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## DETERMINATION OF LEAD IN DOLOMITE BY ZEEMAN ELECTROTHERMAL ATOMIC ABSORPTION SPECTROMETRY

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**Abstract:** A method for the lead determination in dolomite by Zeeman electrothermal atomic absorption spectrometry, is presented. After the dissolution of samples, lead was extracted with sodium diethyldithiocarbamate. The lead-diethyldithiocarbamate complex was extracted into methylisobutyl ketone from a medium of pH 6.0–10.0. The procedure was verified by method of standard additions and by analyzing referent standard samples. A calibration curve (for organic solutions containing up to 1 ng Pb) was made using the proposed extraction procedure for standard solutions of lead. The standard deviation (SD) for 0.5 ng Pb is 0.01 ng and the relative standard deviation ranges from 2.5 to 3.5%. The detection limit of the method, calculated as 3 SD of the blank, was found to be  $1.5 \text{ ng} \cdot \text{g}^{-1}$ . The operation conditions in electrothermal atomic absorption measurements (temperature and time) were: drying –  $90^\circ\text{C}$ , 20 s; charring –  $400^\circ\text{C}$ , 20 s; atomizing –  $1900^\circ\text{C}$ , 3 s; cleaning –  $2650^\circ\text{C}$ , 3 s.

**Key words:** lead; dolomite; electrothermal atomic absorption spectrometry

### INTRODUCTION

The mineral lorandite ( $\text{TlAsS}_2$ ), present in the Alshar deposit (Republic of Macedonia), is a possible solar neutrino detector (Freedman et al., 1976). As result of nuclear reaction between the isotopes of thallium  $^{205}\text{Tl}$  and the solar neutrino,  $^{205}\text{Pb}$  is produced. The aim of the idea is to determine the content of Pb in the lorandite, that could give information for the value of solar neutrino flux over an extended time (Pavićević, 1994).

Because the lorandite is closely associated with other minerals present in the Alshar deposit, it is necessary to determine the lead content in them (Stafilov et al., 1990; Stafilov et al., 1990a; Stafilov et al., 1994) and also the other elements content in the ore samples and the minerals (Stafilov and Todorovski, 1987; Stafilov et al., 1988; Stafilov and Todorovski, 1990; Stafilov et al., 1993; Lazaru and Stafilov, 1993; Stafilov and Lazaru, 1995). These results give data about the purity of the investigated minerals that is important for the geochemistry and for the explanation of the background radiation of Alshar locality.

Up to now, ETAAS has been widely used for lead determination in a variety of materials, so, there are number of papers about it. In a part of the presented papers (Regan and Waren, 1976; Manning and

Slavin, 1978; Hageman et al., 1979; Sedykh et al., 1980; Halliday et al., 1980; Bertenshaw et al., 1982; Bektas and Akman, 1990) the results of the investigations of matrix interference are given. However, in them the contents of Ca and Mg are not in the same concentration ranges. Our previous investigations about the interference of some elements on lead determination by ETAAS (Stafilov et al., 1990) showed that the magnesium in mass ratio with lead up to 500:1 and the calcium up to 1000:1 cause decreasing of the lead absorbance. This fact pointed out to the necessity of lead separation from calcium and magnesium when lead is determined in dolomite by ETAAS. There are many different methods for lead separation from the matrix before its determination by AAS, based on extraction (Arnarez et al., 1982; Ueda et al., 1987), ionic exchange (Freudiger and Kenner, 1972; Korkisch and Gross, 1974; Negi and Das, 1985) or precipitation (Hudnik et al., 1978; Sugimoto et al., 1991).

In this paper we suggest a new method for determination of lead in dolomite ( $\text{CaMg}(\text{CO}_3)_2$ ) using electrothermal atomic absorption spectrometry (ETAAS) after an extraction of lead by Na diethyldithiocarbamate in methylisobutyl ketone (MIBK).

## EXPERIMENTAL

*Apparatus*

A Varian SpectrAA-604Z Zeeman atomic absorption spectrophotometer equipped with a Varian PSD-100 Autosampler was used. The light source was a lead hollow cathode lamp. Pyrolytically coated graphite tubes were used. The instrumental parameters are given in Table 1.

Table 1

*Instrumental parameters for lead determination by ETAAS*

Wavelength	283.3 nm
Spectral width slit	0.5 nm
Calibration mode	Peak height
Lamp current	5 mA
Background correction	Zeeman
DRY	
Temperature	90 °C
Time	20 s
Ramp time	2 s
CHARRING	
Temperature	400 °C
Time	20 s
Ramp time	1 s
ATOMIZING	
Temperature	1900 °C
Time	3 s
Ramp time	0 s
CLEANING	
Temperature	2650 °C
Time	3 s
Ramp time	1 s
GAS	Argon

*Reagents and samples*

All reagents and standards were of analytical grade. The stock solution of lead was prepared by dissolving high purity  $\text{Pb}(\text{NO}_3)_2$  (Merck) in redistilled water. The concentration of lead in this solution was  $1000 \text{ mg}\cdot\text{dm}^{-3}$ , from which all diluted solutions were prepared. Mineral samples were taken from the Alshar mine, Republic of Macedonia.

