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DETERMINATION OF COPPER IN DOLOMITE BY ELECTROTHERMAL ATOMIC ABSORPTION SPECTROMETRY

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Abstract

A method for the copper determination in dolomite by electrothermal atomic absorption spectrometry is presented. After the dissolution of samples, copper was extracted with sodium diethyldithiocarbamate. The copper diethyldithiocarbamate complex was extracted into different organic solvents (carbon tetrachloride, chloroform and methyl isobutyl ketone), the pH of the medium being in the range of 11.0 – 12.0.

Keywords: *Copper, Determination, Dolomite, Electrothermal atomic absorption spectrometry*

Introduction

The first investigations for the determination of copper in geological samples by atomic absorption spectrometry (AAS) refer to the application of flame AAS. Many authors suggested direct determination from the obtained solutions [1-4]. In the cases when the potential interfering elements were present in higher concentrations, matrix modifications were suggested [5]. To remove the potential influences on the determination of copper in different geological samples by flame AAS, the precipitation of copper [6] or the extraction with different compounds was suggested [7-10]. There are different approaches in the determination of copper by ETAAS. Some authors [11-13] suggested direct determination and other proposed separation of copper from the matrix [14].

Continuing our work on the determination of trace elements in different minerals from Alshar mine, Republic of Macedonia [15-19], in this paper we suggest a new method for determination of copper in dolomite using electrothermal atomic absorption spectrometry (ETAAS).

Experimental

Apparatus

A Perkin Elmer 703 atomic absorption spectrophotometer equipped with a Perkin Elmer HGA-400 graphite furnace was used. The light source was a copper hollow cathode lamp. Pyrolytically coated graphite tubes were used. The instrumental parameters are given in Table 1.

Table 1. Instrumental operating conditions for copper determination by ETAAS (deuterium background correction)

Wavelength	324.8 nm
Spectral width slit	0.7 nm
Calibration mode	Peak height
Lamp current	15 mA
Gas	Argon

Parameter	Drying	Charring	Atomization	Cleaning
Temperature (°C)	90	1100	2300	2650
Time (s)	20	20	3	3
Ramp time (s)	2	1	0	1

Reagents and samples

All reagents and standards were of analytical grade. The stock solution of copper was prepared by dissolving high-purity copper metal (Merck) in conc. HNO_3. The concentration of copper in this solution was 1000 mg/dm^3, from which all diluted solutions were prepared. Mineral samples were taken from Alshar mine, Republic of Macedonia.

Procedures

0.1 to 0.5 g of powdered samples of dolomite were dissolved in 10 cm^3 of conc. HCl and 1 cm^3 of conc. H_2O_2. The solution was evaporated almost to dryness and the residue was then dissolved in 2 cm^3 conc. HCl. The solution was filtered and transferred into a separatory funnel. Then, 5 cm^3 of ammonium citrate (50%, m/v) and 5 cm^3 of sodium diethyldithiocarbamate (0.2%) were added. The mixture was shaken for 1 min. Then, the pH was adjusted to about 11 – 12 with a solution of NaOH (20%, m/v) and 5 cm^3 of organic solvent (MIBK, CCl_4 or $CHCl_3$) were added. The mixture was shaken for 2 min and copper was determined by ETAAS in the organic layer using aliquots of 20 mm^3 that were introduced in the graphite furnace.

Results and Discussion

The interference of calcium and magnesium as matrix elements was studied. Series of solutions with the same concentration of copper and various concentrations of interfering elements were prepared so that the concentrations of these elements were similar to the concentrations in the sample solutions. The results show that the interfering elements tend to decrease the absorbance of copper at high concentrations. In order to avoid these interferences, from one hand, and because of the very low concentration of Cu, on the other, it is necessary to separate and concentrate Cu from the samples. For this reason, an extraction method is proposed.

Bode [20] found that copper could be satisfactorily extracted with sodium dithiocarbamate in CCl_4 in the pH region of 5 ÷ 11. It was found that the extraction with sodium dithiocarbamate in CCl_4 is better when ammonium citrate and KCN are added [21]. We found that addition of KCN is

Table 2. Determination of Cu in dolomite by the method of standard additions determined by ETAAS

Solvent	Added (µg/g)	Calculated (µg/g)	Found (µg/g)	Recovery (%)
MIBK	–	–	2.56	–
	1.25	3.81	4.00	104.9
	2.50	5.06	5.31	104.9
$CHCl_3$	–	–	2.47	–
	1.25	3.72	3.63	97.6
	2.50	4.97	4.81	96.8
CCl_4	–	–	1.00	–
	1.25	2.25	2.13	94.7

not necessary to obtain satisfactory extraction rate of copper in the pH range of 11.0 to 12.0. We also found that the extraction of copper with sodium diethyldithiocarbamate can be done with MIBK (in the pH range of 6.0 to 12.0) and $CHCl_3$ (in the pH range of 11.0 to 12.0), too.

To check whether Ca and Mg coextract with Cu, a series of solutions with the same concentration of Cu and different concentrations of interfering elements were prepared and Cu was extracted by the proposed procedure with all three solvents (MIBK, $CHCl_3$ and CCl_4). After the extraction, Cu was determined in the organic phase and no interferences on the copper absorbance were found.

Using this method, some samples of the investigated minerals taken from Alshar mine (with and without standard additions) were extracted and Cu was determined. The results are given in Table 2, which demonstrates satisfactory recovery values.

As it can be seen from the results of Table 2, the content of copper in dolomite samples from Alshar mine ranges from 1 to 2.5 µg/g, which do not contradict to the results obtained by neutron activation analysis (< 15 µg/g) [22].

Further, determination of copper in two referent standard samples (JSS 820-2 and JSS 820-3) was performed. The obtained results (extraction by all three solvents) are compared with certified values of copper for these standards (Table 3). As it can be seen from the results in Table 3, the measured concentrations for copper by the proposed method are very similar to the certified values.

A calibration curve (for organic solutions containing up to 1 ng Cu) was made using the pro-

Table 3. Determination of copper in standard samples

Sample	Certified (µg/g)	Found (µg/g)		
		MIBK	CHCl$_3$	CCl$_4$
JSS 820-2	10.0	10.12	10.08	10.20
JSS 830-3	110.0	–	108.4	108.0

posed extraction procedure for standard solutions of copper. The standard deviation (SD) for 0.5 ng Cu is 0.01 ng. A relative standard deviation for this method ranges from 3 to 5.5%. The detection limit of the method, calculated as 3.SD of the blank, was found to be 0.05 µg/g.

Conclusions

Sodium diethyldithiocarbamate can be successfully applied for copper extraction in MIBK, CCl$_4$ and CHCl$_3$ from dolomite. The method of electrothermal atomic absorption spectrometry was used for determination of copper. The pH of the aqueous medium should be in the range of 11.0 – 12.0.

Acknowledgements

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