

APPLICATION OF COPRECIPITATE FLOTATION AS A METHOD FOR SELECTIVE SEPARATION OF TRACES OF Co, Cu, Ni AND Pb IN DOLOMITE AND GYPSUM AND THEIR DETERMINATION BY ETAAS

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Coprecipitate flotation technique is proposed as a method for selective separation of Co, Cu, Ni and Pb traces as impurities in dolomite and gypsum before their determination by electrothermal atomic absorption spectrometry (ETAAS). Iron(III) hexamethylenedithiocarbamate, Fe(HMDTC)₃, is used as a collector. The effect of hexamethylenedithiocarbamate (HMDTC⁻) amount on flotation recoveries of trace elements present in minerals is studied. The most appropriate surfactant and concentrations of mineral solutions for flotation were investigated because of the reaction of alkaline earth metals with the surfactant and the possibility of flotation suppression. The detection limits of ETAAS method following flotation are found to be 0.008 μg·g⁻¹ for Co, 0.002 μg·g⁻¹ for Cu, 0.006 μg·g⁻¹ for Pb and 0.008 μg·g⁻¹ for Ni.

Keywords: cobalt; copper; nickel; lead; determination; coprecipitate flotation; dolomite; gypsum; ETAAS

INTRODUCTION

Due to the long geological formation of minerals, it is impossible to discover them as absolutely pure species without any traces of extraneous substances in their structure. The traces of elements present in natural minerals as impurities can essentially change their primary physical and chemical characteristics and, consequently, may condition or limit their application in diverse industries. In addition, the kind and amount of impurities can indicate the way of mineral deposit formation. Therefore, the determination of the content of trace elements incorporated in the structure of minerals has a great importance.

Atomic absorption spectrometry (AAS) is one of the most frequently used methods dealing with determinations of trace elements in geological samples [1]. The interferences of matrix elements present in mineral are the main problem of this kind of trace analysis. Thus, during the investigations of trace elements included in dolomite, MgCa(CO₃)₂, and gypsum, CaSO₄·2H₂O, the influ-

ence of the alkaline earth metal (Ca and/or Mg) on their absorbance is possible [2, 3]. The previous papers [4–6] have also proved that these alkaline-earth metals interfere seriously on the determination of trace elements decreasing their absorbance during ETAAS. To overcome this problem, the method of liquid-liquid extraction was applied for separation of trace elements from the alkaline-earth element matrix [4–9]. In some cases diethyldithiocarbamate complexes for the extraction of trace elements from aqueous solution of dolomite [5, 6] or gypsum [7] in the organic phase of methylisobutyl ketone are proposed.

The method presented here is the attempt to eliminate the alkaline-earth metal matrix from dolomite and gypsum aqueous solutions in some other new way. Namely, more than a hundred years the adsorptive bubbles technique called flotation is used for selective separation of valuable substances from ores and minerals. Gradually, except for mining aims, this technique begins to be

used in other fields of chemical engineering for removal of toxic substances, suspended solids, microorganisms *etc.* from residual, industrial, sea and drinking waters. During the time the flotation methods began to be used for analytical chemistry purposes [10–12]. So today there are many flotation methods developed for separation and preconcentration of trace elements from sea and fresh water [10, 12–15], but there is not any successful application for other type of samples. Besides, the developments and studies of these new flotation methods for analysis of traces elements in water systems provide a lot of valuable experience, knowledge and consequently new ideas about further applications of these adsorptive bubbles techniques. Using dithiocarbamates as very suitable colloid precipitate collectors for trace element separation from aqueous solutions with different water hardness, it was found that alkaline-earth metals did not floated under the same conditions as all other heavy metals [16–20].

Therefore the intention of this study is to use a flotation as a procedure for selection of Co, Cu, Ni and Pb impurities in dolomite and gypsum be-

fore their ETAAS determination. Due to the fact that the chelate $\text{Fe}(\text{HMDTC})_3$ (Fig. 1) was shown as a very effective and successful coprecipitate collector for flotation of diverse microelements from waters [16–19], as well as from aragonite [21], it was chosen for the determination of Co, Cu, Pb and Ni impurities in dolomite and gypsum by ETAAS.

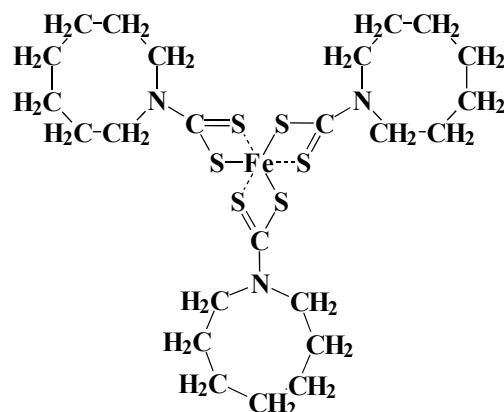


Fig. 1. Iron(III) hexamethylenedithiocarbamate, applied as a collector for trace elements flotation preconcentration

EXPERIMENTAL

Instrumentation

ETAAS determinations of trace elements were performed by Perkin–Elmer 1100 B spectrophotometer equipped with a graphite furnace HGA-700. Calcium and magnesium were deter-

mined by flame AAS (FAAS). Perkin-Elmer hollow cathode lamps were used as the radiation sources. Standard pyrolytically coated graphite tubes and platforms were used. All parameters for AAS determination are presented in Table 1.

