

Letter to Editor

Determination of Strontium in Milk by Flame Atomic Absorption Spectrometry

S. Tautkus*¹, D. Uzdaviniene¹, I. Pakutinskiene¹, R. Kazlauskas¹, E. Zalieckiene²

¹Department of Analytical and Environmental Chemistry, Vilnius University, Naugarduko 24, LT-03225, Vilnius, Lithuania

²Vilnius Gedimino Technical University, Sauletekio al. 11, LT-10223, Vilnius, Lithuania

Received: November 14, 2006

Accepted: April 26, 2007

Abstract

The method for the determination of Sr microamounts in milk by flame atomic absorption spectrometry (FAAS) is suggested. The main characteristics for the determination of this metal have been optimized and investigated: optimum air and gas pressure; the influence of hydrochloric acid and an effect of time on the absorbance of strontium. The selectivity of the determination of strontium was also investigated. The limiting interfering Sr/M ratios (the determination error $\pm 10\%$) have been estimated. The suggested technique is simple, fast, accurate and selective.

Keywords: strontium, milk, flame atomic absorption spectrometry

Introduction

Mercury, lead, cadmium, chromium, copper, nickel, zinc, cobalt, vanadium, molybdenum, beryllium, uranium, strontium, arsenic and many other heavy metals have several negative effects on human health, including carcinogenic, mutagenic and teratogenic effects. The general synergetic impact of metals is especially dangerous when realizing separate concentrations of metals (not higher normative concentration values). Toxic metals and other compounds enter the environment by different means: nuclear tests in atmosphere and strong accidents in atomic energy plants. In this way pollution by radioisotopes of Sr. Strontium is an analogue of calcium, therefore it participates in metabolism of the organism. Sr easily integrates into components of biosphere, migrates

in the biological chain, gains access to human organism with vegetative and animal strain food or fish and can lead to serious problems such as cariosity. So,

toxic doses of strontium have negative effects on human health. The toxicity of this element demands a fast and accurate method for its determination.

Flame photometric method is often used to determine strontium in different samples [1-4]. The essential disadvantage of this method is insufficient selectivity when Fe, Al, Si and Ca are in the investigated sample. Moreover, the results obtained for the determination of Sr by flame photometric method show insufficient reliability. Flame atomic absorption spectrometry (FAAS) is one of the most suitable methods for the determination of Sr. Determination of Cu, Zn, Se, Fe, Pb, Cd, Co, Hg, Mn, and Sb in milk by FAAS method is described previously in articles [5-8]. The determination of strontium in water, alloys, bottom sediments and biological samples by FAAS method is well documented [9-14]. However, the results on the determination of strontium in milk by FAAS are, to our knowledge still not published. Therefore, the aim of the present study was to investigate the experimental parameters for the development of novel method for the determination of strontium in milk by flame atomic absorption spectrometry.

*Corresponding author; e-mail: stasys.tautkus@chf.vu.lt

Experimental

Instrumentation

A Hitachi 170-50 (Japan) flame atomic absorption spectrometer equipped with hollow cathode lamps was used for the analysis. The following conditions for the metal determination by flame AAS method were used: a Sr hollow cathode lamp operating at 460.7 nm was used as radiation source. The lamp current was set at 15 mA. The flame composition was: acetylene (gas pressure $2.69 \cdot 10^4$ Pa), and air (gas pressure $1.18 \cdot 10^5$ Pa).

Materials and Treatments

Double-distilled water and analytical-grade reagents were used in all the experiments.

The standard solution of strontium, 1 mg/ml, was prepared by dissolving 2.4152 g of strontium nitrate (99.9 purity) in double-distilled water and diluted to 1000 ml in volumetric flask.

Working standard solution of strontium. The strontium ions standard solution was diluted daily to obtain a working standard solution of strontium (100 $\mu\text{g/ml}$).

Solutions of K, Na, Ca, Mg, Li, Ba, Cd, Zn, Al, Cu, Mn, Cr, Pb, Fe, Ni, Co and Bi were prepared with 1 g metallic weighing.

Metallic Cd, Cu, Pb, Co, Mn, Fe, ZnO and Ni_2O_3 were dissolved in 10 ml dilute nitric acid (1:1) and heated. CaO and metallic Mg and Al were dissolved in dilute hydrochloric acid (1:1). Metallic Bi was dissolved in the mixture of HNO_3 and HCl acids (3:1). Metallic Cr was dissolved in 10 ml dilute sulphuric acid (4:1).

