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Determination of Micro Minerals in Milk from Farm and Pasture-Reared Cow, Goat and Camel; using Inductively Coupled Plasma-Optical Emission Spectrometry

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ABSTRACT

This study covers raw fresh milk of cow, goat and camel (farm and pasture-reared), in addition to two brands of commercial milk samples, liquid milk of powder origin and drinking yoghurt samples. Camel milk showed a relatively lower pH range (6.15 - 6.46) compared cow, goat and commercial milk. The pH of drinking yoghurt was found (4.35 - 4.47).Microwave digestion, was selected followed by mineral analysis using Inductively Coupled Plasma-Optical Emission Spectrometry. Micro minerals; Cd, Cr, Cu, Fe, Mn and Pb, ranged from not detected to 23.4$\pm$0.52mg/L for Fe while Sr (0.32$\pm$0.005 – 2.51$\pm$0.043 mg/L) and Zn (1.58$\pm$0.01 – 8.91$\pm$0.14 mg/L) in all milk samples.

Key words: cow milk; goat milk; camel milk; microwave digestion; micro minerals; ICP-OES.

INTRODUCTION

The demand for dairy products is increasing in Saudi Arabia, due to improved living status, nutritional awareness and availability of milk and milk product sources. These products are varying in composition, texture and taste. Milk consumption varies, worldwide from about 180 kg yearly per capita in Finland to less than 50 kg in Japan and China[1]. In addition to cow milk as a main source for consumption, in Saudi Arabia; camel and goat milk are also widely available, particularly in rural areas. Raw camel milk usually consumed without pasteurization, while cow and goat milk, after boiling.

Proximate analysis of cow, goat and camel milk showed a protein % of 3.42, 3.26 and 3.26 respectively; a fat content of 4.09, 4.07 and 3.80 respectively and lactose content of 4.82, 4.51 and

4.30 respectively[2-7]. Water content of whole cow, goat and camel milk at Kingdom of Bahrain, reported as 87.4, 87.0 and 87.5 %, respectively[8].

The contribution of milk and milk products to the diet in western countries is significant for sodium, potassium, chloride, calcium, phosphorus, zinc and iodine[9].

Minerals at nutritional standard concentrations in food are necessary for human health. The consumption of food with high mineral contents can cause gastric irritation and diarrehea[10] and might affect other organ systems.

Determination of elements in foods is dependent upon the sample digestion, because of the risks of contamination or losses of analytes[11]. Usually, dry ashing and wet or conventional (hot-plate) methods[12] have been used for mineral analyses but these procedures are time-consuming and give relatively low concentration readings. Microwave digestion provides rapid analysis and satisfactory results for metals in food[13-15].

Minerals determination is an active topic in analytical science. The choice of an analytical technique, is related to a number of factors, including: (1) susceptibility to matrix effects (2) the range of elements covered (3) the detection limits.

Examples of methods are flame photometer, Atomic Absorption Spectrophotometer (AAS)[16] and Inductively coupled Plasma- Optical Emission Spectrometry (ICP-OES)[17]. The latter, is an established analytical technique with large linear dynamic range, low detection limits, high precision and accuracy, which offers automation, rapid multi-element analysis for the determination of major, minor and trace elements in milk samples.

Table 1: The program of microwave digestion

Stage	Power P (W)	Heating-up time t (min)	Operating temperature T (°C)	Operating time t (min)
1	760	5	120	3
2	760	3	150	3
3	760	5	150	15

Table 2: ICP-OES operating conditions

RF (MHz)	40.68
RF power (W)	1300
Gas flow rate (/min)	
Plasma gas	15.0
Auxiliary gas	0.2
Nebulizer gas	0.8
Sample uptake rate (ml/min)	1.5
Observation height (mm)	15
Plasma viewing	Radial
Read time (s)	15
Delay time (s)	30
Wash time (s)	30

In this study, milk samples are obtained from Western region of Saudi Arabia, Taif province, except milk of pasture reared cows which was obtained from Western Sudan, of similar lands and climate. Raw and fresh milk of Cow (*Bos Taurus);* Goat (*Capra aegagrus hircus*) and Camel (*Camelus dromedarius*)*;* farm and pasture-reared; in addition to commercial milk samples and milk products; are evaluated for micro minerals content.