Table 1

Instrumental parameters for AAS determination

ETAAS	Co	Pb	Cu	Ni
Wavelength, nm	240.7	283.3	327.4	232.0
Spectral bandpass, nm	0.7	0.5	0.5	0.7
Lamp current, mA	7	5	4	4
Calibration mode			Peak height	
Background correction			Deuterium	
Drying	100 °C, 25 s	100 °C, 25 s	100 °C, 25 s	100 °C, 25 s
Pyrolysis	900 °C, 25 s	900 °C, 20 s	400 °C, 20 s	900 °C, 20 s
Atomizing	2300 °C, 6 s	2300 °C, 6 s	2100 °C, 6 s	2400 °C, 6 s
Cleaning	2400 °C, 5 s	2400 °C, 5 s	2200 °C, 5 s	2500 °C, 5 s
Sheath gas			Argon	
FAAS		Ca		Mg
Wavelength, nm		422.7		285.2
Spectral banpass, nm		1.3		0.7
Lamp current, mA		10		15
Oxidant/Fuel gas mixture			Air/acetylene	

The pH readings were carried out with Iskra pH-Meter MA 5705 with a combined glass electrode (Iskra Model 0101). The flotation cell, which served to separate the solid precipitate from water phase by means of air bubbles, was a glass cylinder (4×105 cm) with a sintered glass disc (porosity No. 4) at the bottom to generate gas bubbling.

Reagents and samples

By dissolving an appropriate amount of analytical-reagent grade (Merck) $\text{Co}(\text{NO}_3)_2$, $\text{NiCl}_2 \cdot 8\text{H}_2\text{O}$, PbNO_3 , $\text{Ca}(\text{NO}_3)_2$ and $\text{Mg}(\text{NO}_3)_2$ in deionized redistilled water, stock solutions (1 g/l) of Co(II), Ni(II), Pb(II), Ca(II) and Mg(II) were prepared, respectively. The stock solution of Cu(II) was prepared as 1 g/l by dissolving 0.5 g high-purity copper metal (Merck) in concentrated HNO_3 (10 ml) and diluting to 0.5 l by water. Before each investigation, series of metal standard solutions were prepared by diluting these stock solutions. Iron(III) stock solution (30 mg/ml) was prepared as $\text{Fe}(\text{NO}_3)_3$ by dissolving the high-purity iron metal (Merck) in conc. HNO_3 . Diluting this stock solution, series of standards with a concentration of Fe(III) ranging from 2.5 to 100 mg/ml were obtained. The solution of hexamethylenammonium hexamethylenedithiocarbamate (HMA-HMDTC) was 0.1 mol/l in 95 % ethanol. Surfactants used in this study were sodium dodecylsulfate (NaDDS), sodium oleate (NaOL), sodium palmitate (NaPL), sodium stearate (NaST), benzethonium chloride (BTC), cetyltrimethylammonium bromide (CTAB) and triton X-100 (TX-100). NaDDS, NaOL, BTC and CTAB were used as 95 % ethanolic solutions. TX-100 was made as 0.5 % by dissolving appropriate amounts of surfactants in water, while NaPL and NaST in 99.7 % propan-2-ol. For pH adjustment solutions of HNO_3 (0.1 mol/l) and KOH (2.5 and 10 %) were used. The ionic strength (I_c) of the working solutions was regulated by saturated solution of KNO_3 . A solution of 0.1 mol/l NH_4NO_3 served to transfer quantitatively the contents of the beaker into the flotation cell.

The solution of dolomite and gypsum was prepared by dissolving 1 g powdered sample of each mineral in 20 ml concentrated HCl and 5 ml concentrated HNO_3 . A few drops of H_2O_2 (30 %) were added and the mixture was evaporated to near dryness. Then, the residue is dissolved in 5 ml

concentrated HCl and diluted by redistilled water to the volume of 1 liter.

Separation procedure

The separation procedure applied in this work consisted of coprecipitation and flotation. During the coprecipitation, carried out in the beaker, traces of cobalt, copper, lead and nickel were incorporated in the collector particles of $\text{Fe}(\text{HMDTC})_3$. During the flotation, performed in the flotation cell, they were separated from the water phase by air bubbles together with the collector precipitate.