The obtained solutions were diluted with double-distilled water to 50 ml, except Bi, which was diluted with 2 mol/l hydrochloric acid.

KCl, NaCl, Li_2SO_4 and BaCl_2 , which consist of 1 g metals, were dissolved in double-distilled water and diluted to 50 ml in volumetric flasks.

Concentration of metals in all obtain solutions was $2.0 \cdot 10^4$ $\mu\text{g/ml}$.

Solutions of strontium, 0.2 $\mu\text{g/ml}$, along with appropriate amount of interfering ion were prepared for the evaluations of FAAS selectivity. A strontium solution of the same concentration without additives was used as the reference solution.

A calibration curve for the determination of strontium in the milk samples by FAAS was established using the following procedure. First, 0.1, 0.2, 0.4, 0.8, 1.2, 1.6, 2.0, and 2.4 ml of working standard solution of strontium (100 $\mu\text{g/ml}$) were transferred to a 100-ml volumetric flask, then 5 ml 2 mol/l HCl solution was added and filled to the mark with double-distilled water. The calibration solutions were prepared in the concentration range of 0.1–2.4 $\mu\text{g/ml}$. The calibration curve showed a linear correlation within the concentration range of 0.1–2.0 $\mu\text{g Sr/ml}$. The detection limit of Sr was 0.05 $\mu\text{g/ml}$.

For the determination of strontium in milk by FAAS method, 50 ml of the analyzed samples were transferred to the porcelain plate, boiled and fully evaporated. The ashes were washed with double-distilled water, added 5 ml (1:1) HCl and boiled. The obtained solutions were filtered (if not transparent), transferred to a 10-ml volumetric flask and filled to the mark with double-distilled water. Atomic absorption of Sr in the milk was measured. Amount of strontium in the milk was established from the calibration curve.

Results and Discussion

Sr Atomic Absorption

The influence of hydrochloric acid used in the analytical procedure on the absorbance of Sr was estimated. It was determined that the analytical signal of strontium increases about 5% by the addition of HCl up to 4 mmol/l (Fig. 1). The influence of acetylene and air gas pressure on the Sr signals was systematically studied and optimum values were estimated. It was determined that atomic absorption of strontium was dependent on acetylene gas pressure (Fig. 2). The absorbance of strontium is stable in

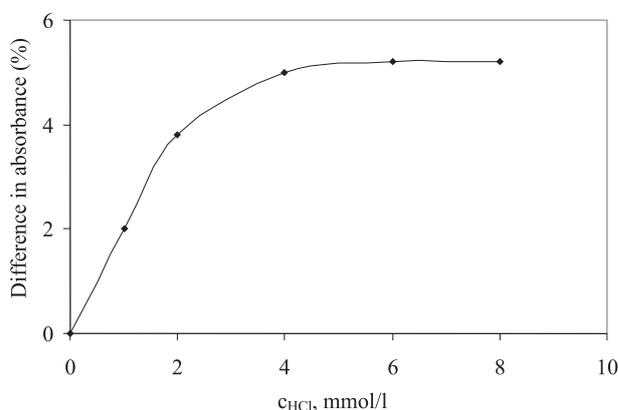


Fig. 1. Correlation between absorption signal and hydrochloric acid ($p_{\text{air}} = 1.18 \cdot 10^5$, $p_{\text{C}_2\text{H}_2} = 2.45 \cdot 10^4$ Pa, $c_{\text{Sr}} = 1$ $\mu\text{g/ml}$).

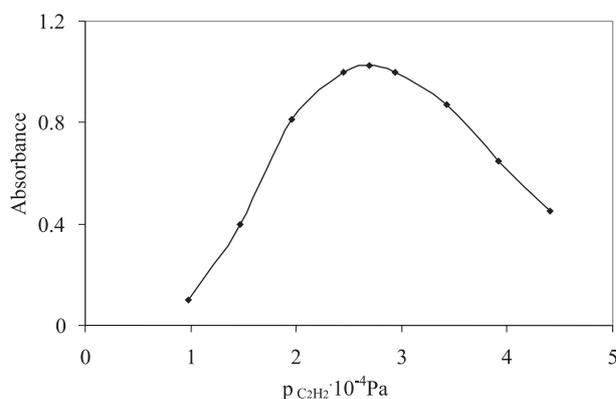


Fig. 2. Correlation between absorbance of strontium and pressure of acetylene ($p_{\text{air}} = 1.18 \cdot 10^5$ Pa, $c_{\text{Sr}} = 1$ $\mu\text{g/ml}$).

narrow acetylene gas pressure interval $(2.45-2.94) \cdot 10^4$ Pa. The absorbance of strontium decreases abruptly at higher and lower values of gas pressure. The optimum air pressure interval for Sr of $1.08 \cdot 10^5$ - $1.37 \cdot 10^5$ Pa was chosen (Fig.3). The effect of time on the absorbance of strontium was also studied. The adsorption of strontium on vessel walls was assessed with reference to absorbance of strontium solutions. It was determined that the absorbance of strontium solutions after three months remains without any changes.

