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Determination of trace elements in dolomite and gypsum by atomic absorption spectrometry: overcoming the matrix interference by flotation separation

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Abstract

The interferences of Ca and Mg as matrix elements in dolomite and gypsum on Ag, Cd, Cr, Mn, Tl and Zn absorbances during their electrothermal atomic absorption spectrometric (ETAAS) determination are investigated. The results reveal that Ca and Mg do not interfere on Zn and Mn, tend to decrease absorbances of Ag, Cd and Cr, while Tl suffers the most significant influence. A flotation separation method is proposed to eliminate matrix interferences. Hydrated iron(III) oxide, $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$, and iron(III) hexamethylenedithiocarbamate, $\text{Fe}(\text{HMDTC})_3$, are applied as flotation collectors. The influence of hydrophobic dithiocarbamate anion, HMDTC, on flotation recoveries of each analyte is studied. The most suitable concentrations of dolomite and gypsum solutions for flotation are determined. To avoid flotation suppression due to the reaction of Ca^{2+} and Mg^{2+} with surfactant ions, a fit foaming agent was selected. The elements present in dolomite and gypsum as traces have been analyzed by ETAAS. Their ETAAS limits of detection following flotation are found to be $0.021 \mu\text{g} \cdot \text{g}^{-1}$ for Ag, $0.019 \mu\text{g} \cdot \text{g}^{-1}$ for Cd, $0.014 \mu\text{g} \cdot \text{g}^{-1}$ for Cr and $0.11 \mu\text{g} \cdot \text{g}^{-1}$ for Tl. The determination of Mn and Zn can be performed by flame AAS (FAAS). The limit of detection for Mn is $1.5 \mu\text{g} \cdot \text{g}^{-1}$, while for Zn $0.8 \mu\text{g} \cdot \text{g}^{-1}$. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Trace elements; Matrix interferences; Dolomite; Gypsum; Flotation separation; AAS; Determination

1. Introduction

The knowledge of the type and amount of trace elements incorporated in the structure of a natural mineral could help to answer many questions about

mineral deposit formation, its physical and chemical properties, crystalline deformations, etc. Because trace elements present in the natural structure basically change the primary physical and chemical characteristics of the minerals, they may limit its application for many useful purposes. Therefore, development of appropriate methods for determination of trace elements in mineral matrices is of great importance.

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Table 1
Instrumental parameters for AAS determination

ETAAS	Ag	Cd	Cr	Tl
Wavelength (nm)	328.1	228.8	357.9	276.8
Spectral bandpass (nm)	0.7	0.7	0.7	0.2
Lamp current (mA)	10	4	25	20
Calibration mode		Peak height		
Background correction		D ₂		
Drying (°C, s)	100, 30	100, 30	100, 25	100, 25
Pyrolysis (°C, s)	500, 25	300, 25	1100, 20	400, 30
Atomizing (°C, s)	2000, 5	1800, 5	2500, 5	2200, 5
Cleaning (°C, s)	2650, 5	2650, 5	2650, 5	2650, 5
Sheath gas		Argon		
FAAS	Ca	Mg	Mn	Zn
Wavelength (nm)	422.7	285.2	279.5	213.9
Spectral bandpass (nm)	2.0	2.0	0.7	0.7
Lamp current (mA)	7	15	10	15
Oxidant/fuel gas mixture		Air/acetylene		

Atomic absorption spectrometry (AAS) is one of the most frequently used methods for determination of trace elements in mineral samples [1]. In the case of dolomite, $\text{MgCa}(\text{CO}_3)_2$, and gypsum, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, the influence of alkaline earth metals (Ca and/or Mg) on absorbances of trace elements is well known [2–8]. To overcome this problem, liquid–liquid extraction [3–7,9–13] was applied and trace elements were separated from the alkaline-earth metal matrix. The method presented in this work, the adsorptive bubble technique called flotation, is an attempt to overcome calcium and magnesium matrix interferences in trace elements present in dolomite and gypsum in some other new way.

