Macro-Elements in Raw Sheep Milk Samples from Şanlıurfa, Turkey

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Abstract: The purpose of this study was to determine the content of macro-elements (calcium, potassium, magnesium, and sodium) in raw sheep milk samples by inductively coupled plasma-optical emission spectroscopy (ICP-OES) after microwave-assisted digestion with nitric acid and hydrogen peroxide. The raw sheep milk samples were gathered from two boroughs (Akçakale, Halfeti) of Şanlıurfa city. The mean concentration of calcium, potassium, magnesium, and sodium were 1450.33 mg L^{-1}, 1245.58 mg L^{-1}, 139.54 mg L^{-1}, 340.8 mg L^{-1}, respectively. The microwave acid digestion method of this study could provide a useful alternative for the characterization of milk and dairy samples. The studied macro-elements were found to be healthy contribution for daily nutrition to consumers.

Keywords: *sheep milk, macro-element, ICP-OES, Şanlıurfa, Turkey*

Şanlıurfa, Türkiye'de Çiğ Koyun Süt Örneklerinde Makro-element İçeriği

Özet: Bu çalışmanın amacı, çiğ koyun süt örneklerinde makro-element (kalsiyum, potasyum, magnezyum ve sodyum) içeriğinin nitrik asit ve hidrojen peroksitle mikrodalga destekli yakma işleminden sonra indüktif eşleşmiş plazma-optik emisyon spektroskopisi (ICP-OES) ile belirlenmesidir. Çiğ koyun sütü örnekleri Şanlıurfa şehrinin iki ilçesinden (Akçakale, Halfeti) toplanmıştır. Ortalama kalsiyum, potasyum, magnezyum ve sodyum konsantrasyonları sırasıyla 1450.33 mg L^{-1}, 1245.58 mg L^{-1}, 139.54 mg L^{-1}, 340.8 mg L^{-1} olarak ölçüldü. Bu çalışmada kullanılan mikrodalgada asit ile yakma yöntemi süt ve süt örneklerinin element karakterizasyonu için faydalı bir alternatif sağlayabilir. Analiz edilen makro-elementlerin, günlük beslenmede tüketici sağlığına olumlu katkı sağladığı bulunmuştur.

Anahtar Kelimeler: *koyun sütü, makro element, ICP-OES, Şanlıurfa, Türkiye*

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INTRODUCTION

Milk is an excellent nutrient for human as a good provenance of protein, fat, micro and macronutrients, including minerals throughout life (1). The importance of milk and dairy products is established in all over the world and they are the main components of the daily human diet, especially for children and nursery mothers (2). Sheep milk differs from human milk and cow milk in having a specific viscosity, titratable acidity, gravity, and refractive index (3). And also sheep milk is an important source for the dairy industry especially in butter and cheese production sector (4).

Macro-elements in animal milk used in the diet should vary due to different factors such as animal species, feeding, breeding, lactation period, climate, geographical location and season (5, 6). Macro-elements have nutritional, biochemical, and structural functions for mammalian body, both physical and mental development (7). On average, macro elements account for 0.01 % of total body mass and also in body fluids such as milk (8). The concentrations of calcium, potassium, magnesium, sodium in sheep milk secerns significantly from the content of blood but when compared to blood, levels of calcium and potassium in milk are more than blood but have less sodium (8). Sodium concentrations in milk do not depend on dietary intake or animal species, it has a positive correlation with lactation period (8). Recommended daily allowances of calcium, potassium, magnesium, sodium for human are described in Table1 (9).

Table-1. Recommended daily allowances of calcium, potassium, magnesium, sodium for human(9)

Category	Age (year)	Ca (mg)	K (g)	Mg (mg)	Na (g)
Infant	0.5-1.0	260	0.7	75	0.37
Child	1-3	700	3	80	1
Female	19-30	1000	4.7	310	1.5
Male	19-30	1000	4.7	400	1.5
Lactation	19-30	1000	5.1	310	1.5

Recent years several studies have been conducted for the distribution and the levels of element contents in various animal milk samples (10, 11, 12, 13). However, there isn't any study report of the element contents of sheep milk produced in Şanlıurfa, Turkey and also little information on the concentrations of macro elements of sheep milk in Turkey.

The purpose of the present study was to assess and compare the macro elements in sheep milk samples collected from Şanlıurfa, Turkey and to compare the results with previously reported values in the worldwide.

MATERIAL AND METHODS

Sampling

A number of 52 raw sheep milk samples were gathered from small family farms throughout two boroughs (Akçakale, Halfeti) of Şanlıurfa city for during 2016. After collection, samples were placed into clean, washed with acid polyethylene bottles and kept at -19 °C until analyses.

Reagents and solution

Whole solutions were arranged with ultrapure water obtained through ultrapure a water purification system (MES MP Minipure, Turkey). The standard solutions of macro elements were procured from standard solution Merck, Germany; Perkin Elmer, USA. Raw milk samples were digested with hydrogen peroxide (30% v/v Merck, Germany) and nitric acid (65% v/v Merck, Germany).