Coprecipitation: A combined glass electrode is immersed into an acidic solution of dolomite *i.e.* gypsum (1 g/l). After adding 6 ml of saturated KNO_3 solution, 10 mg of Fe(III), as a solution of $\text{Fe}(\text{NO}_3)_3$, is put into the beaker and pH of the medium is carefully adjusted to 6.0 by KOH solutions. The yellow-brown precipitate of hydrated iron(III) oxide, $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$, is stirred about 5 minutes by means of a magnetic stirrer. Subsequently, 6 ml of 0.1 mol/l solution of HMA-HMDTC is added to the system. The precipitate gradually changed its color from yellow-brown to black color of $\text{Fe}(\text{HMDTC})_3$. After stirring for 15 minutes 1 ml of NaDDS solution is added. The content of the beaker is transferred quantitatively into the flotation cell using small portions of 0.1 mol/l NH_4NO_3 .

Flotation: A stream of numerous air bubbles (which effluxes from the bottom of the cell with the speed of 50 ml/min) is passed through the solution for 1 min. Gas bubbles raised the black precipitate flakes to the water phase surface. There a frothy layer is formed and the water in the cell became completely clear and free of solid particles. Then, the glass pipette-tube is immersed into the cell through the layer on the liquid surface (a mixture of coagulated precipitate and surfactant foam) and the water phase is sucked off. The solid phase remained in the cell is decomposed by 5 ml hot concentrated HNO_3 . When the liquid in the cell becomes clear yellow, it is sucked off through the bottom of the cell and collected in a volumetric bottle of 25 ml. The cell and the pipette-tube are washed with 4 mol/l HNO_3 solution. The flask is filled up to the mark with 4 mol/l HNO_3 and the sample is ready for AAS measurements.

RESULTS AND DISCUSSION

Matrix interferences on absorbance of trace elements investigated

On account of a high amount of calcium in gypsum, as well as calcium and magnesium concentrations in dolomite, there is a great possibility of their interferences on Co, Cu, Pb and Ni during ETAAS determinations. For that reason it was necessary to examine the influence of these two alkaline earth metals as matrix elements on the magnitude of absorbances of each trace element investigated. Thus, series of solutions with constant concentrations of Co, Cu, Pb and Ni and different calcium *i.e.* magnesium concentrations were prepared

and then tested by ETAAS. The concentration of analytes in the solutions was similar to their concentrations in the sample solutions of minerals.

As it can be seen (Fig. 2), calcium present in higher concentration tends to decrease the absorbance of Co, Cu, Pb and Ni. The influence of magnesium mass on Co, Cu and Ni absorbance is insignificant (Fig. 3), while Pb absorbance suffers the most notable interference. Consequently, to eliminate the matrix interferences on microelements during their ETAAS determination, flotation is proposed as a method for separation of trace elements from water solutions of dolomite and gypsum.

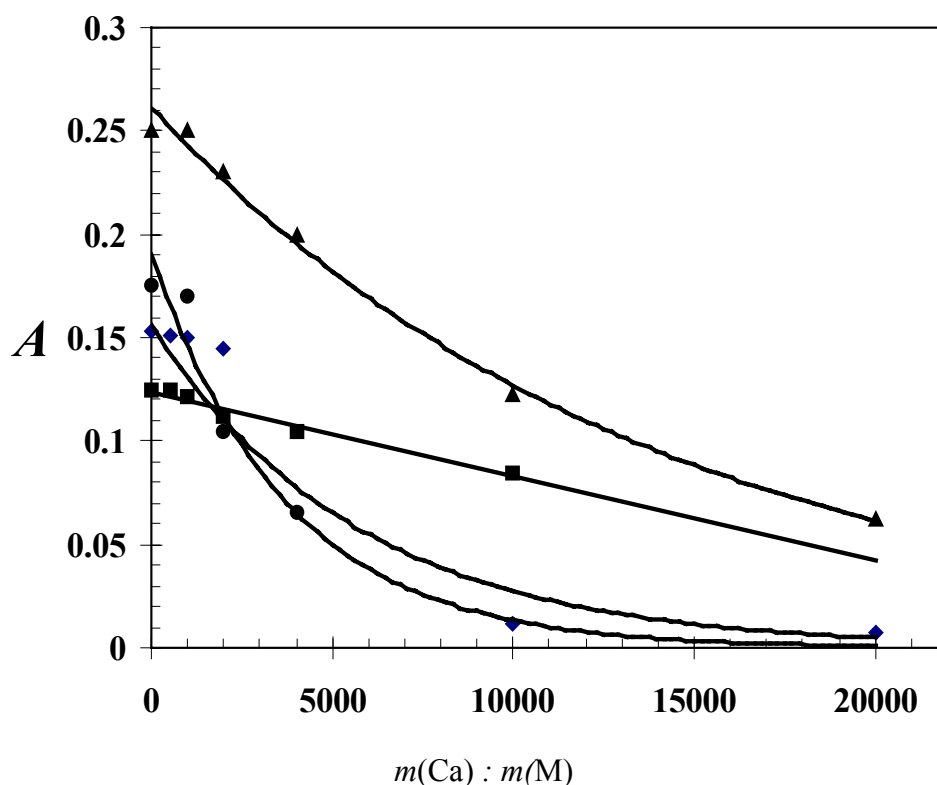


Fig. 2. Influence of Ca as a matrix element on absorbance of Co (—◆—), Cu (—■—), Pb (—▲—) and Ni (—●—); $m(\text{M})$ – trace element mass