Flotation started 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 applications 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, also [14–16]. There are many flotation methods developed for the separation and preconcentration of trace elements from sea and fresh water [14–28], but there is no successful application for other type of samples. However, developments of these new flotation

methods for determination of trace elements in water systems provide a lot of valuable experience and knowledge, and consequently new ideas about further applications of this technique for analytical chemistry. Using dithiocarbamates as very suitable colloid precipitate collectors for trace elements separation from aqueous solutions with different water hardness, it was found that alkaline-earth metals did not float under the same conditions as all other heavy metals [25–28]. Correspondingly, the aim of this study is to separate Ca and Mg matrices from Ag, Cd, Cr, Mn, Tl and Zn, treating acidic aqueous solutions of dolomite and gypsum by flotation, and then make analyses by AAS.

2. Experimental

2.1. Apparatus

A Perkin-Elmer 1100 B spectrometer (Norwalk, USA) equipped with a graphite furnace HGA-700 and Ag, Ca, Cd, Cr, Mg, Mn, Tl and Zn hollow cathode lamps was used for AAS measurements. Instrumental parameters for flame atomic absorption spectrometry (FAAS), as well as for electrothermal atomic absorption spectrometry (ETAAS) were established by extensive testing (Table 1). Standard pyrolytically coated graphite tubes and platforms were used. 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. A pH Meter (Iskra, M 5705, Slovenia) with a combined glass electrode (Iskra, M 0101, Slovenia) was used for pH measurements.

2.2. Reagents and standards

Stock solutions of Ag, Ca, Cd, Cr, Mg, Mn, Tl and Zn nitrates were prepared at a concentration of $1 \text{ g} \cdot \text{l}^{-1}$, using the highest grade pure chemicals (Merck, Germany). Working standards were prepared by diluting stock solutions. The 30 mg ml^{-1} solution of Fe was prepared as $\text{Fe}(\text{NO}_3)_3$ by dissolving of high-purity iron (Merck) in concentrated HNO_3 . A series of standards with a concentration of Fe ranging from 2.5 to 100 mg ml^{-1} were obtained by diluting this stock solution. A solution of HMDTC[−] as $0.01 \text{ mol} \cdot \text{l}^{-1}$ was made by dissolving hexamethylenammonium hexamethylenedithiocarbamate [29] in 96% ethanol. The foaming reagents tested for the procedure 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% aqueous, while NaPL and NaST as 99.7% propan-2-olic solutions. To adjust the pH of the medium, solutions of HNO_3 (0.1 mol l^{-1}) and KOH (2.5 and 5%) were used. The ionic strength was regulated by saturated solution of KNO_3 . A solution of $0.1 \text{ mol} \cdot \text{l}^{-1}$ NH_4NO_3 served to transfer quantitatively the contents of the beaker into the flotation cell.

To obtain a solution of the natural mineral, 1 g of powdered dolomite or gypsum sample was dissolved in a mixture of 20 ml of concentrated HCl and 5 ml of concentrated HNO_3 . Then, 1–2 ml of H_2O_2 (30%) were added and the mixture was evaporated near to dryness. Later, the residue was dissolved with 5 ml concentrated HCl, diluted with redistilled water to 1 l. The obtained solution is then ready for flotation.

