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Determination of Trace Elements in Cow's Milk in Saudi Arabia

S.M. FARID, M.A.ENANI and S.A. WAJID
Nuclear Engineering Department, King Abdulaziz University, Jeddah, Saudi Arabia
manani@kaau.edu.sa

ABSTRACT. Milk and its products are very common in our food list due to its nutrient value, since it is a source of some vitamins and a lot of mineral constituents which are necessary for proper development and functioning of different tissues and organs. However, overdose of these vitamins and mineral constituents can be harmful. This study was directed to measure the concentrations of Zinc (Zn), Cadmium (Cd), Chromium (Cr), Copper (Cu) and Lead (Pb) in cow's milk samples available commercially in Saudi Arabia using Graphite Furnace Atomic Absorption Spectrometer. Two types of milk samples were analyzed. These were - fresh cow's milk and liquid milk prepared from cow's milk powder. The mean elemental concentration values in ppb of Cr, Cu, Zn, Cd, and Pb in fresh cow's milk were : (31.4 ± 0.4), (48.9 ± 0.6), (944.9 ± 2.4), (4.7 ± 0.2) and (3.5 ± 0.2) respectively. Those in cow's milk powder were : (20.6 ± 0.8), (36.9 ± 1.1), (956.8 ± 3.2), (3.1 ± 0.3), and (2.2 ± 0.2) respectively. These values are compared with Recommended Dietary Allowance (RDA) values and also with the corresponding values of different countries available in the literature.

KEYWORDS: atomic absorption spectrometer; cadmium; chromium; copper; lead; zinc; cow's milk

1. Introduction

Elements are essential micro-nutrients and have a variety of biochemical functions in all living organisms. Some of them form an integral part of several enzymes [1, 2]. Although they are essential, they can be toxic when taken in excess; both toxicity and necessity vary from element to element and from species to species [2]. Thus, information on the intake of heavy metals through food chain is important in assessing risk to human health.

Increasing environmental pollution has given rise to concern on the intake of heavy metals in humans. These metals enter the human body mainly by two routes namely : inhalation and ingestion. The intake of heavy metals through ingestion depends on the food habit [2]. Milk and dairy products make an important contribution to the supply of nutrients for the human diet. The ash of cow's milk contains some major elements such as calcium, phosphorus and magnesium, in addition to potassium, sodium and chlorine and a wide range of trace elements including zinc, copper, iron, manganese and iodine. Thus cow 's milk is an important source of protein, minerals and vitamins in the human diet [3, 4].

The aim of the present study is to determine the concentrations of some trace elements, namely Zinc (Zn), Cadmium (Cd), Chromium (Cr), Copper (Cu) and Lead (Pb) in cow's milk available in markets of Saudi Arabia. The studied milk samples were fresh cow's milk and liquid milk prepared from cow 's milk powder available in Saudi market. A total of 155 samples were analyzed after" Wet digestion" for five trace elements using Graphite Furnace Atomic Absorption Spectrometer (AAS). The obtained mean elemental concentrations were compared with the corresponding values of different countries available in the literature. The daily intake of these elements are also compared with the Recommended Dietary Allowance (RDA) values set by different international organizations.

2. Experimental Procedure

2.1 Collection of milk samples

For the present study, the commercially available fresh cow's milk samples and liquid milk prepared from cow's milk powder were collected from different supermarkets in Jeddah, Makkah, Medina and Gassim cities. One sample was collected from King Saud University at Riyadh. An amount of 1 liter of milk in a paper cartoon was collected for each sample. The milk samples of different brands analyzed in the present study are listed in Tables 1 and 2.

2.2 Reagents and Glasswares

Atomic absorption spectroscopic standard solutions for Zn, Cd, Cr, Cu, and Pb were purchased from Fisher Scientific Company, USA. Working standard solutions were prepared by diluting the stock solution. Sulfuric acid, perchloric acid and nitric acid were all of AR quality (BDH, England). All glass wares (conical flask, volumetric flask, watch glass, pipette, measuring cylinder, etc.) were of borocylicate (England). De-ionized water has been used when required.