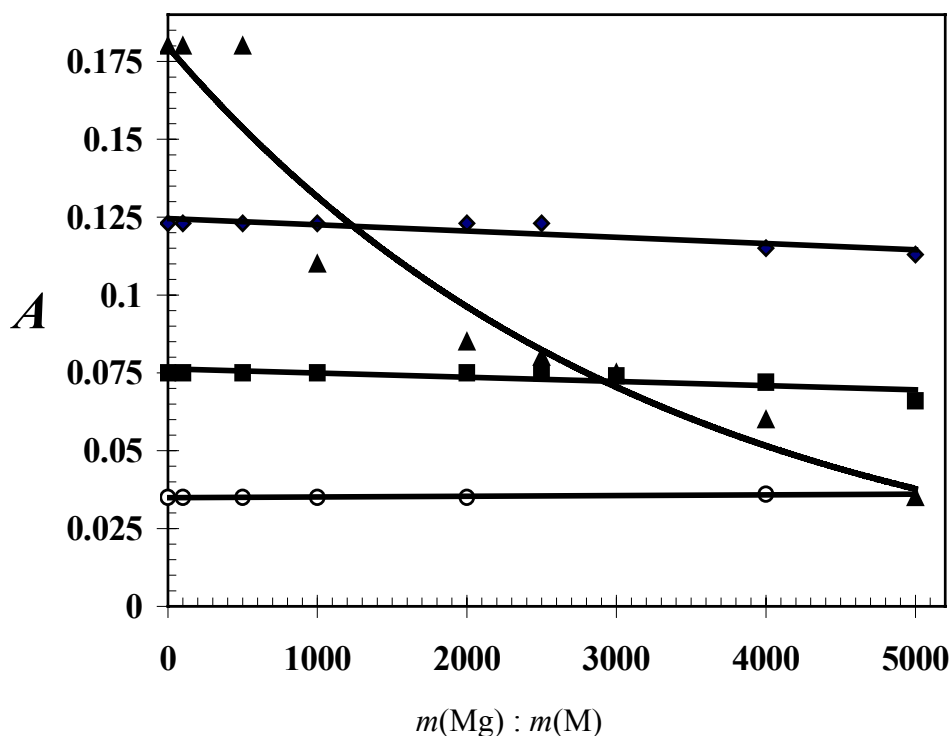


Fig. 3. Influence of Mg as a matrix element on absorbance of Co (—◆—), Cu (—■—), Pb (—▲—) and Ni (—●—); $m(\text{M})$ – trace element mass

Selection of pH and ionic strength of medium

The pH and ionic strength (I_c) of the medium were shown as very important variables for coprecipitation of trace elements in precipitate of $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ and $\text{Fe}(\text{HMDTC})_3$, as well as for flotation separation. For dolomite and gypsum the values of pH and I_c were used from the results of the earlier investigations [17]. Therefore, the flotation of Co, Cu, Pb and Ni from the aqueous solutions of minerals investigated was performed at pH 6.0 and I_c 0.02 mol/l, regulating by saturated solution of KNO_3 .

Influence of dithiocarbamate on flotation process

The previous studies of trace elements flotation in natural water samples [16–20] have shown that dithiocarbamates applied as collectors can have a significant influence on the values of investigated analyte recoveries. So the effect of

HMDTC^- on flotation recoveries of microelements enclosing in the structure of dolomite was studied, floating series of solutions (1 liter) containing mixture of 0.2 g calcium and 0.1 g magnesium. To each solution a different amount of HMDTC^- (0.13–0.6 mmol) was added, while pH (6.0), I_c (0.02 mol/l), Fe(III) mass (10 mg) were kept constant (Fig. 4) The mass of iron (10 mg) for these investigations was accepted from the previous studies [16, 17]. To ascertain the influence of HMDTC^- on flotation separation of analytes present in gypsum, solutions containing 0.2 g/l calcium were floated under the same conditions as in the case of dolomite (Fig. 5).

The results show that the addition of more amount of dithiocarbamate raises the recoveries values of all trace elements investigated (Figs. 3 and 4). When larger quantities of HMDTC^- were put into the reaction system, trace elements of minerals floated better reaching significant recoveries of 97.4 to 100.0 %. Thus 0.6 mmol of HMDTC^- was chosen for flotation procedure.