2.3. Flotation procedure

A combined glass electrode was immersed into 1 l of dolomite or gypsum solution. After adding 6 ml of saturated KNO_3 solution, 10 mg of Fe as $\text{Fe}(\text{NO}_3)_3$ solution were introduced and the pH of the medium was carefully adjusted to 6.0 with KOH solutions (5% and 2.5% at the end). The red-brown precipitate of $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ was stirred for approximately 5 min by means of a magnetic stirrer. Subsequently, 6 ml of $0.1 \text{ mol} \cdot \text{l}^{-1}$ solution of HMDTC[−] was added to the system and the black precipitate of $\text{Fe}(\text{HMDTC})_3$ was formed. After a 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_4NO_3 solution. Then, a stream of air bubbles, which effluxes from the bottom of the cell, was passed through the solution for 1 min with a flow of 50 ml/min. Gas bubbles ensure the separation of the solid from the liquid phase 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. The solid phase remained in the cell was decomposed and dissolved with 5 ml of hot concentrated HNO_3 . The strong acidic solution was sucked off by a vacuum through the bottom of the cell and collected in a 25-ml volumetric flask. The cell and the pipette-tube were washed with 4 mol l^{-1} HNO_3 solution. The bottle was filled up to the mark with 4 mol l^{-1} HNO_3 and the sample was ready for AAS measurements.

3. Results and discussion

3.1. Matrix interferences

To check the influence of Ca and Mg on the absorbance of trace elements present in the minerals as impurities, series of solutions with the constant concentration of Ag, Cd, Cr, Mn, Tl and Zn and different concentration of Ca and Mg were prepared. The amounts of these analytes, as well as the mass ratios calcium/analyte, $m(\text{Ca})/m(\text{M})$, and magnesium/analyte, $m(\text{Mg})/m(\text{M})$, were similar to those in the aqueous solutions of natural

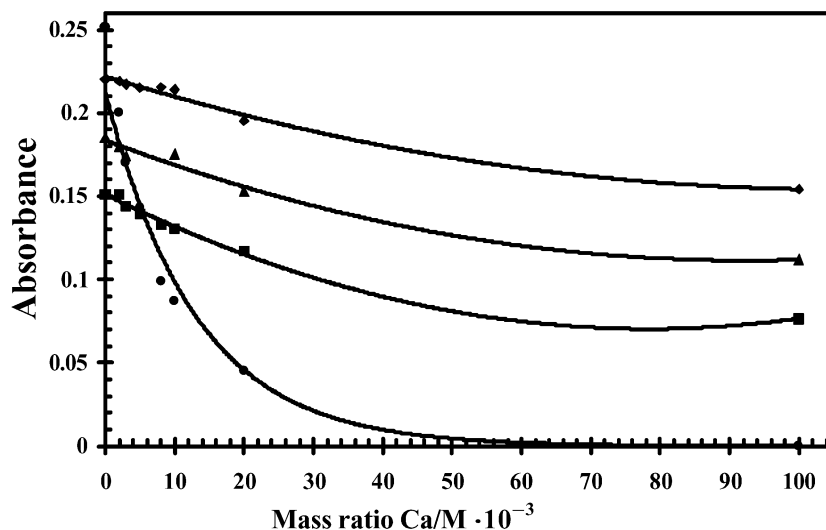


Fig. 1. Influence of Ca as matrix element on Ag (♦) Cd (■), Cr (▲) and Tl (●) absorbance (M-trace element).

minerals. AAS results show that Ca and Mg does not interfere on absorbance of Mn and Zn, but there is the tendency of decreasing the absorbances of Ag, Cd, Cr and Tl (Figs. 1 and 2). Among them, Tl absorbance suffers the most notable interference. Thus, Mn and Zn can be determined directly in the acidic aqueous solutions of dolomite

or gypsum without any previous separation by FAAS. The lower concentration of Ag, Cd, Cr and Tl have to be determined by ETAAS and this cannot be performed without previous elimination of the matrix elements. Therefore, the flotation method using $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ and $\text{Fe}(\text{HMDTC})_3$ as collectors is proposed to separate and precon-