MATERIALS AND METHODS

This study, carried out in Taif University, Western Saudi Arabia from August to November

2015. Twelve milk and milk product samples collected:

1) Fresh, raw cow milk (farm -rearing); 2) Fresh, raw cow milk (pasture-rearing);3) Fresh, raw goat milk (farm -rearing); 4) Fresh, raw goat milk (pasture-rearing); 5) Fresh, raw camel milk (farm -rearing); 6) Fresh, raw camel milk (pasture-rearing); 7) Commercial fresh cow milk, Sample 1; 8) Commercial fresh cow milk, Sample 2; 9) Commercial liquid milk, whole, prepared from cow's milk powder, Sample 3; 10) Commercial liquid milk, fat free, prepared from cow's milk powder Sample 4; 11) Commercial drinking yoghurt (cow milk source) Sample 1; 12) Commercial drinking yoghurt (cow milk source), Sample 2.

Table 3: The pH of raw milk of farm and pasture-reared cow, goat and camel; commercial fresh milk (samples 1 and 2), liquid milk prepared from milk powder (samples 3 and 4) and drinking yoghurt (samples 1 and 2)

Raw milk source; fresh milk and yoghurt samples	pH
Cow (Farm fed)	6.68 (6.69, 6.68, 6.67)
Cow (Pasture fed)	6.78 (6.79, 6.78, 6.77)
Goat (Farm fed)	6.45 (6.46, 6.45, 6.44)
Goat (Pasture fed)	6.58 (6.54, 6.60, 6.61)
Camel (Farm fed)	6.46 (6.45, 6.46, 6.47)
Camel (Pasture fed)	6.15(6.13,6.15, 6.17)
Commercial Sample 1	6.69 (6.70, 6.67, 6.69)
Commercial Sample 2	6.73 (6.73, 6.72, 6.73)
Commercial Sample 3	6.59 (6.59, 6.6, 6.59)
Commercial Sample 4	6.58 (6.57, 6.58, 6.59)
Commercial Yoghurt 1	4.35 (4.36, 4.33, 4.35)
Commercial Yoghurt 2	4.47 (4.48, 4.47, 4.47)

Reagents and glass wares

All reagents and chemicals were of analytical grade obtained from Merck (Darmstadt, Germany, www.merck.de). Nitric acid of analytical grade R. Was used, 69–72 % (m/m) HNO3 (d = 1.41–1.51 kg l-1), De-ionized doubly distilled water (DDDW) was also used throughout the analyses for preparing reagents, standard and sample solutions. DDDW also used for washing and rinsing of all apparatus and glassware. Acid-washed polyethylene bottles used for preparing and storing solutions. All solutions were stored in the refrigerator until needed for analysis.

Microwave digestion using MARS 5 instrument

The MARS 5, instrument was programmed for digestion as shown in Table 1. The program involved 760 W, power at 120 ºC for 5 min, 760 W at 150 ºC for 15 min. and 0 W for 30 min to cool down polypropylene volumetric flasks (Corning NY Mexico). The contents, then diluted with de-ionized water and analyzed[18].

Table 4: Concentration (mg/L) of micro minerals (Cd, Cr, Cu, Fe, Mn, Pb, Sr and Zn) in milk from farm and pasture -reared cow [1, 2]; goat [3, 4] and camel [5, 6].

	Cd	Cr	Cu	Fe	Mn	Pb	Sr	Zn
1	0.025b ±0.024	0.732c ±0.005	ND	23.32a 23.32a	0.575 ±0.002	0.167b ±0.010	1.452b ±0.014	7.814a ±0.141
2	ND	ND	ND	1.42c ±0.076	ND	ND	1.141c ±0.003	7.437a ±0.140
3	0.094a ±0.032	6.656a ±0.581	ND	13.05b ±1.484	0.406 ±0.005	0.266a ±0.004	2.294a ±0.040	2.964b ±0.140
4	0.009b ±0.018	ND	ND	1.85 c ±0.410	ND	ND c	1.172c ±0.004	3.405b ±0.049
5	0.089a ±0.065	0.193c ±0.084	ND	ND	ND	ND	1.517b ±0.015	1.580c ±0.039
6	0.007b ±0.012	ND d	0.265a ±0.088	0.049d ±0.036	ND	ND	0.885d ±0.002	7.39a ±0.144

*Same letter in any column (mineral) signs for non-significant difference.

