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MAGNESIUM AS A MARKER IN DETECTION AND QUANTIFICATION OF ADULTERATION WITH DOLOMITE IN DOMIATI CHEESE

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ABSTRACT

This work presents novel and very simple method for the simultaneous determination and detection of magnesium as a marker element that contained in adulterated domiati cheese with dolomite. Formulated domiati cheese samples were prepared with 0, 3, 6 and 9% commercial Dolomite. Six cheese samples were collected from the local market in two different governorates Cairo and Giza. Three methods have been used to determine elements in the cheese samples, plasma ICP-spectrometry, atomic absorption and titration method with EDTA (disodium dihydrogen-ethylene diamine tetraacetate). Ca, Mg, Mn, Fe, Na, K, Ni, Cu, Zn and Pb elements were detected by atomic absorption. Titration with EDTA and ICP methods used to detect Ca and Mg elements. Values that measured by ICP method was found to be not correlated with the percent of dolomite contained in the spiked samples. Strong correlation coefficient (0.968) of Mg concentration and dolomite percentage was reported in titration with EDTA method which is a simply and clearly detect the possible adulteration with dolomite via Ca and Mg concentration in tested cheese samplaes.

KEYWORDS: Ca, Mg, Minerals, Atomic Absorption, ICP, Titration with EDTA, Adultration, Domiati Cheese

INTRODUCTION

Product authenticity and authentication are emerging topics within the food sector (Karoui *et al.*, 2004). It is a major concern not only for consumers, but also for producers and distributors (Fernandez *et al.*, 2003).

Milk and milk products are important components of the human diet. Cheese being one of the basic dairy products, is rich in protein, fat, calcium, riboflavin and some other vitamins (Scott, 1981; Yüzbaşi *et al.*, 2003). The mineral content of the milk depends on numerous factors, such as genetic characteristics, the stage of lactation, environmental conditions, type of pasture and soil contamination among others (Cichoscki *et al.*, 2002; Lucas *et al.*, 2006a, 2006b, 2008; Park, 2000; González-Martín *et al.*, 2011). The minerals like sodium, potassium, calcium and magnesium and the anionic constituents, phosphate, citrate, chloride, carbonate and sulphate are found in the milk or associated to the casein micelle (Moreno-Rojas *et al.*, 1994). The heavy metal in the cheese is fundamentally related to the manufacturing practices and possible contamination from the equipment during the process (Mendil, 2006).

Milk adulteration creates significant problems for the dairy industry. It leads to economic losses, deterioration of the quality of the end products and is a risk to consumer's safety (Haza *et al.*, 1996).

Dolomite is a natural product that contains the two more important cations; calcium and magnesium. Their origin is mainly sedimentary and it provides a great quantity of applications. In pharmaceutical industry it has been used to obtain calcium nutritional supplements. Various impurities in dolomite composition confer its potential toxicity when it is used as an ingredient of pharmaceutical products (Hodgson and Levi, 1987).

In the Drug Research and Development Center (CIDEM), a calcium and magnesium supplement as chewable tablets containing dolomite was developed. This nutritional supplement is intended for use in lacking the states of calcium and magnesium that occur during pregnancy, nursing, maturation and ageing. Significant toxicity in oral acute tests was not observed with chewable tablets. In an oral subchronic 90 days toxicity study, a physiologic hypercellularity of thyroid cells and histopathological disorders in the kidney were observed (Lagarto *et al.*, 2008). Percentage of calcium and magnesium in dolomite is widely variable and dependent mainly on several factors, source and manufacturing is the most effective factors. Commercial dolomite content of Calcium and magnesium ranged from 20-35% and 18-30% respectively, Gaydou and Arrivets (1989).

In the present study, Atomic absorption spectrometry, plasma ICP-optical spectroscopy and titrimetric EDTA analytical methods was used to detect the mineral profile of prepared cheese samples spiked with different levels of dolomite in addition to commercial samples that was collected from local markets from deferent regions. The study also designed to assess the relationship between the dolomite level in cheese and Mg element to serve as a marker in detection of adulteration with dolomite in Domiati cheese.

