U.E.for El-NasharCo.Jeddah
Green Farms	14-7-2012	26-12-2013	Alesayi Marketing Co L.T.D.
Saudia	2-6-2012	5-12-2013	U.E.forSadafcoCo.K.S.A.
Luna	7-4-2012	1-9-2013	National Food Industries L.T.D Jeddah K.S.A
Cheese			
Kraft	21-6-2012	13-12-2012	Kraft Food Bahrain.
President	25-4-2012	28-4-2013	United Food Industries Corp.K.S.A.
Bega	1-11-2011	1-1-2013	Bega cheese L.T.D. Australia
Almarai	8-10-20111	7-10-2012	Almarai Company K.S.A.
Labena			
Ulker	6-6-2012	4-12-2012	Turkey
Kiri	3-3-2012	28-9-2012	Poland for Fromageries Bed-pariscedex-France
Forsana	15-7-2012	7-1-2013	Prod. By Forsana Foods Factories in K.S.A.
Almarai	23-9-2012	7-10-2013	Almarai Company K.S.A.
Alsafi	13-7-2012	8-1-2013	Turkey for Al-safiDanon Co. L.T.D.K.S.A.

Table 5: Concentrations of heavy and trace elements in different milk samples (mg/kg)

Sample	Minerals concentration in Powdered milk (mg/kg)							
	Cd	CO	Cr	Cu	Fe	Pb	Zn	Ni
Luna	0.004	0.001	0.009	0.12	0.06	0.02	3.47	0.07
Rainbow	0.003	0.001	0.011	0.42	0.08	0.07	3.67	0.01
Nido	0.004	0.002	0.016	0.19	1.13	0.02	6.48	0.07
Velor	0.003	0.002	0.012	0.16	0.06	0.02	2.81	0.01

Anchor	0.004	0.003	0.019	0.24	0.25	0.02	3.14	0.02
Minerals concentration in Evaporated milk (mg/kg)								
Almarai	0.002	0.004	0.004	0.11	0.05	0.02	1.36	0.007
Al-Taie	0.002	0.0002	0.004	0.16	0.12	0.02	1.18	0.031
Rainbow	0.003	0.002	0.003	0.22	0.08	0.01	1.29	0.008
Bonney	0.002	0.0004	0.003	0.12	0.07	0.01	1.13	0.005
Luna	0.029	0.003	0.035	0.20	0.08	0.02	1.98	0.025

Table 6: Concentrations of heavy and trace elements in different milk products samples (mg/kg)

Sample	Minerals concentration in Cream (mg/kg)							
	Cd	CO	Cr	Cu	Fe	Pb	Zn	Ni
Almarai	0.011	0.0003	0.006	0.12	0.04	0.03	1.57	0.009
Al-Tag	0.003	0.0005	0.007	0.17	0.12	0.20	1.68	0.006
Green-Farm	0.002	0.0004	0.003	0.12	0.04	0.10	0.39	0.002
Saudi	0.005	0.0006	0.003	0.11	0.05	0.01	0.48	0.003
Luna	0.001	0.0002	0.003	0.14	0.07	0.01	0.35	0.003
Minerals concentration in Cheese (mg/kg)								
Krart	0.007	0.003	0.027	1.78	0.10	0.06	2.71	0.017
President	0.003	0.002	0.023	0.56	0.06	0.04	2.90	0.010
Bega	0.004	0.004	0.025	0.79	0.28	0.06	3.12	0.025
Almarai	0.005	0.003	0.032	0.89	0.10	0.04	2.98	0.018
Minerals concentration in Labneh (mg/kg)								
Ulker	0.003	0.002	0.004	0.31	0.03	0.02	0.73	0.07
Kiri	0.004	0.001	0.015	0.38	0.07	0.02	0.97	0.01
Forsana	0.004	0.002	0.004	0.17	0.02	0.02	0.15	0.01
Almarai	0.002	0.0001	0.003	0.21	0.03	0.01	0.78	0.003
Alsafi	0.005	0.001	0.005	0.29	0.03	0.02	0.77	0.01

4. Discussion:

The dry ashingprocedure (**ItodoU.A.and ItodoU.H, 2010)** has proved to be precise and accurate sample preparation procedure for multi-element determination of Pb, Cd, Cu, Zn, Fe, Ni, Co and, Cr in milk and milk products samples.

The results of this study showed that the studied canned cream (Green-Farm and Al-Tag) and cheese samples contained lead in concentrations over permissible limit. On other hand only Luna evaporated milk showed high level of Cd content. Cheese samples were rich in Cu content followed by powdered milk and Labenh samples, lowest levels were detected in evaporated milk and cream samples. Nido powdered milk contains higher concentration of Iron; other minerals were present in smallest concentration regard to mentioned before.

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