Table 1: Elemental concentration in fresh cow's milk in Saudi Arabia

Type of Milk	Brand name	Concentration (µg / kg)				
		Chromium	Copper	Zinc	Cadmium	Lead
Fresh Cow's Milk	Al-Safi	30.2 ± 1.3	51.1 ± 2.0	599.2 ± 6.7	1.0 ± 0.0	1.1± 0.1
	Al-Marai	22.0 ± 0.8	53.0 ± 1.9	352.3 ± 5.2	2.0 ± 0.2	1.1 ± 0.2
	Al-Hanah	12.1 ± 0.9	53.1 ± 2.1	1115.1 ± 8.6	4.1 ± 0.5	3.2 ± 0.4
	KAAU	58.6 ± 1.8	43.1± 1.7	1144.3 ± 8.9	2.0 ± 0.4	1.0 ± 0.0
	KSU	24.2 ± 1.3	27.2 ± 1.	1180.0 ± 9.2	5.1 ± 0.6	1.0 ± 0.1
	Gassim (Gassim area)	14.1 ± 1.0	41.0 ± 1.6	990.2 ± 7.3	5.1 ± 0.8	5.2 ± 1.0
	Gassim (Burayda area)	30.3 ± 1.2	80.1 ± 2.7	1235.2 ± 9.3	1.0 ± 0.4	4.3 ± 0.9
	Najayah	18.3 ± 1.1	37.0 ±.3	1046.3 ± 8.5	18.2 ± 1.3	5.2 ± 1.2
	Nadec	28.4 ± 1.3	23.1 ±1.0	623.2 ± 5.8	7.2 ± 0.7	0.0
	Tabiah	48.6 ± 1.7	42.0 ±1.4	908.4 ± 6.1	2.0 ± 0.3	1.0 ± 0.2
	Assafwa	58.6 ± 1.9	88.1 ±3.1	1200.1 ± 9.8	4.1 ± 0.6	15.2 ±.6
Mean		31.4 ± 0.4	48.9 ± 0.6	944.9 ± 2.4	4.7 ± 0.2	3.5 ± 0.2

Table 2: Elemental concentration in liquid milk prepared from cow's milk powder in Saudi Arabia.

Type of milk	Brand name	Concentration (µg / kg)				
		Chromium	Copper	Zinc	Cadmium	Lead
Liquid milk prepared from cow's milk powder	Al-Rabie	6.2 ± 1.1	35.0 ± 2.2	978.2 ± 7.4	12.3 ± 1.9	1.0 ± 0.0
	Saudia	24.4 ± 2.0	20.1± 2.1	891.3± 7.1	1.1± 0.1	1.1± 0.1
	Cortina	30.1± 2.0	38.0± 3.1	482.0± 6.1	1.0± 0.0	1.2± 0.1
	Jamjoom	34.6± 2.4	24.2± 2.0	1078.1±8.7	1.0± 0.0	1.0± 0.0
	Danya	17.0± 1.7	29.1± 2.4	1111.3±8.9	1.1± 0.2	5.4± 1.0
	Noor	11.1± 1.6	75.3± 3.8	1200.4±9.3	2.2± 0.6	3.2± 0.5
Mean		20.6± 0.8	36.9± 1.1	956.8± 3.2	3.1± 0.3	2.2± 0.2

2.3 Sample Digestion and Preparation of Analyte Solution for AAS

The milk sample needs to be brought into clear solution for analysis by the Atomic Absorption Spectrometer. For this reason the milk sample was first digested with chemicals where the organic matrix of milk was destroyed and left the element into a clear solution. " Wet Digestion" method (i.e. digestion with nitric, sulfuric and perchloric acids) has been used in the present study. The detailed procedure is available in the papers [5 - 8].

