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## FLOTATION SEPARATION OF Cd, Co, Cr, Cu, Ni AND Tl FROM CALCIUM MINERALS AND THEIR DETERMINATION BY INDUCTIVELY COUPLED PLASMA-ATOMIC EMISSION SPECTROMETRY

Vesna Zajkova-Paneva<sup>1</sup>, Trajče Stafilov<sup>2</sup>, Blažo Boev<sup>1</sup>

<sup>1</sup>*Faculty of Mining and Geology, Sts. Cyril and Methodius University, Štip, Republic of Macedonia*

<sup>2</sup>*Institute of Chemistry, Faculty of Science, Sts. Cyril and Methodius University, POB 162, MK-1001 Skopje, Republic of Macedonia; E-mail: trajcest@iunona.pmf.ukim.edu.mk*

**Abstract:** The method of inductively coupled plasma-atomic emission spectrometry (ICP-AES), is developed for determination of Cd, Co, Cr, Cu, Ni and Tl in traces in calcite and gypsum. The interferences of Ca as matrix element on Cd, Co, Cr, Cu, Ni and Tl intensities during their ICP-AES determination are investigated. The results reveal that Ca does not interfere on intensities of Cr, but tends to decrease the intensity of the other elements. To eliminate those matrix interferences of Ca on trace element intensities a flotation separation method is proposed. Lead(II) hexamethylenedithiocarbamate, Pb(HMDTC)<sub>2</sub>, is applied as a collector for flotation of trace elements from acidic solutions of mineral samples. The most suitable concentrations of calcite and gypsum solutions for flotation are ascertained. The detection limits of ICP-AES method following flotation of elements present in calcite and gypsum as impurities are determined: 0.022 and 0.061  $\mu\text{g}\cdot\text{g}^{-1}$  for Cd, 0.071 and 0.042  $\mu\text{g}\cdot\text{g}^{-1}$  for Co, 0.026 and 0.132  $\mu\text{g}\cdot\text{g}^{-1}$  for Cr, 0.164 and 0.149  $\mu\text{g}\cdot\text{g}^{-1}$  for Cu, 0.289 and 0.095  $\mu\text{g}\cdot\text{g}^{-1}$  for Ni and 0.645 and 0.766  $\mu\text{g}\cdot\text{g}^{-1}$  for Tl, respectively.

**Key words:** ICP-AES; cadmium; cobalt; chromium; copper; nickel; thallium; calcite; gypsum; matrix interferences; flotation separation; ICP-AES

### INTRODUCTION

The most of minerals occurring in the nature are not chemically pure substances. They contain extraneous substances. The knowledge of the kind and of elements incorporated in the structure of a natural mineral as impurities could help to answer on many questions about mineral deposit formation, its physical and chemical properties, crystalline deformations, *etc.* As trace elements present in natural structure essentially change the primary physical and chemical characteristics of minerals, they may limit their application for many useful purposes. Therefore, development of appropriate methods for determination of trace elements in minerals has a great importance.

ICP-AES has been used as a method for geological analysis (Walsh and Howie, 1986; Gomez Goedo and Vallie Frients, 1985; Fernandez Chanchez et al., 1984; Walsh, 1980; Russell et al., 1979). During ICP-AES determination of trace elements in calcite,  $\text{CaCO}_3$ , and gypsum,  $\text{CaSO}_4\cdot 2\text{H}_2\text{O}$ , the influence of Ca on intensities of analytes can be ex-

pected (Blades and Horlick, 1981; Maessen et al., 1982). To overcome this problem liquid-liquid extraction has been applied to separate trace elements from alkaline-earth metal matrix (Russell et al., 1979; Hoffer et al., 1984). The method presented here is the attempt to overcome this problem by removing calcium matrix interferences in some other new way using the adsorptive bubble technique called flotation as separation and preconcentration method.