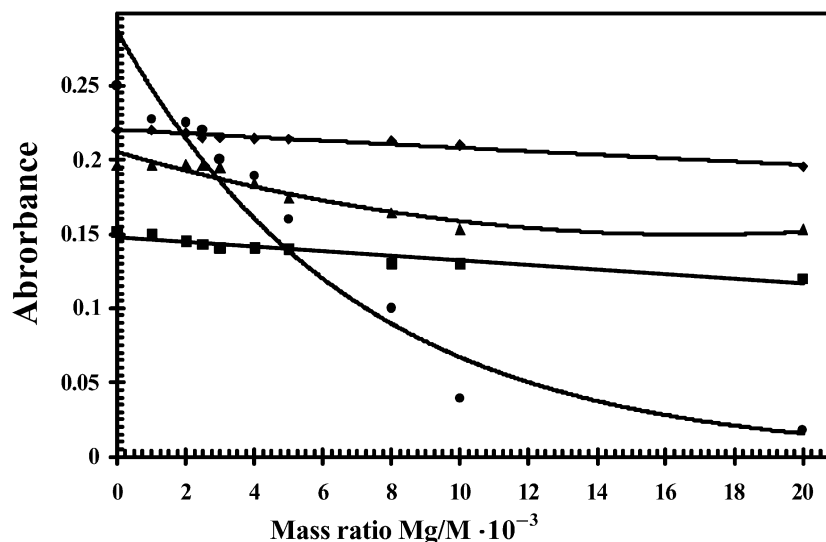


Fig. 2. Influence of Mg as matrix element on Ag (♦) Cd (■), Cr (▲) and Tl (●) absorbance (M-trace element).

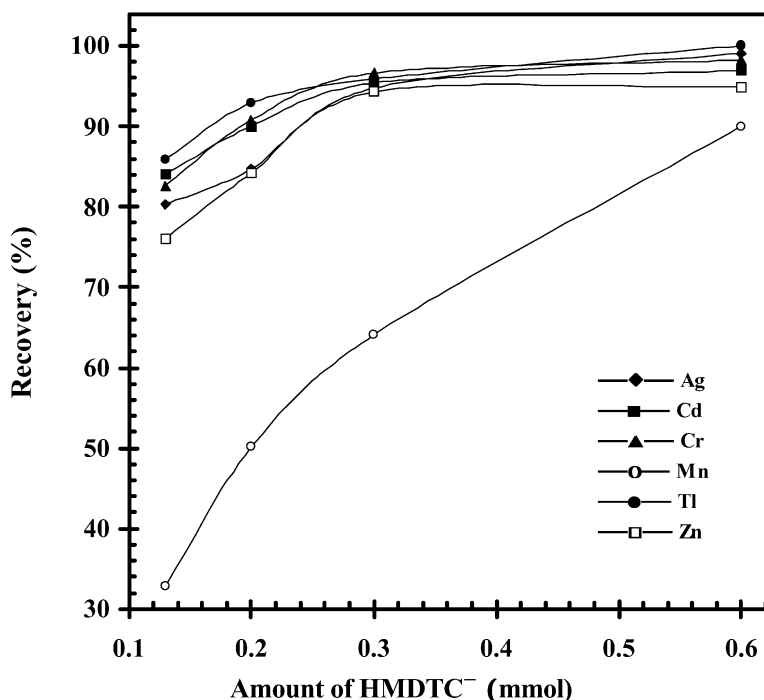


Fig. 3. Effect of the amount of HMDTC[−] on flotation recoveries of Ag, Cd, Cr, Mn, Tl and Zn in dolomite.

trate trace elements from dissolved mineral samples.

3.2. Selection of pH and ionic strength

To ensure the effective incorporation of trace elements in the precipitate mixture of $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ and $\text{Fe}(\text{HMDTC})_3$, as well as to perform a successful flotation separation, pH and ionic strength (I_c) of the medium must be selected very carefully. For dolomite and gypsum we used the values of pH and I_c from the results of earlier investigations [27]. Therefore, flotations of Ag, Cd, Cr, Mn, Tl and Zn from mineral solutions were performed at pH 6.0 and I_c 0.02 mol l^{-1} , regulating by a saturated solution of KNO_3 .