2.4 Calibration Curve

The VARIAN Atomic Absorption Spectrometer (AAS), Model Spectra AA 30 P consisting of a double beam, four lamp Turrent Spectrometer with a Deuterium background corrector and a temperature programmable Graphite Tube Furnace Assembly (GTA 96) was used in this study. Temperature program of the furnace was optimized to obtain the best signal during the atomization process. The drying time and ashing temperature for each element was determined earlier. All these data were fed into the computer associated with the AAS machine. The range of linearity of the concentration vs. absorbance curve is of great importance in determining the elemental concentration of the milk samples. Standard aqueous solutions of different elements obtained from Fisher Scientific Company, USA were used to calibrate the AAS machine.

The calibration curves were drawn for Zn, Cd, Cr, Cu, and Pb by Macintosh Microcomputer using linear regression analysis of the concentrations of the standard solutions versus absorbance values. A new calibration curve was plotted for each element every time a new batch of milk samples was arranged for analysis. Each standard solution was measured at least three times and the mean was plotted.

The sensitivity of the AAS machine was tested by using 10 ppb standard Lead (Pb) solution. The mean absorbance value of several measurements was found to agree well with the manufacturer' s stated value with a relative standard deviation (RSD) of 1.6 %.

2.5 Measurement of elemental concentration in milk samples

Ten µl aliquot of milk samples, obtained after wet digestion, was injected into the graphite tube of the AAS with the help of an auto-sampler, and the elemental concentration was read from the output of the printer connected to the computer. Each sample was repeated three times for each element. At least three milk samples of each brand collected at different times of the year were analyzed for each element. The concentrations of Zn, Cd, Cr, Cu and Pb were determined for each sample. A total of 155 milk samples were analyzed in the present study.

3. Results and Discussions

The range of linearity of concentration vs. absorbance curve is of great importance in determining the elemental concentration of the milk samples. The calibration curves for Chromium (Cr) and Copper (Cu) are shown in Fig. 1 (a)

and (b) respectively. Similar curves were also drawn for Zn, Cd, and Pb but they are not shown here. The calibration curves obtained for Zn, Cd, and Pb were fairly linear.

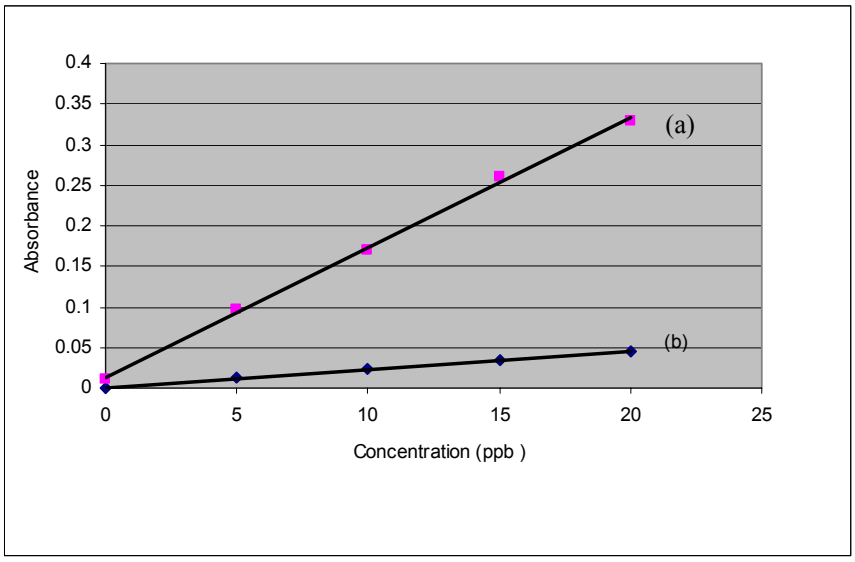

Fig. 1 Concentration versus absorbance curves for (a) chromium and (b) copper.