The selectivity of the determination of strontium was investigated. The limiting interfering Sr/M ratios were considered as limiting when the error of the determination did not exceed $\pm 10\%$. The amount of additive metal was reduced if the error of the determination exceeded 10%. The selectivity studies are summarized in Figs. 4-8.

Evidently, Li, Mg, K, Zn, Cr and Ca have the lowest influence on the absorbance of strontium (Fig. 4). These metals did not interfere with the determination of strontium by FAAS even if their concentrations were 20,000 times higher than that of Sr. Secondly, about 8,000 times higher concentrations of Cu, Ni, Mn and Fe have no influence on the absorbance of strontium as well (Figs. 5 and 6). Na and Cd did not interfere with the determination of strontium if their concentration were 4,000 times higher than that of Sr (Fig. 7). Slightly higher influence on

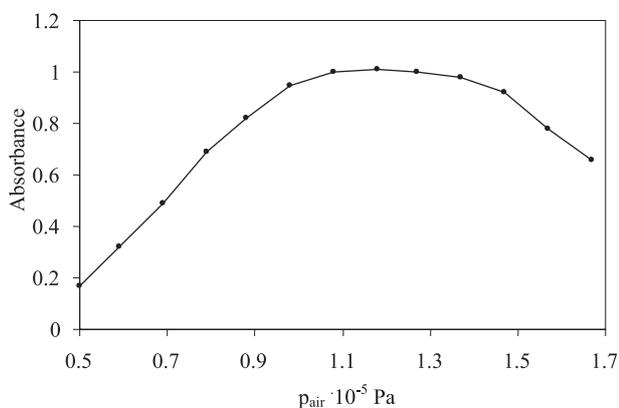


Fig. 3. Correlation between absorbance of strontium and air pressure ($p_{C_2H_2} = 2.45 \cdot 10^4$ Pa, $c_{Sr} = 1 \mu\text{g/ml}$).

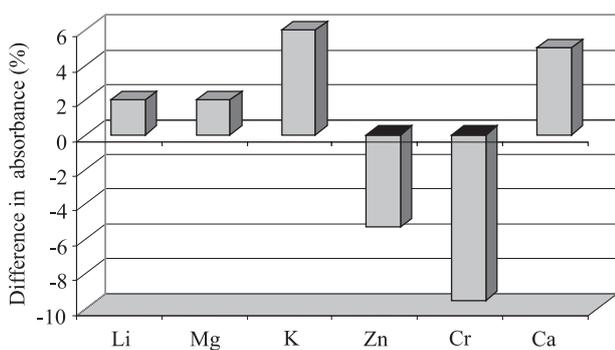


Fig. 4. Effect of the concentration of Li, Mg, K, Zn, Cr and Ca ions on the analytical signal of Sr (Sr:M = 1:20,000).

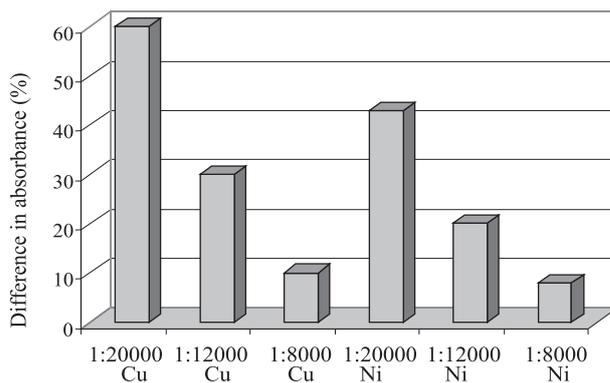


Fig. 5. Effect of the concentration of Cu and Ni ions on the analytical signal of Sr.