The flotation began to be used for selective separation of valuable substances from ores and minerals a hundred years ago. Step by step, except for mining aims, this technique has found an application in other fields of chemical engineering for removal of harmful substances, microorganisms, suspended solids, *etc.* from waste, industrial, sea and drinking waters. Gradually, flotation has received an interest in analytical chemistry as separation and enrichment procedure (Mizuike, 1983; Kuzmin and Zolotov, 1988; Caballero et al., 1990). There are many flotation methods developed for

separation and preconcentration of trace elements from sea and fresh water (Mizuike, 1983; Kuzmin and Zolotov, 1988; Caballero et al., 1990; Nakashima and Yagi, 1983; Feng and Ryan, 1984; Cabezon et al., 1984; Stafilov and Čundeва, 1996, 1998; Čundeва and Stafilov, 1997; Pavlovska et al., 1998, 2001; Stafilov et al., 1998; Čundeва et al., 2000a; 2000b; Zendelovska et al., 2000), but there is no successful application for other type of samples. However, the developments of these new flotation methods for analyses of trace elements in water systems provide a lot of valuable experience, knowledge and consequently new ideas about further applications

of this adsorptive bubbles technique for analytical chemistry intentions. Using dithiocarbamates as very suitable colloid precipitate collectors for trace elements separation from aqueous solutions, it was found that alkaline-earth metals did not floated under the same conditions as all other heavy metals (Čundeва et al., 2000a; 2000b; Zendelovska et al., Pavlovska et al., 2001). Therefore, the idea of this study is to eliminate Ca from acidic aqueous solutions of minerals by means of  $Pb(HMDTC)_2$  as a flotation collector. After Ca flotation removing, correct ICP-AES analyses of Cd, Co, Cr, Cu, Ni and Tl in traces would be made.

## EXPERIMENTAL

### Apparatus

Inductively coupled plasma-atomic emission spectrometry (ICP-AES) was carried out by Varian spectrometer Model Liberty 110. Instrumentation and operating conditions for ICP-AES system are given in Table 1. The electrokinetic ( $\zeta$ ) potential of the surface particles of collector was determined electrophoretically by means a device analogous to

Chaikovskii's equipment (Eggert et al., 1960; Grigorov et al., 1964). The flotation cell, which served to separate the solid precipitate from water phase by means of air bubbles, was a glass cylinder ( $4 \times 105$  cm) with a sintered glass disc (porosity No. 4) at the bottom to generate gas bubbling. A pH Meter (Iskra, M 5705) with the combined glass electrode (Iskra, M 0101) was used for pH measurements.

Table 1

### Instrumentation and operating conditions for ICP-AES system

ICP system	Varian, Liberty 110						
<b>RF generator</b>							
Operating frequency	40.68 MHz						
Coupling	Direct Serial Coupling – DISC ( $\approx 70\%$ efficiency)						
Spectrometer							
Optical arrangement	Czerny Turner 0.75 m focal length						
Grating	Holographic						
Groove density	1800 Lines/mm						
<b>Introduction area</b>							
Sample Nebulizer	V- groove						
Spray Chamber	Inert Sturman-Masters						
Peristaltic pump	12 rollers, 1 turn/min increment						
<b>Conditions for program</b>							
RFG Power	1.0 kW	Pump speed	25 rpm				
Plasma Ar flow rate	15 L/min	Stabilization time	30 s				
Auxiliary Ar flow rate	1.5 L/min	Rinse time	30 s				
Nebulizer Ar flow rate	150 kPa	Sample delay	30 s				
Background correction	dynamic	High in plasma	Optimized on SBR				
<b>Conditions for line</b>							
El.	Wavelength/ nm	Search window/ nm	Integrated time	Replicates	Filter	Order	PMT/V
Tl	351.924	0.02	7	3	6	1	650
Ni	352.45	0.02	5	3	6	1	650
Cr	267.72	0.01	5	3	6	2	650
Cu	324.75	0.01	5	3	6	2	650
Cd	226.50	0.007	5	3	1	3	650
Co	228.62	0.007	5	3	6	1	650