3.3. Influence of dithiocarbamate on flotation process

The influence of HMDTC[−] on flotation recoveries of metals present in dolomite was studied by floating series of solutions (1 l) containing 0.2 g

calcium and 0.1 g magnesium. The mass of Ag, Cd, Cr, Mn, Tl and Zn were similar to those in solutions of the natural dolomite. Flotations were carried out by different amounts of HMDTC[−] (0.13–0.6 mmol), while pH (6.0), I_c (0.02 mol l^{-1}) and Fe(III) mass (10 mg) were kept constant (Fig. 3). The mass of iron (10 mg) for these investigations was adopted from the previous investigation [28]. To study the effect of HMDTC[−] on flotation separation of analytes present in gypsum, solutions containing 0.2 g l^{-1} calcium were floated under the same conditions as in the case of dolomite (Fig. 4). Here also, the mass of analytes was similar to those in the aqueous solutions of natural gypsum.

The results show that the increase of $n(\text{HMDTC}^-)$ rises the recoveries of all analytes. As can be seen in Figs. 3 and 4, the total recovery for manganese is not achieved. They are smaller (90.0–91.1%) than those for Ag, Cd, Cr, Tl and Zn (94.9–100.0%). The explanation for that is the nature of Mn, which behaves different by that all

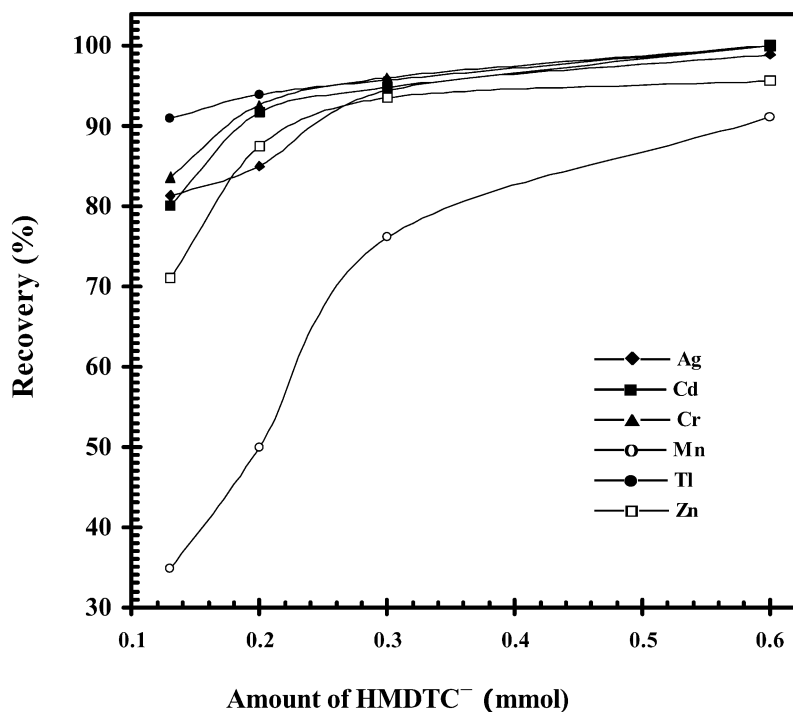


Fig. 4. Effect of the amount of HMDTC⁻ on flotation recoveries of Ag, Cd, Cr, Mn, Tl and Zn in gypsum.

other heavy metals during the used procedure [28]. However, its recoveries, as the recoveries of all other analytes, could be enlarged, if greater amounts of dithiocarbamate were added. Therefore, the amount of 0.6 mmol of HMDTC⁻ was chosen for further investigations.

3.4. Surfactants and suitable concentration of mineral aqueous solutions for flotation

The addition of foaming agents is very advantageous, because they transform the hydrophilic surface of the species floating in hydrophobic, and so they facilitate the separation of the solid from the liquid phase of the system.

To select properly an appropriate surfactant for procedure, several foaming reagents was tested at pH 6.0 and I_c 0.02 mol l⁻¹. The contents of Ag, Cd, Cr, Mn, Tl and Zn in each solution investigated were similar to those in the aqueous solutions of natural minerals. The flotations were carried out with 10 mg of Fe(III), 0.6 mmol HMDTC⁻ and by 1 ml of surfactant solution (0.5%).