Analytical determinations

The macro element contents were analyzed by inductively coupled plasma optical emission spectrometry (ICP-OES, Optima 7000 S10, Perkin Elmer, USA) after microwave-assisted acid digestion with operation conditions described in Table 2. All plastic and glassware were cleaned with %10 (v/v) nitric acid solution for 24 hours and flushed with ultrapure water. 1.0 mL of each milk sample was digested with 4.0 mL of 65% (v/v) HNO_3 and 2 mL of 35% (v/v) H_2O_2 in high-pressure Teflon digestion vessels. The vessels were put into microwave system (MARS X-press 5, CEM). Two blank digests were performed in an equal method. Digestion circumstances for the microwave system performed were: up to 90 °C for 7 min and then fixed for 5 min; up to 170 °C in 5 min and fixed for 5 min; up to 210 °C in 20 min and then fixed 5 min finally, a cooling stage (30 min) was conducted to 22°C and dilution completed to 50 mL with ultrapure water.

Table-2. Operating conditions for ICP-OES

Analyte	**Macro-elements (Ca, K, Mg, Na)**
Nebulizer type	Concentric glass
Spray chamber type	Glass cyclonic spray chamber
RF power (W)	1450
Sample uptake rate (mL/min)	1.5
Gas flow rates (L/min)	0.60 L/min
Viewing mode	Radial
Read time	1-5 s
Measurement replicates	3
Plasma argon flow rate	17 L/min
Auxiliary argon flow rate	0.2 L/min
Nebulizer argon flow rate	0.6 L/min
Emission lines	Ca=317,933 nm
	K=766,490 nm
	Mg=285,213 nm
	Na=330,237 nm

Statistical analysis

The statistical analysis of the results was performed using the SPSS 24.0 Software package (SPSS Inc., Chicago, USA). Relations between macro-elements were made with Pearson correlation coefficient.

RESULTS and DISCUSSION

The concentrations of four macro-elements in sheep milk samples are summarized in Table 3**.** The mean concentrations of calcium, potassium, magnesium, and sodium were 1450.33 mg L^{-1}, 1245.58 mg L^{-1}, 139.54 mg L^{-1}, 340.8 mg L^{-1}, respectively.

Table-3. Statistical description of raw sheep milk samples (mg L^{-1})

Sample		Ca	K	Mg	Na
Sheep milk (n=52)	Median	286.5	223.6	43.8	89.4
	Min	553.5	427.1	83.6	158.9
	Max	2389.0	1704.0	267.3	630.2
	Mean	1450.33	1245.58	139.54	340.8
	Std dev	320	220	115	207

Calcium is a macro element which is responsible for muscle contraction, enzyme activation, and cardiac rhythm (14). Calcium concentrations of raw sheep milk samples of our study is between 553.5 - 2389.0 mg L^{-1}. Previous studies calcium concentrations were in the range of 1360-2000 mg L^{-1}, so the calcium levels of this study are parallel with the other studies (10). Elbagermi et al. (2014) reported a mean calcium level (478 mg L^{-1}) in Misurata-Libya which is lower than our study (12). Antunović et al.(2016) reported a mean calcium level (2067.97 mg L^{-1}) of 23 Croatian sheep milk and the result of their study is higher than our results (15). Khan et al (2006) reported 551 mg L^{-1} for winter and 900 mg L^{-1} for summer mean calcium level in Semiarid Region of Pakistan (16). A comparison of calcium content of sheep milk samples in the present study with available literature for caprine milk showed that it was higher than reported by Sing et al. (17) (344.8 mg L^{-1}) and parallel with Guler (18) (1342 mg L^{-1}).

Potassium is an intracellular cation which is important for blood pressure, transmission of nerve impulses and bone metabolism (8). The mean potassium level of sheep milk samples in this study is 1245.58 mg L^{-1} which is higher than the Slovenian sheep milk samples with a mean potassium level of 920 mg L^{-1} (10). Khan et al. (2006) reported that the mean potassium level of 1166 mg L^{-1} for winter and 1079 mg L^{-1} for summer in the semiarid region of Pakistan (16). Zamberlin et al. (2012) reported the mean potassium level of 1334.99 mg L^{-1} for sheep milk which is higher than our mean potassium concentration (1245.58 mg L^{-1})(8).

The content of magnesium in raw milk is not depending on dietary intake (14) and plays a role in protein metabolism, blood pressure regulation, and neuromuscular transmission (8). The concentration ranges of magnesium in sheep milk samples are in 83.6-267.3 mg L^{-1} which is parallel with the literature data 80-190 mg L^{-1} (8). Coni et al. (1999) reported a mean level of magnesium (442 mg L^{-1}) content of Italian sheep which is so higher than this study results (19). Khan et al. (2006) reported the mean magnesium concentration of 112 L^{-1} for winter and 104 mg L^{-1} for summer which is lower than our study's mean magnesium level (139.4 mg L^{-1}) (16).In this study, there are strong positive correlations between magnesium and calcium (rho: 0.737; *P<0.01*) and between magnesium and sodium (rho:0.615; *P<0.01*).

Sodium is responsible cation in extracellular fluids which attendant for acid-base balance, and osmotic pressure (8). Sodium levels in this study are in the range of 158.9- 630.2 mg L^{-1}. Zamberlin et al. (2012) stated sodium concentrations of sheep milk samples were in a range of 209-310 mg L^{-1} (8). In Southern Punjab region of Pakistan, Khan et al. (2006) reported 422 mg L^{-1} for winter and 358 mg L^{-1} for summer mean level of sodium which is similar this study's sodium mean levels (16).

In conclusion, raw sheep milk samples from Şanlıurfa are rich with macro element content so the quality of sheep milk from this city is good and suitable for the production of dairy products such as Urfa cheese. When considering the importance of sheep milk for human nutrition, farmers should be encouraged to increase the production of sheep milk in Şanlıurfa, Turkey.

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