The stock solutions of Cd, Co, Cr, Cu, Ni and Tl nitrates were prepared at a concentration of 1 g/L, using the highest grade (multielemental standards with concentration of 1000 µg/ml of each element) pure chemicals (Merck). Lead(II) stock solution was prepared as 1 g/l Pb(NO<sub>3</sub>)<sub>2</sub>. By diluting these stock solutions before each investigation working solutions were freshly prepared. A 0.1 mol/l solution of hexamethylenedithiocarbamate, HMDTC<sup>-</sup>, was made by dissolving an appropriate amount of the crystalline hexamethylenammonium-hexamethylenedithiocarbamate, HMA-HMDTC, in 96 % ethanol. Sodium dodecylsulfate, NaDDS, was made as 0.5 % ethanolic solution. Solution of HNO<sub>3</sub> (0.1 mol/l) and KOH (2.5 %, 5 % and 10 %) were used to adjust the pH of the media. The regulation of the ionic strength was performed by saturated solution of KNO<sub>3</sub>. A solution of 0.1 mol/l NH<sub>4</sub>NO<sub>3</sub> served to transfer quantitatively the contents of the beaker into the flotation cell. All aqueous solutions were prepared in deionized redistilled water.

### Procedure

*Calcite.* To obtain appropriate solution of natural mineral for flotation 0.5 g of powdered calcite sample was dissolved in of 12 ml of HNO<sub>3</sub> (1:1). Then, 3.5 ml of H<sub>2</sub>O<sub>2</sub> (30 %) were added and the mixture was evaporated near to dryness. Later, the residue was dissolved by 5 ml concentrated HNO<sub>3</sub>, diluted with redistilled water to 1 liter and then the solution was ready to be treated by flotation.

*Gypsum.* Powdered gypsum sample (0.4 g) was dissolved with 20 ml HNO<sub>3</sub> (1:1), and 12 ml of H<sub>2</sub>O<sub>2</sub> (30 %). The following procedure is the same as for calcite samples.

### Matrix interferences

To check the interferences of Ca as matrix elements, on the intensities of trace elements present in calcite and gypsum, series of solutions with the constant concentration of Cd, Co, Cr, Cu, Ni and Tl and different concentration of Ca were prepared. The amounts of these analytes, as well as the mass ratios calcium/analyte,  $m(\text{Ca})/m(\text{M})$ , were similar to those in the aqueous solutions of calcite

The procedure employed in this work has consisted of coprecipitation and flotation. During the coprecipitation (which was carried out in the beaker) element traces were incorporated in the collector particles, and then by flotation (which was performed in the flotation cell) they were separated from the water phase together with the collector.

*Coprecipitation:* A combined glass electrode is immersed into 1 liter of acidic solution of mineral. After adding 6 ml of saturated KNO<sub>3</sub> solution, 10 mg of Pb as Pb(NO<sub>3</sub>)<sub>2</sub> solution were introduced. The pH of the medium was carefully adjusted to 6.0 with KOH solutions (10, 5 and 2.5 % at the end). Next, 3 ml of 0.1 mol/l solution of HMDTC<sup>-</sup> was added to the system. A white precipitate of Pb(HMDTC)<sub>2</sub> was obtained. After 15 min stirring, 1 ml of NaDDS solution was added. The content of the beaker was removed quantitatively into the flotation cell by 5–6 ml of NH<sub>4</sub>NO<sub>3</sub> solution, 0.1 mol/l.

*Flotation:* A stream of numerous air bubbles, which effluxes from the bottom of the cell, was passed through the solution for 1 min by the speed of 50 ml·min<sup>-1</sup>. Gas bubbles separated the solid from the liquid phase of the system forming a layer (a mixture of coagulated precipitate and foam) at the top of the water column. The glass pipette-tube was immersed into the system through the scum and the processed aqueous solution was sucked off. By 5 ml of hot concentrated HNO<sub>3</sub> the solid phase remained in the cell was decomposed and dissolved. The cell and the pipette-tube were washed 3 times with 5 ml, 4 mol/l HNO<sub>3</sub> solution. The strong acidic solution was sucked off by vacuum through the bottom of the cell and collected in a volumetric bottle of 25 ml. The bottle was filled up to the mark with 4 mol/l HNO<sub>3</sub> and the sample was ready for ICP-AES measurements.