It was found that the cationic surfactants BTC and CTAB, as well as non-ionic tenside TX-100, were inadequate (Table 2). They frothed well at pH 6.0, but they did not help to separate the solid phase from the processed solution.

Among anionic surfactants singly tested (NaDDS, NaOL, NaPL and NaST) and in pairs (NaDDS/NaOL, NaPL/NaOL and NaST/NaOL), NaDDS was the most helpful (Table 2), achieving the highest recovery values of 94.8–100.0% for Ag, Cd, Cr, Tl, Zn and 90.8–91.5% for Mn. The results obtained by the pair NaDDS/NaOL were also satisfactory, but this combination of reagents formed too much scum, which was very difficult to decompose by acid. When NaDDS was used as a single reagent, the dissolution of the froth precipitate was easier and faster. Therefore NaDDS was selected for the procedure.

Because calcium and magnesium salts of NaDDS are soluble in water, this detergent foams very well in aqueous media. Nevertheless, in the case of flotation of dolomite and gypsum solutions, NaDDS must be added into a system with very

Table 2

Flotation recovery of various foaming reagents for separation of heavy metal amounts from dolomite and gypsum aqueous solutions at pH (6.0), I_c (0.02 mol l⁻¹), by addition of 10 mg Fe(III), 0.6 mmol HMDTC⁻ and 1 ml 0.5% surfactant solution per liter

	Ag	Cd	Cr	Mn	Tl	Zn
<i>Dolomite</i>						
Cationic surfactants			Recovery (%)			
BTC			Foam, no flotation			
CTAB			Foam, no flotation			
Anionic surfactants			Recovery (%)			
NaDDS	95.4	95.9	100.0	90.8	94.8	100.0
NaOL	96.2	93.7	89.5	92.7	93.3	94.8
NaPL	84.7	94.1	79.3	90.0	89.4	93.7
NaST	78.9	89.7	80.4	90.0	87.8	88.9
Non-ionic surfactants			Recovery (%)			
TX-100			Foam, no flotation			
Pairs of anionic surfactants			Recovery (%)			
NaDDS/NaOL	96.2	95.6	94.8	93.6	94.4	96.3
NaST/NaOL	87.7	94.7	94.3	91.7	93.7	89.9
NaPL/NaOL	84.9	94.4	89.8	92.1	94.0	94.9
<i>Gypsum</i>						
	Ag	Cd	Cr	Mn	Tl	Zn
Cationic surfactants			Recovery (%)			
BTC			Foam, no flotation			
CTAB			Foam, no flotation			
Anionic surfactants			Recovery (%)			
NaDDS	96.9	100.0	99.7	91.5	95.7	99.9
NaOL	97.0	88.5	86.5	89.1	92.6	95.3
NaPL	79.9	94.3	80.3	79.9	89.4	94.4
NaST	88.7	91.1	81.1	68.4	86.7	89.8
Non-ionic surfactants			Recovery (%)			
TX-100			Foam, no flotation			
Pairs of anionic surfactants			Recovery (%)			
NaDDS/NaOL	96.8	94.8	95.2	89.0	94.9	95.4
NaST/NaOL	94.7	93.9	92.5	76.0	96.0	93.9
NaPL/NaOL	89.9	90.3	90.9	80.2	94.6	94.9

high concentrations of alkaline-earth metals. Ca²⁺ and Mg²⁺ concentrations in dolomite and gypsum solutions are elevated so that a reaction among them and NaDDS anions is very possible. Consequently the flotation process could be restrained. For this reason, it was necessary to find the most suitable concentration of aqueous solution of dolomite and gypsum in solution.