The results of the present study for five trace elements in milk samples collected from different areas in Saudi Arabia are given in Tables 1 and 2. The elemental concentrations in fresh cow's milk samples are presented in Table 1, while the concentrations in liquid milk prepared from cow's milk powder are given in Table 2.

In fresh cow's milk, the mean concentration of Zn is the highest (44.9 ± 2.4) ppb followed by Cu (48.9 ± 0.6) ppb, Cr (31.4 ± 0.4) ppb, Cd (4.7 ± 0.2) ppb and the last Pb (3.5 ± 0.2) ppb. The same trend is also observed for liquid milk prepared from cow's milk powder. The distribution of concentrations of five trace elements in both milk samples are shown in Fig. 2. The elemental concentrations in fresh cow's milk are higher than the corresponding values in liquid milk prepared from cow's milk powder except for Zn concentration. The Zn concentration is higher in liquid milk prepared from milk powder than in fresh milk.

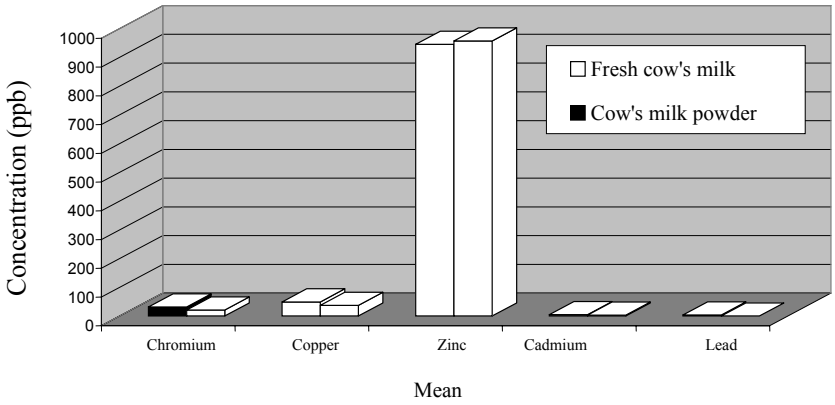

Fig. 2. Distribution of concentration of five trace elements in fresh cow's milk and in liquid milk prepared from cow's milk powder

There is wide variations in the published data for the elemental concentrations of cow's milk of different countries [2, 6, 9 -18]. Some of the results are recorded in Table 3 for comparison with the present values. The Cr and Cu concentrations of the present study are well comparable with the published data. But the present value of Zn concentration is the lowest compared with the corresponding values of other countries. This shows that the cow's milk in Saudi Arabia is a poor source of Zinc. The cow's milk in Saudi Arabia is also a poor source of Cd and Pb.

Table 3 : Comparison of the elemental concentrations of fresh cow's milk in Saudi Arabia with the published values

Country	Concentration (μg / kg)					Reference
	Cr	Cu	Zn	Cd	Pb	
Japan	--------	100.0	3000.0	1.0	50.0	[17]
Germany	--------	49.9	3730.0	0.1	5.5	[11]
India	55.2	56.0	3100.0	0.1	1.6	[2,18]
Spain	33.9	9.7	1419.3	----	49.3	[15]
Poland	38.0	90.0	3770.0	15.0	20.0	[14]
USA	29.1	19.4	2235.2	9.7	34.0	[9, 12]
Bangladesh	------	97.2	1214.8	-----	------	[12]
Saudi Arabia	31.4	48.9	944.9	4.7	3.5	Present study

The daily intake of the metals depends on both the concentration and the amount of food consumed. The daily dietary intake of milk for an average Mumbai (India) population is 113 g [2, 18]. The reported values of daily milk consumption in USA and Spain are respectively 224 g and 124 g [9, 15].

Table 4: Comparison of daily intakes of metals from 124 g of milk by Saudi population with the recommended values from all food intake.