## RESULTS AND DISCUSSION

and gypsum. Then, analytes were tested by ICP-AES. The results are expressed as recoveries (R, %). The data show that Ca does not interfere on intensity of Cr, but there is the tendency of decreasing the intensities Cd, Co, Cu, Ni and Tl, which are present in minerals as trace impurities (Fig. 1). To overcome these interferences it is necessary to separate and preconcentrate trace elements from water solutions of minerals. For those purpose a flotation method using Pb(HMDTC)<sub>2</sub> as collector is suggested.

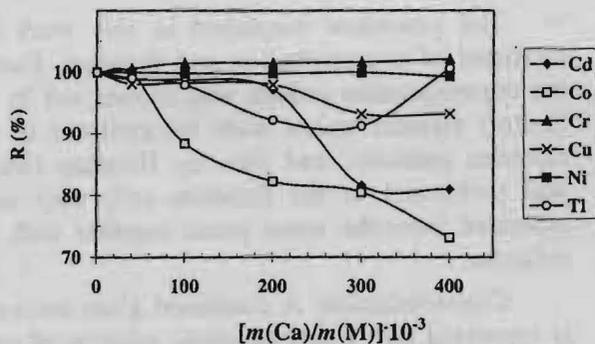


Fig. 1. Influence of Ca as matrix element on Cd, Co, Cr, Cu, Ni and Tl recoveries;  $m(\text{Ca})$  – mass of calcium;  $m(\text{M})$  – mass of metal investigated

### Selection of pH and ionic strength

The effective incorporation of trace elements in the precipitate of  $\text{Pb}(\text{HMDTC})_2$  and successful flotation separation depend of the correctly selected pH and ionic strength ( $I_c$ ) of the medium. For calcite and gypsum the values of pH and  $I_c$  were used from the results of the earlier investigations (Zendelovska et al., 2000). Therefore, the flotations of Cd, Co, Cr, Cu, Ni and Tl from acidic aqueous solutions of minerals investigated were performed at pH 6.0 and  $I_c$  0.02 mol/l, regulating by saturated solution of  $\text{KNO}_3$ .

### $\zeta$ potential of collector particle surface and choice of surfactant

A very important parameter, which can condition the choice of surfactant, is the electrokinetic or  $\zeta$  potential of the collector particle surfaces. Therefore, series of electrophoretic measurements of  $\zeta$  potential of the solutions with the new flotation collector  $\text{Pb}(\text{HMDTC})_2$  were performed.

The results of  $\zeta$  potential could be obtained within the pH interval where the system was in the colloid state. At the moment when the system reached the pH value at which its coagulation began (about 5.5), all further electrophoretic measurements using a device analogous to Chaikovskii's equipment were impossible. So the  $\zeta$  potential values of the  $\text{Pb}(\text{HMDTC})_2$  flocs had been obtained only for the pH's of 3.5 to 5.15. Within that pH range  $\text{Pb}(\text{HMDTC})_2$  flocs have  $\zeta$  potentials of 80.6 - 86.1 mV (Čundeveva et al., 2000b). The positive charge of the  $\zeta$  potentials signifies that the surfactant, which could be used for flotation, should have opposite charge *i.e.* should be anionic surfactant.

The experimental tests of the surfactants confirmed the suggestion of  $\zeta$  potential investigations. The anionic surfactants were the most suitable. Among all foaming reagents investigated, the recoveries obtained by the detergent NaDDS were the highest and this detergent was selected to be a reagent for flotation of calcite and gypsum.

### Detection limits

The limit of detection,  $LOD$ , of the method for each element was estimated as three values of the standard deviation,  $s$ , of the blank. For that purpose ten blanks were floated by the recommended procedure. Then the concentrations of analytes were determined by AES-ICP. The precision of the method was expressed by means of the relative standard deviations,  $sr$  (Table 2).