MATERIALS AND METHODS

Materials

Dolomite powder was obtained from Multi-Minerals Company for industrial minerals, Egypt. Full cream milk powder was purchased from local market, while sodium chloride, Hydrogen peroxide and nitric acid was purchased from El-Gomhoreya Company, Cairo, Egypt.

METHODS

Cheese Samples

Six domiati cheese samples were collected from different marketing regions around Cairo and Qaliubiya governorates. Samples were kept in refrigerator until examination which was undertaken just after getting the samples into the laboratory.

Domiati Cheese Making

Four batches (one Kg each) of Domiati cheese were made from pasteurized (65 °C/30 min) and salted (6% w/w) reconstituted full cream milk powder following the method described by Fahmi and Sharara (1950). Batch one kept as control, while other three batches spiked with dolomite powder at 3, 6, and 9 % respectively as replacement from full cream milk powder.

Analytical Procedure

All reagents were of analytical reagent grade unless otherwise stated. Double deionized water was used for all dilutions HNO_3 and H_2O_2 were of superior quality. Elements were estimated using three different analytical methods to evaluate the best way and the easiest and available for the quantitative estimation Ca and Mg. Commercial standard

solution for atomic absorption spectrometer. The samples of ground cheese are submitted to desiccation with a heater at 105°C for 24 hours. Once dry, they are ground and submitted to mineralization in a microwave system measuring the composition in the resulting solution by plasma ICP-optical spectroscopy (AOAC, 2005). The calcium and magnesium estimate plasma method at the National Center for Research. A comparison was made of four methods for the determination of magnesium by titration with EDTA (disodium dihydrogen-ethylene diamine tetraacetate) method. Jackson (1973)

Statistical Analysis

The statistical analysis was performed Using SPSS (2001) package and the descriptive correlation coefficients (r) were estimated between different analytical methods.

RESULTS AND DISCUSSIONS

The concentration level (mg/Kg) of the elements and minerals (Ca, Mg, Mn, Fe, Na, K, Ni, Cu, Zn and Pb) measured in the nine plus control different typical cheese samples by atomic absorption are given in Table 1. Data presented shows that the cheese samples taken from different regions contain different element profiles. The calcium values of the samples varied from 45800-2858 mg/kg and the highest average values were found in cheese sample spiked with 9% dolomite and cheese sample collected from region 5. Similar findings for Ca value were reported by Park (2000).

Mean Mg concentrations ranged from 172 to 2243 mg/kg. The maximum and minimum Mg levels were found in cheese samples collected from region 2 and 6. The maximum Zn, Fe, Mn and Cu levels were 430.43, 226.09, 21.74 and 105.65 mg/kg, respectively in cheese sample collected from region 2. Nickel and lead contents were reported to be 101.16-194 and 0-7 mg/kg, respectively. The FAO/WHO has set a limit for heavy metal intakes based on body weight. For an average adult (60 kg body weight), the provisional tolerable daily intakes (PTDI) for lead, iron, copper and zinc are 214 lg, 48 mg, 3 mg and 60 mg, respectively according to (JECFA, 1999; Yüzbaşi *et al.*, 2003). Maximum sodium and potassium levels were found in cheese sample collected from region 4 cheese and cheese sample spiked with 9% dolomite (5084 and 616.85 mg/kg), respectively. These values are in agreement with data recorded by (Merdivan *et al.*, 2004 and Park, 2000).

Table 1: The concentration levels of elements (mg/Kg) in cheese samples by atomic absorption.