Elemental Concentration (μ g / day)	Fresh cow's milk	Cow's milk powder	Recommended / Permissible value (μ g / day)
Chromium	3.8	2.5	50 - 200
Copper	5.9	4.4	2000 - 3000
Zinc	113.9	115.3	12000 - 15000
Cadmium	0.6	0.4	57 - 72
Lead	0.4	0.3	429

Table 5 : Percentage of recommended/permissible dietary allowances per 124 g of cow's milk .

Elements	USA	Spain	India	Saudi Arabia
Chromium	7. 2	8.4	13.7	7.6
Copper	0.3	0.1	0.3	0.3
Zinc	2.3	1.5	3.2	0.9
Cadmium	2.1	----	0.1	1.0
Lead	0.9	1.4	0.1	0.1

Assuming a value of 124 g / day for milk consumption in Saudi Arabia, the daily intake of these metals are determined and are depicted in Table 4. The last column shows the Recommended Dietary Allowance (RDA) as set by different international organizations [2, 19 - 22]. Percentage of Recommended Dietary Allowance per 124 g of cow's milk for different countries are presented in Table 5. The present values of Cr and Cu of cow's milk are well comparable with the values for some other countries. But the cow's milk in Saudi Arabia are poor sources of Zn, Cd, and Pb supplying less than 1% of the estimated RDA in a 124 g serving.

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قياس كمية بعض المواد ضئيلة الوجود في حليب البقر المتواجد في أسواق المملكة العربية السعودية

سيد محمد فريد، محمد عبدالصمد عناني ، سبحان عبدالواجد

قسم الهندسة النووية، كلية الهندسة، جامعة الملك عبد العزيز جدة، المملكة العربية السعودية

المستخلص: يُعتبر الحليب ومشتقاته من أكثر المواد الغذائية تواجدًا في أطعمتنا وذلك لأهمية القيمة الغذائية المتواجدة فيها. إن العناصر الموجودة في الحليب ومشتقاته تلعب دورًا هامًا في نمو جسم الإنسان وصحته بصفة عامة. إن الزيادة أو النقصان لبعض العناصر المتواجدة في الحليب بكميات ضئيلة تؤدي إلى ظهور بعض الأعراض الجانبية. في هذا البحث تم قياس تركيز بعضًا من هذه العناصر المتواجدة في حليب البقر بكميات ضئيلة مثل الكروم، النحاس، الزنك، الكادميوم، الرصاص، وذلك باستخدام جهاز مطايف الامتصاص الذري المتواجد بقسم الهندسة النووية وقد تمت هذه القياسات على عينات مختلفة من حليب البقر المتواجد في المملكة العربية السعودية. هذه العينات تمثلت في حليب الأبقار الطازج وحليب الأبقار المعد من مسحوق حليب البقر المجفف. لقد تم تحليل العينات التي جمعت من مناطق مختلفة في المملكة العربية السعودية وكان متوسط تركيز الكروم، النحاس، الزنك، الكادميوم والرصاص (بوحدة الجزء من كل بليون جزء) في عينات

حليب البقر الطازج كما يلي : ٣١,٤ ± ٠,٤، ٤٨,٩±٠,٦، ٩٤٤,٩±٢,٤, ٤,٧±٠,٢، ٣,٥±٠,٣ . بينما كان متوسط تركيز تلك المواد المذكورة آنفا (حسب الترتيب) في عينات الحليب المعد من مسحوق حليب الأبقار هو: ٢٠,٦±٠,٨, ٣٦,٩±١,١, ٩٥٦,٨±٣,٢, ٣,١±٠,٣ ، ٢,٢±٠,٢ جزء من بليون جزء. هذه النتائج قورنت بالكميات التي ينصح بأخذها في غذاء الفرد اليومي من قِبَل بعض منظمات الصحة وكذلك بتركيز تلك العناصر في الحليب المتواجد في البلدان الأخرى والمبينة في طيات هذا البحث.