From each. 1.5 ml sample was taken in 250 ml beaker, heated on hot surface (about 95 °C) to near dryness.12 ml nitric acid followed by 2 ml hydrogen peroxide were used to transfer the sample from the beaker to the poly-tetrafluoroethylene (PTFE) (MF 100) digestion vessel.

After microwave digestion and cooling for 30 minutes, the contents were transferred to a 250 mL beaker, heated on a hot plate at temperature not exceeding 95°C,up to about 1 ml is remaining in the beaker. After cooling, about 10 ml double distilled water (DDW) added and transferred to a 25 ml volumetric flask; more DDW added to rinse the

Table 5: Concentration (mg/L) of micro minerals (Cd, Cr, Cu, Fe, Mn, Pb, Sr and Zn) in investigated commercial milk samples,1,2,3 and 4; milk products (drinking yoghurt) 1 and 2.

	Cd	Cu	Fe	Pb	Sr	Zn	Mn	Cr
Milk Sample 1	0.223a	1.658a	21.68a	3.338a	1.306a	2.36 c	0.224c	0e
	±0.007	±0.011	±3.070	±0.080	±0.017	±4.469	±0.009	±0
Milk Sample 2	0.027e	0.0	0.0	0.040e	1.164b	2.56b	0.502a	0.782c
	±0.001	d	d	±0.007	±0.051	±0.038	±0.373	±0.016
Milk Sample 3	0.042d	0.0	0.0	0.434b	0.223c	2.71b	0.0	0.224d
	±0.001	d	d	±0.019	±0.005	±0.692	d	±0.007
Milk Sample 4	0.027e	0.0	11.517c	0.0	1.173b	2.342e	0.603a	1.947a
	±0.032	d	±0.119	f	±0.045	±0.032	±0.051	±0.142
Milk Produt 1	0.054c	0.985b	16.17b	0.256c	1.153b	7.64a	0.318b	1.173a
	+0.005	+0.093	+2.423	+0.008	+0.054	+0.210	+0.009	+0.013
Milk Product 2	0.083b	0.484c	0.0	0.146d	1.521b	2.00d	0.0	1.126b
	+0.005	+0.008	d	+0.041	+0.076	+0.045	d	+0.010

*Same letter in any column (mineral) signs for non-significant difference.

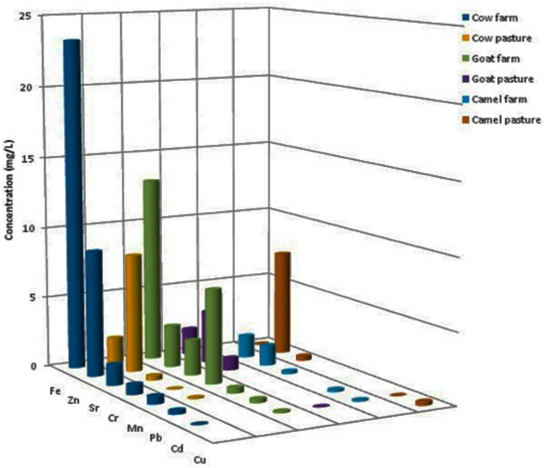

Fig. 1: Concentration (mg/L) of micro minerals (Cd, Cr, Cu, Fe, Mn, Pb, Sr and Z) in milk of farm or pasture -reared cow, goat and camel milk