*Procedures*

0.1 to 1.0 g of powdered samples of dolomite was dissolved in 10 mL of concentrated HCl and 1 mL of concentrated  $\text{HNO}_3$ . The solution was evaporated almost to dryness and the residue was then dissolved in 2 mL concentrated HCl and adding of 13 mL redistilled water. The solution was filtered and transferred into a separatory funnel. 5 mL of ammonium citrate (50 % w/v) were added and the pH value was adjusted to about 9 with NaOH (20 %). Then, 5 mL of sodium diethyldithiocarbamate (0.2 %) were added and the mixture was shaken for 1 min. After 15 min, 5 mL of organic solvent were added. The mixture was shaken for 2 min, and lead was determined by ETAAS in the organic layer using aliquots of 20  $\mu\text{L}$  that were introduced in the graphite furnace.

## RESULTS AND DISCUSSION

Bode (1954) found that lead could be satisfactory extracted with sodium diethyldithiocarbamate in  $\text{CCl}_4$  in pH region of 5–11. It was found that the extraction with sodium dithiocarbamate in  $\text{CCl}_4$  is better when ammonium citrate and KCN are added (Bode, 1954). We found that addition of KCN is not necessary to obtain satisfactory extraction rate of lead in the pH range of 11.0 to 12.0. Also, we found that the extraction of lead with sodium diethyldithiocarbamate can be made with MIBK in the pH range of 6.0 to 10.0, too.

To check whether Ca and Mg coextract with Pb, series of solutions with the same concentration of Pb and different concentrations of interfering

elements were prepared and Pb was extracted by the proposed procedure. After the extraction, Pb was determined in the organic phase and no interference on the lead absorbance were found. Also, aliquot of organic layer was separated, evaporated to dryness and the residue dissolved in 2 mL of conc. HCl. Using flame AAS, it was found that extracted amounts of Ca and Mg were in range that have not influence on Pb absorbance.

Using the method, some samples of the investigated minerals taken from Alshar mine, with standard additions, were extracted and lead was determined. The results given in Table 2 show that satisfactory recovery results were obtained.

Table 2

*Determination of lead in dolomite by method of standard additions, determined by ETAAS*

Samples	Pb added ( $\mu\text{g}\cdot\text{g}^{-1}$ )	Pb calculated ( $\mu\text{g}\cdot\text{g}^{-1}$ )	Pb found ( $\mu\text{g}\cdot\text{g}^{-1}$ )	Recovery (%)
1-1	-	-	1.53	-
1-2	4.97	6.50	6.54	100.60
1-3	9.93	11.45	11.48	100.26
2-1	-	-	1.24	-
2-2	4.97	6.21	6.35	102.3

There is only one data for the Pb content in the dolomite from the Alshar mine given by Frantz et al. (1994) obtained by neutron activation analysis ( $0.189 \mu\text{g}\cdot\text{g}^{-1}$  Pb). Using the proposed method we find that the content of lead in different samples of the mineral range from 1 to  $2.5 \mu\text{g}\cdot\text{g}^{-1}$ .

The determination of lead was also performed for two referent standard samples (SU1 and 204J E).

The results of measured and certified values for lead content are given in Table 3. As it can be seen, the measured concentrations for lead are very similar to the certified values.

Table 3

*Determination of lead in standard samples*

Standard sample	Certified value ( $\mu\text{g}\cdot\text{g}^{-1}$ )	Value found ( $\mu\text{g}\cdot\text{g}^{-1}$ )
SU 1	0.01	0.0085
204J E	0.002	0.0017

A calibration curve (for organic solutions containing up to 1 ng Pb) was made using the proposed extraction procedure for standard solutions of lead. The standard deviation (SD) for 0.5 ng Pb is 0.01 ng. A relative standard deviation for this method range from 2.5 to 3.5 %. The detection limit of the method, calculated as 3 SD of the blank, was found to be  $1.5 \text{ ng}\cdot\text{g}^{-1}$ .

## CONCLUSION

It was shown that sodium diethyldithiocarbamate can be successfully applied for lead extraction in MIBK from dolomite. The extraction was per-

formed from a medium of pH 6.0 - 10.0. The method of Zeeman electrothermal atomic absorption spectrometry was used for determination of lead.

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## Резиме

## ОПРЕДЕЛУВАЊЕ НА ОЛОВО ВО ДОЛОМИТ СО ЗЕЕМАН-ОВА ЕЛЕКТРОТЕРМИЧКА АТОМСКА АПСОРПЦИОНА СПЕКТРОМЕТРИЈА

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**Клучни зборови:** олово; доломит; електротермичка атомска апсорпциона спектрометрија

Во трудот е предложен метод за определување на олово во доломит со Zeeman-ова електротермичка атомска апсорпциона спектрометрија. По растворањето на пробите оловото се екстрахира со натриум-диетилдитиокарбамат. Оловно-дितिокарбаматниот комплекс се екстрахира во метилизобутил кетон при pH од 6,0 до 10,0. Постапката е потврдена со методот на стандардни додатоци и со анализа на референтни стандардни проби. Калибрациониот дијаграм (за органски раствори кои содржат до 1 ng Pb) е подготвен

со примена на предложената постапка за стандардни раствори од олово. Стандардната девијација (SD) за 0,5 ng Pb изнесува 0,01 ng, додека релативната стандардна девијација се движи од 2,5 до 3,5 %. Границата на детекција на методот, пресметана како 3 SD на слепа проба, е 1,5 ng·g<sup>-1</sup>. Оптималните услови за определувањето на оловото со електротермичката атомска апсорпциона спектрометрија (температура и време) се: сушење – 90 °C, 20 s; жарење – 400 °C, 20 s; атомизација – 1900 °C, 3 s; чистење – 2650 °C, 3 s.