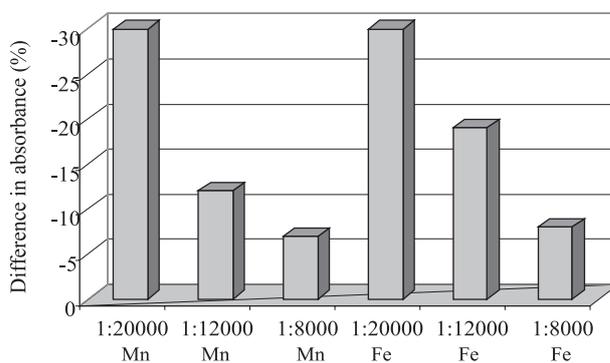


Fig. 6. Effect of the concentration of Mn and Fe ions on the analytical signal of Sr.

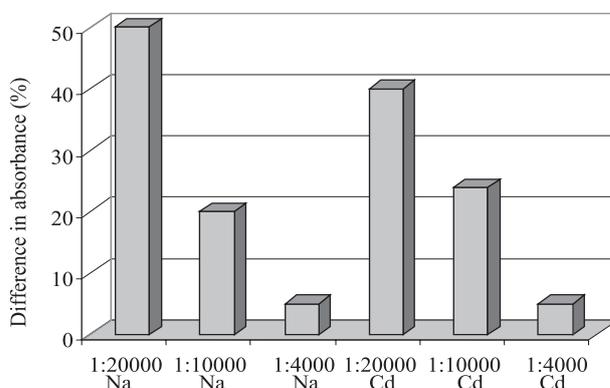


Fig. 7. Effect of the concentration of Na and Cd ions on the analytical signal of Sr.

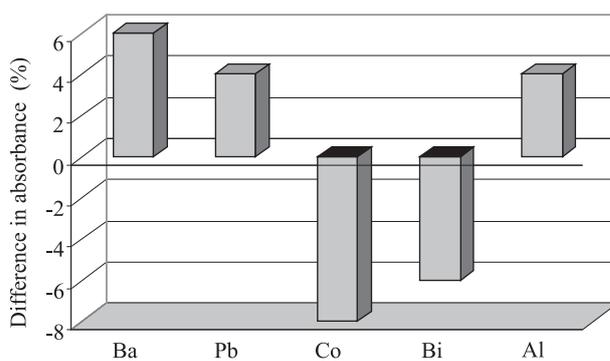


Fig. 8. Effect of the concentration of Ba, Pb, Co, Bi and Al ions on the analytical signal of Sr (Sr:M = 1:2,000).

Table 1. FAAS results for the determination of strontium in milk.

Milk	Amount of strontium, mg/l (n = 5)	S _r , %
VP Market "Saulės pienas"	0.055	3.0
AB Mažeikių dairy "Labas rytas"	0.041	2.9
AB Utenos milk "Žalioji karvutė"	0.024	2.3
AB Mažeikių dairy "Ūpas"	0.028	2.7
AB Rygos milk "Margė"	0.032	2.0

Table 2. Results obtained for the determination of strontium in milk by the additive method.

Milk	Amount of strontium, mg/l		total	Abstraction, %
	Sr found by the FAAS method	additive		
VP Market "Saulės pienas"	0.055	0.2	0.259	98
AB Mažeikių dairy "Labas rytas"	0.041	0.2	0.245	102
AB Utenos milk "Žalioji karvutė"	0.024	0.2	0.224	100
AB Mažeikių dairy "Ūpas"	0.028	0.2	0.232	102
AB Rygos milk "Margė"	0.032	0.2	0.229	99

the determination of strontium was observed for Ba, Pb, Co, Bi and Al (Fig. 8). 2,000 times higher concentrations of these metals have no influence on the absorbance of strontium. All metals can be put in order of obstruction characteristics: Ba, Pb, Co, Bi, Al > Na, Cd > Mn, Fe, Cu, Ni > Li, Mg, K, Zn, Cr, and Ca.

Determination of Sr in Milk

Determination of Sr by FAAS method was investigated and optimized. Analysis of different milk samples was performed. The content of strontium was determined in several milk samples from different dairies: VP market "Saulės pienas," Mažeikių dairy "Labas rytas," AB Utenos milk "Žalioji karvutė," AB Mažeikių dairy

"Ūpas" and AB Rygos milk "Margė." Analytical process was described in the "Experimental" part. The results obtained for strontium determination by the suggested FAAS method are summarized in Table 1. Accuracy of the results was assessed by additive method (Table 2). As can be seen from Table 1, the highest concentration of strontium was found to be in the milk from VP market "Saulės pienas," the lowest in the milk from Utenos milk "Žalioji karvutė." As can be seen from Table 2, the results obtained for the determination of Sr by FAAS method are very accurate.