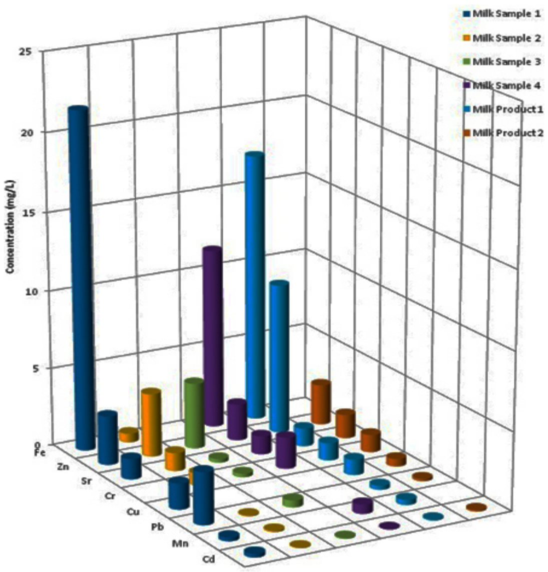

Fig. 2: Concentration (mg/L) of micro minerals (Cd, Cr, Cu, Fe, Mn, Pb, Sr and Zn) in investigated commercial milk samples and milk products (drinking yoghurt)

beaker and complete the flask to mark; ready for analysis. Blank solutions prepared by the procedure above without sample[18], with modifications).

Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES)
Instrument and conditions

A Varian 725–ES inductively coupled plasma-optical emission spectrometer (ICP–OES), with radial viewing configuration (Perkin Elmer, USA), was used to analyze the standard and the sample solutions of Cd,, Cr, Cu, Fe, Mn, Pb, Sr, Zn. The ICP-OES operating conditions well optimized and carefully selected in order to maximize the sensitivity for the desired elements and to obtain the best precision and accuracy. Details of the operating conditions summarized in Table 2.

To ensure that no contamination and/or loss of elements occurs during sample preparations and measurement methodology, a multi-element standard solution was prepared in DDDW and treated in a similar way to samples solutions. Table 4 and Figure 1 show the concentration values of micro minerals (Cd, Cr, Cu, Fe, Mn, Pb, Sr and Zn) in raw milk from farm and pasture -reared cow; goat and camel.

Statistical Analysis

Statistical analysis was carried out by Sigma Stat for Windows version 2.0 (Jandel Scientific, USA). Data expressed as Mean ±SEM. Statistical analysis was performed using one way analysis of variance followed by Tukey post hoc test. The criterion for statistical significance was $p<0.05$. Results expressed as $x \pm s$, where x mean values and s is standard deviation.

RESULTS AND DISCUSSION

pH Determination

The instrument; Microprocessor pH meter (Hanna, pH 211) used in this study.

As shown in Table 3, the pH range of raw fresh cow (farm and pasture-reared) milk and commercial cow milk samples is (6.45 - 6.78). Goat milk pH range (6.45-6.58) while camel milk showed a relatively lower pH range (6.15 - 6.46). The pH of drinking yoghurt found (4.35 - 4.47).

Table 5 and Figure 2 show the concentration values of micro minerals (Cd, Cr, Cu, Fe, Mn, Pb, Sr and Zn) of commercial milk samples, 1 and 2; sterilized milk; samples prepared from milk powder; sample 3 (fat free) and sample 4 (whole); in addition to milk products (drinking yoghurt) samples 1 and 2.

For minerals of investigated raw milk samples, correlation factors of Fe and Sr (r=0.80); Cd and Mn (r=0.84). For commercial milk samples and products: Fe and Zn (r=0.92); Cd and Pb (r=0.96); Cd and Cu (r=0.84) indicated strong correlations between concentration of these minerals.

The Cd-Cu and Cd-Mn correlations were noteworthy for the association of a highly toxic element (Cd) with nutritionally important elements (Cu and Mn). Cd, Cu, Pb, Mn, and Cr concentrations in raw milk of pasture-reared cow, goat and camel are notably lower than those farm-reared. This can be attributed to farm utensils, which possibly contain these minerals.

Variations in milk mineral content, can be attributed to animal breed differences, feeding and analytical procedures[19] in addition to water intake[20].

Present study show that milk can contribute a considerable proportion of the supply of micro minerals in the human diet.

CONCLUSION

The selection of microwave digestion for sample preparation and ICP-OES for determination of cadmium, chromium, copper, iron, manganese, lead, strontium and Zinc as micro minerals proved relevant for the analysis of raw milk, fresh milk and drinking yoghurt. Mineral concentrations were found within recommended values. The concentrations of minerals in studied samples were relatively: Zn > Sr > Fe. These results are comparable to previous studies and confirm the nutritional contribution of milk and drinking yoghurt to the human diet, with concentration values below tolerable upper levels.

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