Samples	Concentration Levels (mg/Kg)									
	Ca	Mg	Zn	Fe	Mn	Cu	Ni	Pb	Na	K
Control	3150.00	168.00	47.60	10.00	1.45	28.00	135.95	0.50	4460.80	530.35
Spiked 3%	4090.91	241.36	33.00	9.09	1.14	4.91	101.16	0.00	4428.00	267.18
Spiked 6%	13849.96	278.24	61.67	18.14	1.03	7.79	185.10	1.00	4534.60	189.07
Spiked 9%	45800.00	876.00	53.20	62.50	2.90	42.00	194.85	7.00	4915.90	616.85
Region 1	3480.39	774.51	46.67	36.76	1.42	27.45	140.25	0.00	3181.60	379.60
Region 2	28695.65	2243.48	430.43	226.09	21.74	105.65	139.30	5.00	4797.00	204.40
Region 3	3600.00	297.30	38.50	26.00	2.50	12.15	116.65	5.50	4715.00	202.58
Region 4	3350.00	312.30	80.85	14.00	1.25	6.75	108.55	6.00	5084.00	226.30
Region 5	2858.44	230.85	37.43	9.07	1.13	8.58	189.80	5.50	4100.00	343.10
Region 6	3350.00	172.00	41.30	10.00	1.45	42.00	144.85	0.00	2488.70	405.15

Data presented in Table 2 show the estimated levels of calcium and magnesium by EDTA method. The highest value of calcium was recorded in cheese sample collected from region 6 compared to the control. The higher the value of magnesium was found in the cheese sample spiked with 9% dolomite. Mendil, (2006) were reported that the Mg level in different cheese samples was ranged from 28.9 to 127 mg/Kg.

Table 2: The Concentration of Ca and Mg (mg/Kg) in Cheese Samples by Titration with EDTA Method

Samples	Concentration Levels (mg/Kg)	
	Ca	Mg
Control	110.00	18.00
Spiked 3%	174.00	135.60
Spiked 6%	272.00	328.80
Spiked 9%	200.00	684.00
Region 1	150.00	600.00
Region 2	180.00	396.00
Region 3	70.00	270.00
Region 4	120.00	246.00
Region 5	40.00	231.60
Region 6	380.00	600.00

Data in Table 3 show the concentration level of Ca and Mg in Cheese species by plasma ICP-spectroscopy. The maximum of Ca and Mg levels were found in cheese samples spiked with 3% and 9% dolomite.

Table 3: The Concentration Levels of Ca and Mg (mg/Kg) in Cheese Samples by Plasma ICP-Spectroscopy

Samples	Concentration Levels (mg/Kg)	
	Ca	Mg
Control	12486.50	748.50
Spiked 3%	78770.00	940.00
Spiked 6%	4102.00	1143.00
Spiked 9%	20156.00	2038.00
Region 1	9753.50	589.50
Region 2	4580.00	1140.50
Region 3	4227.50	1184.50
Region 4	5094.00	1379.50
Region 5	6909.50	1723.00
Region 6	10807.00	1261.50

Data in Table 4 and Figure 1 presents a comparison between the three methods for estimating the calcium and magnesium in cheese samples spiked with dolomite. The maximum value was recorded by using plasma ICP- spectroscopy and Atomic methods and there was no correlation between the percentage of dolomite content and the levels of Ca and Mg elements. In the manner of detection a marker element(s) as a result of adulteration with dolomite, these methods showed no reliability and the possibility of their use in rapid detection of elements is very limited. On the other hand, the EDTA method is a simple and rapid analytical method for identification of calcium and magnesium. There is a strong correlation ($R^2 = 0.968$) between the concentration of calcium and magnesium and the percentage of dolomite used in present work.

Table 4: Comparison between the Three Methods for Estimating the Calcium and Magnesium in Cheese Spiked with Dolomite

Methods	ICP		Versen		Atomic	
	Ca	Mg	Ca	Mg	Ca	Mg
Control	12486.50	748.50	111.00	19.00	3150.00	168.00
Spiked 3%	78770.00	940.00	171.50	136.60	4092.11	241.36
Spiked 6%	4102.00	1143.00	272.00	325.80	13849.96	278.24
Spiked 9%	20156.00	2038.00	201.50	684.00	45800.00	876.00