Conclusions

1. The influence of different parameters on strontium atomic absorption was systematically studied. The influence of hydrochloric acid used in the analytical procedure on the absorbance of Sr was estimated. It was determined that the analytical signal of strontium increases about 5% by the addition of HCl up to 4 mmol/l. The influence of acetylene and air gas pressure on Sr signals was systematically studied and optimum values were estimated. The absorbance of strontium is stable in narrow acetylene gas pressure interval (2.45-2.94)·10⁴ Pa. The effect of time on the absorbance of strontium was also studied. It was determined that the absorbance of strontium solutions after three months shows no changes.
2. The selectivity of the determination of strontium was investigated. The limiting interference by Sr/M ratios (determination error ±10%) have been estimated. All metals can be put in order by obstruction characteristics: Ba, Pb, Co, Bi, Al > Na, Cd > Mn, Fe, Cu, Ni > Li, Mg, K, Zn, Cr, and Ca.
3. A simple method for the flame atomic absorption spectrometry determination of Sr in milk has been suggested. The methodological approach is fast and not labour consuming. Besides, this method showed excellent reproducibility, sufficient accuracy (S_r 2–3%) and high selectivity.

References

1. LURJE YU. YU. Analytical chemistry of industrial effluent. Moscow. Chemistry, **1984**.
2. Drinking-water. Analytical methods. Moscow. **1984**.
3. ANDERSEN N. R., HUME D. N. Determination of barium and strontium in sea water. *Analytica Chimica Acta*. **40**, 207, **1968**.
4. WEBB M. S. W., WORDINGHAM M. L. The direct flame photometric determination of strontium:calcium ratios in the ash of human bones and teeth. *Analytica Chimica Acta*. **28**, 450, **1963**.
5. CLESIA C. NASCENTES, MARKO A. Z. ARRUDA, ANA RITA A. NOGUIRA, JOAQUIM A. NOBREGA. Direct determination of Cu and Zn in fruits juices and bovine milk by

- thermospray flame furnace atomic absorption spectrometry. *Talanta*. **64**, 912, **2004**.
6. POLIANA C. ALEIXO, JOAQUIM A. NOBREGA. Direct determination of iron and selenium in bovine milk by graphite furnace atomic absorption spectrometry. *Food Chemistry*. **83**, 45, **2003**
 7. PALMINGER HALLEN I., JORHEM L., JON LA-GERKVIST B., OSKARSSON A. Lead and cadmium levels in human milk and blood. *Science of the Total Environment*. **166**, 149, **1995**
 8. IYENGAR G. V., KASPEREK K., FEINENDEGEN L. E., WANG Y. X., WEESE H. Determination of Co, Cu, Fe, Hg, Mn, Sb, Se and Zn in milk samples. *The Science of the Total Environment*. **24**, 267, **1982**.
 9. BURGUERAM.,BURGUEAJ.L.,RONDONC.,BERNARDO M. L., GALLIGNANI M., NIETO E., SALINASJ. Appraisal of different electrothermal atomic absorption spectrometric methods for the determination of strontium in biological samples. *Spectrochimica Acta Part B54*, pp 805–818, **1999**.
 10. ARSLAN Z., TYSON J. F. Determination of calcium, magnesium and strontium in soils by flow injection flame atomic absorption spectrometry. *Talanta*. **50**, 929, **1999**.
 11. HELSBY Ch. A. Determination of strontium in human tooth enamel by flameless atomic- absorption spectrometry. *Talanta*. **24**, 46, **1977**.
 12. MENDES-BEZERRA A. E., PAIVA M. E. D., MARTINS M. M. C. An atomic-absorption study of strontium. *Anal. Proc.* Vol. **23** (6), 233, **1986**.
 13. DEFFRAWY M. M., KHALIFA M. E., ABDALLAH A. M., AKI M. A. Removal of phosphate and silicate interferences in the determination of magnesium, calcium and strontium by atomic absorption spectrometry. *J. Analyt. Atom. Spectrom.* **2** (3), 333, **1987**.
 14. SEN GUPTA J. G. Determination of barium, strontium and nine minor and trace elements in impure barite and strontianite by inductivelycoupled plasma atomic-emission spectrometry after dissolution in disodium ethylenediaminetetraacetate. *Talanta*. **38**, 1083, **1991**.