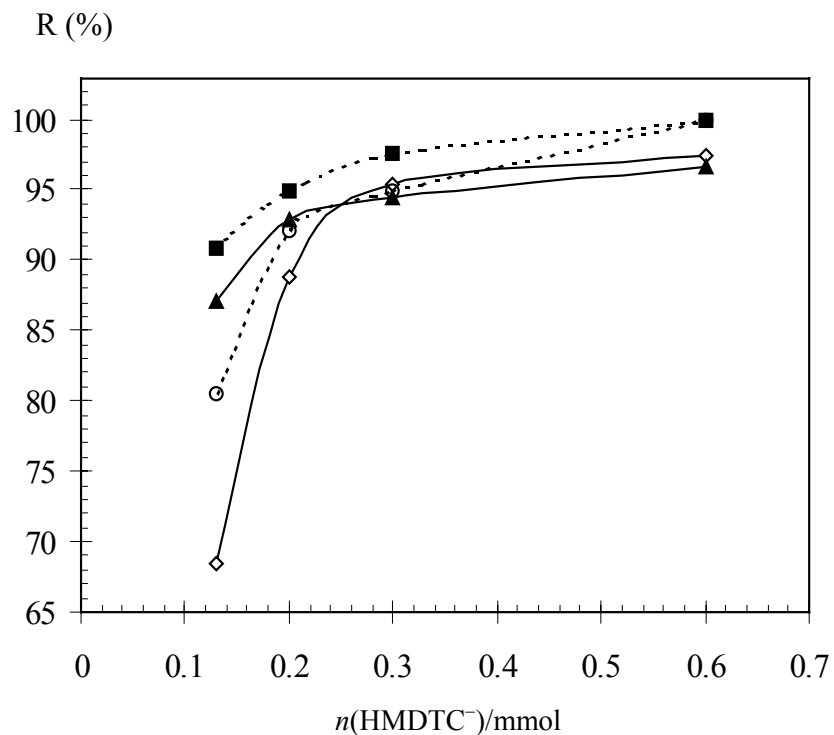


Fig. 4. Effect of $n(\text{HMDTC}^-)$ on flotation recoveries (R) of Co (—◆—), Cu (—○—), Pb (—▲—) and Ni (—■—) in dolomite ($\text{pH} = 6.0$, $I_c = 0.02 \text{ mol/l}$, 10 mg of iron added to 1 liter of solution containing 1 g dolomite)

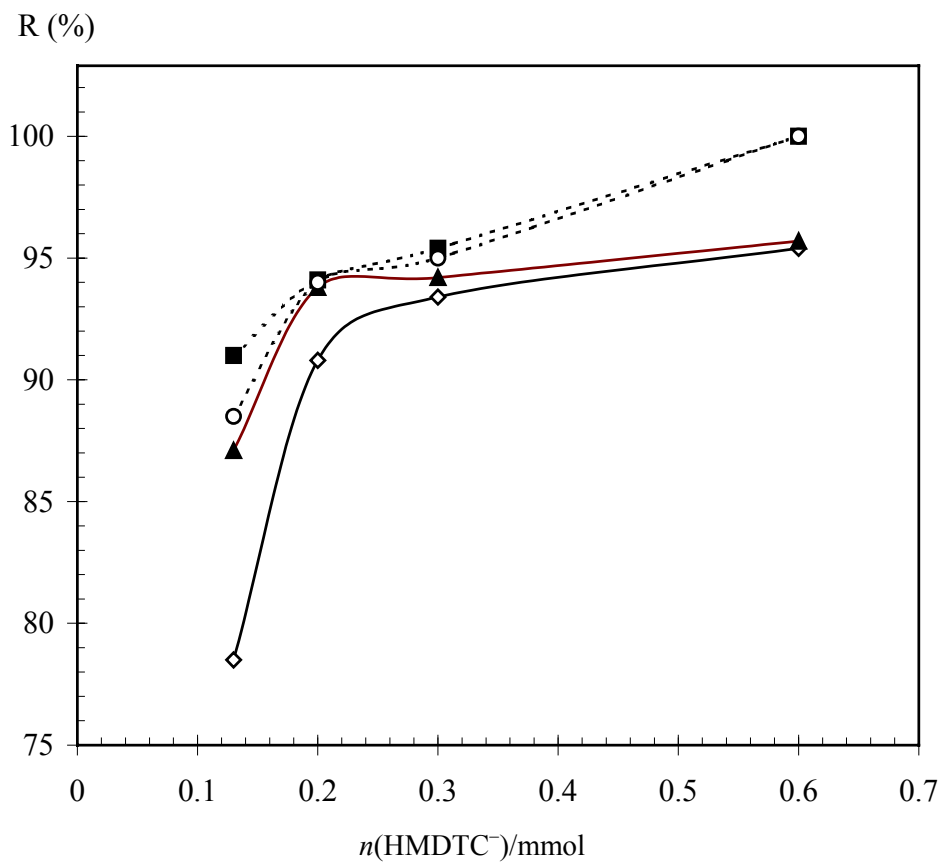


Fig. 5. Effect of $n(\text{HMDTC}^-)$ on flotation recoveries (R) of Co (—◆—), Cu (—○—), Pb (—▲—) and Ni (—■—) in gypsum ($\text{pH} = 6.0$, $I_c = 0.02 \text{ mol/l}$, 10 mg of iron added to 1 liter of solution containing 1 g gypsum)