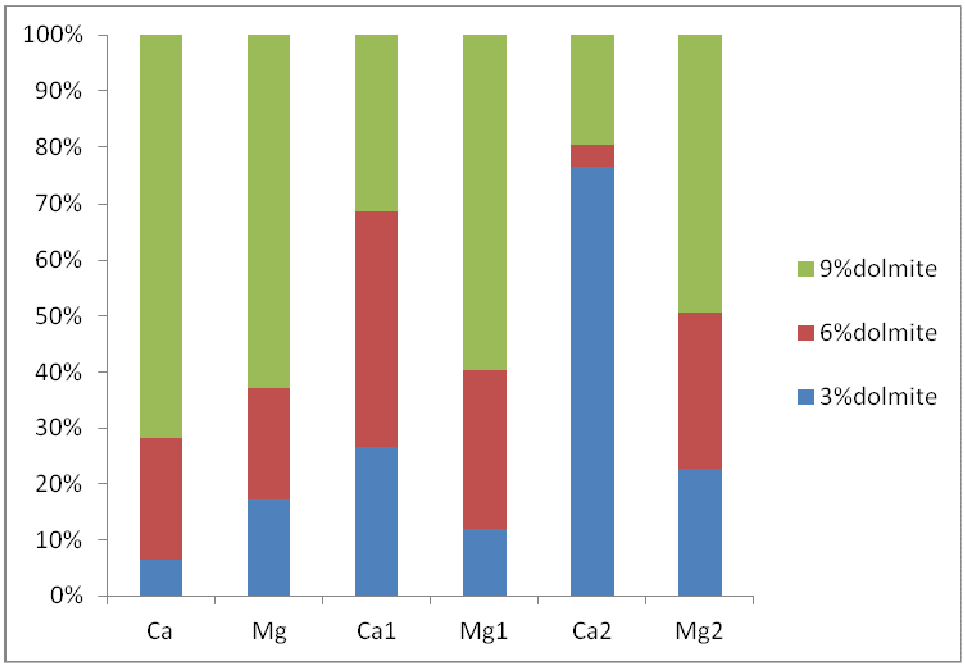

Figure 1: Distribution of Mg and Ca in Cheese: Ca and Mg Determined with Plasma ICP-spectroscopy, Ca1 and Mg1 Determined by Titration with EDTA Method and Ca2 and Mg2 Determined with Atomic Absorption

Commercial dolomite used in present study is containing up to 22% calcium and 18% magnesium as reported in its data sheet. While, the pure dolomite contain up to 98% of $CaCO_3.MgCO_3$. LD_{50} of the dolomite is 6.5g/Kg (rats, oral) has been identified for pure dolomite Lagarto *et al.*, (2008). Safety data for dolomite identified $CaCO_3.MgCO_3$ as a non-carcinogenic material but traces of crystalline silicate was found to be carcinogenic Material Safety Data Sheet (2008).

The main objective of this work was to determine the content of magnesium and calcium in different cheese sample using the methods applied, to estimate the interrelationship and dependence on cheese properties and source. For comparison between the three methods for estimating the calcium and magnesium is done by including the correlation coefficient. Results in the table 5 shows the correlation coefficient between the three methods and demonstrates that the titrimetric EDTA method is the best way to estimate the correlation coefficient EDTA high significant element magnesium.

The correlation established between magnesium content determined by methods were very strong 0.46–0.96. The method is clear for the third estimate of calcium and magnesium from the best ways to estimate where given a high correlation coefficient where they can provide possibilities and easy to estimate. The values without star shows no significant (R^2=0.069).

Table 5: The correlation Coefficient of Estimating Methods between Calcium and Magnesium

Method	Ca	Mg
Atomic	Y=5251x-8221 R^2=0.84*	Y=82.13x+0.764 R^2=0.774*
EDTA	Y=13.06x+126.9 R^2=0.46*	Y=81.74x-96.91 R^2=0.968**
ICP	Y=2554x+41013 R^2=0.069	Y=153.4x+488.6 R^2=0.88*

* Values are significant 95% confidence level.
** Values are significant 99% confidence level.

CONCLUSIONS

Based on the above results, it could be concluded that the detection of adulteration with dolomite could be assessed by a simple titrimetric EDTA method. There was a strong positive correlation between the level of magnesium and the percentage of dolomite in the spiked cheese samples in comparison with other analytical methods.

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