For this purpose, a series of solutions (1 l) containing different masses of dolomite and gypsum (5.0, 4.0, 3.0, 2.0 and 1.0 g) were treated by the recommended flotation procedure under previously optimized conditions (pH 6, I_c 0.02 mol/l, 10 mg iron, 0.6 mmol of dithiocarbamate) using NaDDS. These experiments showed that a higher mass of calcium and magnesium had no significant effect on the formation of precipitates F₂O₃·xH₂O

and Fe(HMDTC)₃ during the step of coprecipitation, but had a negative effect on the process of flotation separation. The solutions of dolomite, as well as gypsum at concentrations of 5.0–2.0 g l⁻¹ could not be floated. Increasing amounts of NaDDS and HMDTC⁻ could not ameliorate the flotation efficiency. Therefore, it was ascertained that aqueous solution at concentration of 1 g l⁻¹ dolomite, as well as gypsum was the most suitable for this procedure.

3.5. Alkaline-earth metals, flotation process and matrix interferences

The solutions of dolomite and gypsum, prepared as 1 g l⁻¹, yet contained a lot of Ca and Mg. According to the fact that during the flotation the

Table 3

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

Sample of mineral	Before flotation mg l ⁻¹ Ca	After flotation mg l ⁻¹ Ca	Flotability <i>R</i> (%)
Dolomite	220 ^a	1.83	0.83
Gypsum	230 ^a	2.28	0.99
	mg l ⁻¹ Mg	mg l ⁻¹ Mg	<i>R</i> (%)
Dolomite	130 ^b	1.23	0.95

^a Concentration of Ca estimated in 1 g of dolomite or gypsum.

^b Concentration of Mg estimated in 1 g of dolomite.

concentrations of all solutes, including these macro elements, would be increased 40 times, it should expect significant effect of matrix elements on analyte absorbances during AAS.

To find out what happened with calcium and magnesium as macro elements during the process of separation, their concentrations in the final solutions concentrated by flotation were determined by FAAS and the recoveries were estimated. The data of these investigations showed that the recoveries of Ca (0.83, 0.99%) and of Mg (0.95%) were minor. It is obvious that these macro elements could not be separated from the aqueous solutions under conditions recommended for all other analytes (Table 3). Their concentrations in final solutions, preconcentrated by flotation method, cannot cause any interference on absorbances of Ag, Cd, Cr, Mn, Tl and Zn during their AAS determinations.

3.6. Detection limits

Ten blanks were floated by the adopted procedure and concentrations of Mn and Zn were determined by FAAS, while Ag, Cd, Cr, and Tl concentrations by ETAAS. The detection limit (LOD) of the method for each element 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 deviations (s_r). These data are presented in Table 4.

3.7. Determination trace elements in dolomite and gypsum

The developed method was applied to determine the concentrations of Ag, Cd, Cr, Mn, Tl and Zn

present as impurities in dolomite and gypsum. After flotation under optimized conditions, Mn and Zn were determined by FAAS, and Ag, Cd, Cr and Tl by ETAAS. The concentrations were calculated using external calibration curves. To verify the validity of the results, standard addition method was also applied. To aliquots of 1 g l⁻¹ aqueous solution of dolomite or gypsum known amounts of Ag, Cd, Cr, Mn, Tl and Zn were added. Recoveries are higher than 95% for each heavy metal determined in dolomite and gypsum. Comparing the results obtained by external calibration with those by the method of standard additions, it can be seen that they are equally valid (Tables 5 and 6). This is one proof that the recommended method for separation and preconcentration of analytes from aqueous solutions of minerals investigated was successful.