Concentration of alkaline-earth metals and flotation process

To perform a more effective flotation separation of desired species the introduction of foaming reagent was necessary. Nevertheless, if calcium and magnesium ions are present in higher concentrations in the system, the reaction among them and surfactant anions will be possible, what could repress the process of flotation separation. Therefore it would be necessary to ascertain the most appropriate concentration of dolomite *i.e.* gypsum solution for flotation. For this purpose series of solutions with different mass of dolomite and gypsum (5.0, 4.0, 3.0, 2.0 and 1.0 g/l) were prepared according to the proposed procedure of the experimental part. Dolomite solutions contained 1.09, 0.87, 0.65, 0.43 and 0.22 g/l calcium *i.e.* 0.66, 0.53, 0.40, 0.26 and 0.13 g/l magnesium. The calcium concentrations in gypsum solutions were 1.16, 0.93, 0.70, 0.47 and 0.23 g/l. After treating of these solutions by the recommended procedure, it was evident that very high masses of calcium and magnesium had no significant effect on the formation of $\text{Fe}(\text{HMDTC})_3$ precipitate during the step of coprecipitation, but had a negative effect on the process of flotation separation. The dolomite solutions by calcium concentration of 1.09 to 0.43 g/l and magnesium concentration of 0.66–0.26 g/l could not be floated. The solutions of gypsum with calcium concentration of 1.16 to 0.47 g/l had not floated either. The enlarging of amount of NaDDS and HMDTC⁻ had not any influence on flotation efficiency. Consequently, it was ascertained that the concentration of 1 g/l dolomite *i.e.* gypsum was the most suitable concentration for flotation of the aqueous solution of dolomite and gypsum.

However, the solution of dolomite *i.e.* gypsum prepared as 1 g/l yet contained a lot of calcium and magnesium. To find out what happened with these macro metals during the process of separation, the concentrations of calcium and magnesium in the final solutions concentrated by flotation were determined by FAAS and their recoveries were estimated. According to the data of these investigations (recoveries for calcium 0.63, 1.07 % and for magnesium 1.01 %), it was clear that these macro metals could not be separated from the aqueous solutions under conditions recommended for cobalt, copper, lead and nickel (Table 2). Their quantities present in the final solutions, preconcentrated by the flotation method, are such that they could not cause any interference on absorbances of

microelements during their ETAAS determinations.

Table 2

Recovery (R) of calcium and magnesium present in dolomite and gypsum: pH 6.0; I_c 0.02 mol/l; 10 mg/l of Fe; 0.6 mmol/l HMDTC⁻; 1 ml 0.5 % solution of NaDDS.

Sample of mineral	Before flotation	After flotation	Flotability
	mg/l Ca	mg/l Ca	R (%)
Dolomite	220 ^a	1.39	0.63
Gypsum	230 ^b	2.46	1.07
	mg/l Mg	mg/l Mg	R (%)
Dolomite	130 ^c	1.31	1.01

^{a, b}Concentration of Ca estimated in 1 g of dolomite or gypsum.

^cConcentration of Mg estimated in 1g of dolomite.

Selection of foaming reagent

To select the most appropriated foaming reagent for procedure, several surfactants were tested at pH 6.0 and I_c 0.02 mol/l. Each 1 liter solution was floated by 10 mg of Fe(III), 0.6 mmol HMDTC⁻ and 1 ml of 0.5 % solution of surfactant.

The cationic surfactants BTC and CTAB, as well as non-ionic tenside TX-100, were shown as useless (Table 3). They frothed well at pH 6.0, but they could not help to separate the solid phase of the system from the water phase. Abundant white foam was formed at the surface of the water, but the black precipitate of $\text{Fe}(\text{HMDTC})_3$ remained in the liquid phase in the flotation cell. These investigations suggest that the surface of $\text{Fe}(\text{HMDTC})_3$ particles might be the same charge as the cationic surfactants.