Table 2

Standard deviation,  $s$ , relative standard deviation,  $s_r$ , and detection limit,  $LOD$ , of AES-ICP method following flotation of trace elements present in calcite and gypsum

Element	Mineral	$s/\mu\text{g}\cdot\text{g}^{-1}$	$s_r(\%)$	$LOD/\mu\text{g}\cdot\text{g}^{-1}$
Cd	Gypsum	0.0069	4.41	0.022
	Calcite	0.0204	8.51	0.061
Co	Gypsum	0.0238	3.27	0.071
	Calcite	0.0140	4.68	0.042
Cu	Gypsum	0.0547	3.42	0.164
	Calcite	0.0498	4.44	0.149
Ni	Gypsum	0.0993	1.45	0.298
	Calcite	0.0316	0.87	0.095
Cr	Gypsum	0.0088	1.39	0.026
	Calcite	0.0440	7.54	0.132
Tl	Gypsum	2.1496	11.08	0.645
	Calcite	2.5523	11.07	0.766

### Trace elements in calcite and gypsum

After flotation preconcentration analytes were determined by AES-ICP. The method standard additions were used to verify the procedure. For that purpose known amounts of Cd, Co, Cr, Cu, Ni and Tl were added to aliquots of 1 g/l aqueous solution of calcite *i.e.* gypsum and then were determined by AES-ICP. The recovery of each heavy metal present in calcite and gypsum as impurity is higher than 95.0 %. Comparing the results obtained by calibration curves and those by the method of standard additions, it can be seen that they are equally

valid (Tables 3, 4). This is the proof that the recommended method for separation and preconcentration of analytes from aqueous solutions of minerals investigated was successful. The obtained

data for the same minerals are in agreement with those obtained by atomic absorption spectrometry (Stafilov and Lazaru, 1996; Lazaru and Stafilov, 1997; T. Stafilov and Zendelovska, 2000).

Table 3

*AES-ICP determinations of trace elements in calcite after separation and preconcentration by flotation with Pb(HMDTC)<sub>2</sub> verified by the method of standard additions*

Added m/μg·g <sup>-1</sup>	Estimated μg·g <sup>-1</sup>	Found μg·g <sup>-1</sup>	R %	Added m/μg	Estimated μg·g <sup>-1</sup>	Found μg·g <sup>-1</sup>	R %
Cd				Cr			
–	–	1.61	–	–	–	4.12	–
0.798	2.41	2.41	100.08	0.798	4.92	4.87	98.95
1.974	3.21	3.21	100.08	1.974	5.72	6.05	105.87
Co				Cu			
–	–	0.431	–	–	–	3.758	–
0.798	1.229	1.233	100.26	0.798	4.556	4.56	100.1
1.974	2.028	2.019	99.54	1.974	5.36	5.369	100.3
Ni				Tl			
–	–	0.661	–	–	–	15.32	–
0.798	1.459	1.546	105.95	7.987	23.308	23.467	100.68
1.974	2.258	2.236	99.01	15.974	31.296	31.884	101.88

Table 4

*AES-ICP determinations of trace elements in two types of gypsum (plate and stick) after separation and preconcentration by flotation with Pb(HMDTC)<sub>2</sub> verified by the method of standard additions*

Added m/μg	Estimated μg·g <sup>-1</sup>	Found μg·g <sup>-1</sup>	R %	Added m/μg	Estimated μg·g <sup>-1</sup>	Found μg·g <sup>-1</sup>	R %
Cd				Co			
Plate gypsum							
–	–	0.0533	–	–	–	0.693	–
1.009	1.062	1.054	99.27	1.009	1.702	1.682	98.85
2.002	2.070	2.038	88.396	2.002	2.711	2.694	99.38
Stick gypsum							
–	–	0.201	–	–	–	0.61	–
Cr				Cu			
Plate gypsum							
–	–	0.806	–	–	–	0.075	–
1.009	1.815	1.814	99.23	1.009	1.084	1.109	102.3
2.002	2.824	2.835	100.4	2.002	2.093	2.177	103.99
Stick gypsum							
–	–	0.79	–	–	–	0.05	–
Ni				Tl			
Plate gypsum							
–	–	1.35	–	–	–	62.75	–
1.009	2.360	2.449	103.7	10.09	72.89	73.42	100.73
2.002	3.369	3.283	97.43	20.17	82.98	83.72	100.89
Stick gypsum							
–	–	2.33	–	–	–	35.07	–