4. Conclusion

This study has affirmed our earlier conclusions about the possibility of direct analysis of Zn and

Table 4

Standard deviation (s), relative standard deviation (s_r) and detection limit (LOD) of AAS method after flotation for elements present in dolomite and gypsum ($n=10$)

Element	s (μg·g ⁻¹)	s_r (%)	LOD (μg·g ⁻¹)
Ag	0.007	1.95	0.021
Cd	0.006	4.73	0.019
Cr	0.0046	3.56	0.014
Mn	0.5	4.54	1.5
Tl	0.037	6.32	0.110
Zn	0.27	3.95	0.8

Table 5

AAS determination of trace elements in dolomite by the method of standard additions after separation and preconcentration by flotation

Added $m \mu\text{g}^{-1}$	Estimated $\mu\text{g}\cdot\text{g}^{-1}$	Found $\mu\text{g}\cdot\text{g}^{-1}$	Recovery (%)	Added $m \mu\text{g}^{-1}$	Estimated $\mu\text{g}\cdot\text{g}^{-1}$	Found $\mu\text{g}\cdot\text{g}^{-1}$	Recovery (%)
Ag				Cd			
–	–	4.51	–	–	–	2.09	–
5.0	9.51	9.24	97.2	12.5	14.59	14.11	96.7
10.00	14.51	14.34	98.8	25.0	27.09	26.81	99.0
Cr				Mn			
–	–	1.24	–	–	–	987.7	–
5.0	6.24	6.16	98.7	125.0	1112.7	1107.5	99.5
10.0	11.24	11.08	98.6	250.0	1237.7	1249.5	101.0
Tl				Zn			
–	–	111.25	–	–	–	14.50	–
12.5	123.75	123.56	99.9	50.0	64.50	61.50	95.4
25.0	136.25	136.03	99.8	100.0	114.50	112.75	98.5

Mn in acidic aqueous solutions of dolomite [30] and gypsum [31] without any previous separation from the system. Investigations in the frame of this work have also proved, that flotation can be applied to overcome problems with Ca and Mg matrix interferences on Ag, Cd, Cr and Tl in the ETAAS analysis. Dissolving an appropriate amount of powdered mineral in a mixture of acids, a system suitable for a flotation was obtained. After incorporation of all trace elements in the structure of $\text{Fe}_2\text{O}_3\cdot x\text{H}_2\text{O}/\text{Fe}(\text{HMDTC})_3$ precipitate mixture and addition of NaDDS, the solid

phase of the system were separated from the liquid phase by air bubbling. It has been proved that under the appropriate conditions for flotation of Ag, Cd, Cr, Mn, Tl and Zn, most of the Ca and Mg could not float and was left in the processed aqueous solution of mineral. Thus, amounts of Ca and Mg in the final solutions, could not interfere on Ag, Cd, Cr and Tl absorbances. The achieved flotation recoveries for all analytes (higher than 95.0%) verify the proposed method and indicate that it could be applied for analysis of other trace metals included in the structure of other calcium

Table 6

AAS determination of trace elements in gypsum by the method of standard additions after separation and preconcentration by flotation

Added $m \mu\text{g}^{-1}$	Estimated $\mu\text{g}\cdot\text{g}^{-1}$	Found $\mu\text{g}\cdot\text{g}^{-1}$	Recovery (%)	Added $m \mu\text{g}^{-1}$	Estimated $\mu\text{g}\cdot\text{g}^{-1}$	Found $\mu\text{g}\cdot\text{g}^{-1}$	Recovery (%)
Ag				Cd			
–	–	0.84	–	–	–	0.07	–
0.50	1.34	1.31	97.8	1.25	1.32	1.30	98.5
1.00	1.84	1.80	97.6	2.50	2.57	2.55	99.2
Cr				Mn			
–	–	0.60	–	–	–	3.95	–
0.50	1.10	1.08	98.2	12.5	16.45	16.25	98.8
1.00	1.60	1.58	98.8	25.0	28.95	28.58	98.7
Tl				Zn			
–	–	<0.1	–	–	–	1.87	–
1.25	1.25	1.19	95.2	5.0	6.87	6.65	96.8
2.50	2.50	2.50	100.0	10.0	11.87	11.78	99.2

and magnesium minerals. The major advantage of this separation method is the rapidity of procedure, the use of inexpensive devices and the possibility to obtained low detection limits for all analytes investigated.

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