Anionic surfactants were investigated singly (NaDDS, NaOL, NaPL and NaST) and in pair (NaDDS/NaOL, NaPL/NaOL and NaST/NaOL). Among them NaDDS as a single reagent has been shown as the most effective (96.7 - 98.8 % for Co, 100.0 % for Cu, 98.0 - 100.0 % for Pb and 96.7 - 97.8 % for Ni). The explanation is the nature of NaDDS. It is a detergent whose calcium and magnesium salts are soluble in water media, that provides a good foaming and effective flotation. Therefore, it was selected to be a foaming reagent for the method. The recoveries obtained by the pair NaDDS/NaOL (96.0 - 96.0 %) were also satisfac-

tory, but this combination of surfactants gave unnecessarily too copious scam, which was very difficult to destroy with conc. HNO_3 . When NaDDS was used as a single reagent, the destroying of the scam was easier.

Table 3

Applicability of divers surfactants for flotation separation of trace elements in dolomite and gypsum expressed as flotation recovery effectiveness (R) at constant pH (6.0), I_c (0.02 mol/l) with 10 mg iron and 0.6 mmol HMDTC⁻

Dolomite	Co	Cu	Pb	Ni
Cationic surfactants				
R (%)				
BTC	Foam, no flotation			
CTAB	Foam, no flotation			
Anionic surfactants				
R (%)				
NaDDS	98.8	100.0	100.0	97.8
NaOL	90.4	94.1	95.1	89.9
NaPL	71.4	92.0	82.0	53.3
NaST	71.3	83.1	80.1	64.5
Non-ionic surfactants				
R (%)				
TX-100	Foam, no flotation			
Pairs of anionic surfactants				
R (%)				
NaDDS/NaOL	95.7	100.0	94.4	95.3
NaST/NaOL	72.4	93.6	72.8	85.7
NaPL/NaOL	91.4	95.5	88.3	91.3
Gypsum	Co	Cu	Pb	Ni
Cationic surfactants				
R (%)				
BTC	Foam, no flotation			
CTAB	Foam, no flotation			
Anionic surfactants				
R (%)				
NaDDS	96.7	100.0	98.0	96.7
NaOL	92.4	95.1	94.1	90.1
NaPL	61.9	94.0	89.0	63.3
NaST	71.3	84.1	93.1	84.5
Non-ionic surfactants				
R (%)				
TX-100	Foam, no flotation			
Pairs of anionic surfactants				
R (%)				
NaDDS/NaOL	88.7	100.0	98.4	95.4
NaST/NaOL	72.4	92.4	96.4	93.7
NaPL/NaOL	94.4	94.9	95.4	92.3

Detection limit

To determine the standard deviations of the method, ten blanks were floated by the recommended procedure and then the concentration of cobalt, copper, lead and nickel was determined by ETAAS. The detection limit (L_d) of the method was estimated as three values of the standard deviation (s) of the blank. The precision of the method was expressed by means of the relative standard deviation (s_r). The values of these parameters are presented in Table 4.

Table 4

Standard deviation (s), relative standard deviation (s_r) and detection limit (w_L) of ETAAS method following flotation separation of cobalt, copper, lead and nickel from dolomite and gypsum

Element	$s/\mu\text{g}\cdot\text{g}^{-1}$	s_r (%)	$w_L/\mu\text{g}\cdot\text{g}^{-1}$
Co	0.0028	2.48	0.0084
Cu	0.0007	4.99	0.0021
Pb	0.0020	4.37	0.0060
Ni	0.0027	3.99	0.0081

Analysis of trace elements in minerals

After flotation in accordance with the proposed procedure, ETAAS determination of analytes was performed using a calibration curve. To verify the method to 1 liter aliquots of the aqueous solution containing 1 g of mineral known amounts of Co, Cu, Pb and Ni were added. Both measurements (by the calibration curve and by standard additions) seem to be equally valid (Tables 5 and 6). The recoveries of dolomite analysis (98.6 – 99.5 % for Cu, 98.0 – 99.4 % for Pb and 99.9 – 99.7 % for Ni), as well as those of gypsum determinations (100.0 % for Co, 98.4 – 99.1 % for Cu and 99.7 – 99.4 % for Ni) show that the separation of these analytes using the proposed method of flotation is satisfactory.

The method was also checked by its application on dolomite (GBW 07114) and limestone (NIST 88 b) reference materials (Table 7). It can be seen that values obtained by flotation method are similar to the certified values.

Table 5

Results of ETAAS determinations of trace elements in dolomite after flotation separation by the method of calibration curve and standard additions

Cu			
Added $m(\text{Cu})/\mu\text{g}$	Estimated $\mu\text{g}\cdot\text{g}^{-1}\text{ Cu}$	Found $\mu\text{g}\cdot\text{g}^{-1}\text{ Cu}$	R (%)
–	–	0.35	–
0.50	0.85	0.84	98.6
1.00	1.35	1.34	99.5
Pb			
Added $m(\text{Pb})/\mu\text{g}$	Estimated $\mu\text{g}\cdot\text{g}^{-1}\text{ Pb}$	Found $\mu\text{g}\cdot\text{g}^{-1}\text{ Pb}$	R (%)
–	–	2.38	–
5.00	7.38	7.23	98.0
10.00	12.38	12.30	99.4
Ni			
Added $m(\text{Ni})/\mu\text{g}$	Estimated $\mu\text{g}\cdot\text{g}^{-1}\text{ Ni}$	Found $\mu\text{g}\cdot\text{g}^{-1}\text{ Ni}$	R (%)
–	–	4.37	–
25.0	29.37	29.33	99.9
50.0	54.37	54.21	99.7

Table 6

Results of ETAAS determinations of trace elements in gypsum after flotation separation by the method of calibration curve and standard additions

Co			
Added $m(\text{Co})/\mu\text{g}$	Estimated $\mu\text{g}\cdot\text{g}^{-1}\text{ Co}$	Found $\mu\text{g}\cdot\text{g}^{-1}\text{ Co}$	R (%)
–	–	0.20	–
0.50	0.70	0.70	100.0
1.00	1.20	1.20	100.0
Cu			
Added $m(\text{Cu})/\mu\text{g}$	Estimated $\mu\text{g}\cdot\text{g}^{-1}\text{ Cu}$	Found $\mu\text{g}\cdot\text{g}^{-1}\text{ Cu}$	R (%)
–	–	0.11	–
0.50	0.61	0.60	98.4
1.00	1.11	1.10	99.1
Ni			
Added $m(\text{Ni})/\mu\text{g}$	Estimated $\mu\text{g}\cdot\text{g}^{-1}\text{ Ni}$	Found $\mu\text{g}\cdot\text{g}^{-1}\text{ Ni}$	R (%)
–	–	1.26	–
2.5	3.76	3.75	99.7
5.0	6.26	6.22	99.4

Table 7

Determination of Co, Ni, Pb and Cu in referent standards samples (given in $\mu\text{g}/\text{g}$)

Co		Cu		Pb		Ni	
GBW 07114							
Certified	Found	Certified	Found	Certified	Found	Certified	Found
3.88	3.75	241	232	4.44	4.50	30.2	27.5
NIST 88b							
Certified	Found	Certified	Found	Certified	Found	Certified	Found
1.02	1.07	–	–	–	–	–	–

CONCLUSION

On the basis of our previous experiences of determination of trace elements in natural waters by flotation and taking into account the similar properties of water systems with a higher concentration of calcium and magnesium and those of diluted aqueous solutions of dolomite and gypsum, ETAAS methods for determination of trace impuri-

ties of Co, Cu, Pb and Ni were developed. It was proved that copper, lead and nickel included in dolomite, and cobalt, copper and nickel present in gypsum can be separated successfully from alkaline-earth matrices by the precipitate flotation procedure using $\text{Fe}(\text{HMDTC})_3$ as a collector. In that way the possible interferences during ETAAS are

avoided. The investigations in the frame of this work show that Co, Cu, Pb and Ni in traces can be floated simultaneously at pH 6.0, I_c 0.02 mol/l by addition of 10 mg of Fe(III) and 0.6 mmol of HMDTC⁻ to 1 liter of acidic solution of mineral with

a concentration of 1 g/l. The achieved flotation recoveries of about 100.0 % verify the proposed method and indicate that it could be applied for analysis of other trace metals included in the structure of other calcium and magnesium minerals.

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Резиме

ПРИМЕНА НА ТАЛОЖНАТА ФЛОТАЦИЈА КАКО МЕТОД ЗА СЕЛЕКТИВНА СЕПАРАЦИЈА НА ТРАГИ ОД Co, Cu, Ni И Pb ВО ДОЛОМИТ И ГИПС И НИВНО ОПРЕДЕЛУВАЊЕ СО ЕТААС

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Клучни зборови: кобалт; бакар; никел; олово; определување; таложна флотација; доломит; гипс; ЕТААС

Таложната флотација е предложена како метод за сепарирање на траги од Co, Cu, Ni и Pb во доломит и гипс и нивно определување со електротермичка атомска апсорпциона спектрометрија (ЕТААС). Како колектор се користи железо(III)хексаметилентетраамин, Fe(HMDTC)₃. Испитуван е ефектот на количеството на хексаметилентетрааминот (HMDTC⁻) на флотационите извлекувања на елементите во траги присутни во

минералите. Испитувана е примената на различни тензиди, како и нивната концентрацијата во растворите за флотација поради реакцијата на земноалкалните метали со тензидите и можноста од супресија врз самата флотација. Границата на детекција за определување на испитуваните елементи со ЕТААС изнесува: 0,008 $\mu\text{g}\cdot\text{g}^{-1}$ за Co, 0,002 $\mu\text{g}\cdot\text{g}^{-1}$ за Cu, 0,006 $\mu\text{g}\cdot\text{g}^{-1}$ за Pb и 0,008 $\mu\text{g}\cdot\text{g}^{-1}$ за Ni.