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Gorica Pavlovska[a]; Katarina Čundeva[a]; Trajče Stafilov[a]; Dragica Zendelovska[b]
[a] Institute of Chemistry, Faculty of Science, Sts. Cyril and Methodius University, Skopje, Macedonia [b] Institute of Preclinical and Clinical Pharmacology with Toxicology, Faculty of Medicine, Sts. Cyril and Methodius University, Skopje, Macedonia

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Flotation Method for Selective Separation of Silver, Cadmium, Chromium, Manganese, Thallium, and Zinc from Aragonite Before Atomic Absorption Spectrometric Determination

Gorica Pavlovska,[1] Katarina Čundeva,[1,*] Trajče Stafilov,[1] and Dragica Zendelovska[2]

[1]Institute of Chemistry, Faculty of Science, and [2]Institute of Preclinical and Clinical Pharmacology with Toxicology, Faculty of Medicine, Sts. Cyril and Methodius University, Skopje, Macedonia

ABSTRACT

Selective separation of impurities contained in aragonite ($CaCO_3$) before their determination by atomic absorption spectrometry (AAS) was performed by the method of flotation. At proper selected pH, Ag, Cd, Cr, Mn, Tl, and Zn present in an aqueous solution of aragonite, unless Ca, were incorporated in the mass of the collector mixture consisting of hydrated iron(III) oxide, $Fe_2O_3{\cdot}xH_2O$, and iron(III) hexamethylenedithiocarbamate, $Fe(HMDTC)_3$. By addition of surfactant, the collector precipitate was separated from liquid phase by air bubbles. After dissolving, the analytes were tested by, atomic absorption spectrometry

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*Correspondence: Katarina Čundeva, Institute of Chemistry, Faculty of Science, Sts. Cyril and Methodius University, POB 162, 1000 Skopje, Macedonia; Fax: +389 2 226 865; E-mail: kcundeva@iunona.pmf.ukim.edu.mk.

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(AAS). To ascertain optimal concentration of aragonite solution suitable for flotation, preliminary tests were performed. Flotation suppression because of the reaction among calcium and surfactant ions was very possible, and therefore, the most appropriate foaming reagent was selected. The detection limit of AAS method following flotation was found to be 0.024 $\mu g\, g^{-1}$ for Ag, 0.019 $\mu g\, g^{-1}$ for Cd, 0.016 $\mu g\, g^{-1}$ for Cr, and 0.117 $\mu g\, g^{-1}$ for Tl, determined by electrothermal atomic absorption spectrometry (ETAAS), and 1.596 $\mu g\, g^{-1}$ for Mn and 0.792 $\mu g\, g^{-1}$ for Zn, determined by flame AAS.

Key Words: Aragonite; Trace elements; Silver; Cadmium; Chromium; Manganese; Thallium; Zinc flotation; Atomic absorption spectrometry.

INTRODUCTION

For 100 years, the separation and preconcentration bubble methods called flotations have been used in mining and metallurgical industry to exploit valuable minerals from natural resources. Except for mining aims, these techniques have found a great application for separating and removing many kinds of harmful impurities from different polluted liquid systems. Today there are several attempts to apply flotation for trace analysis.[1–17]

There are many differences between an industrial flotation processes, where the materials floated are relative massive grains of ores, and flotation as an analytical method, where the particles are invisible ions or molecules. However, for both procedures the same principles and laws are valid.[1–4] For both types of separations the pH of the working system must be carefully selected. It is necessary to use the stream of gas bubbles and foaming reagents to successfully remove one kind of species from others.

For the analytical purposes flotation was mostly used for preconcentration of heavy metals from water samples (sea, fresh, tap, underground, waste, etc.).[1–16] Nevertheless, the development of the new flotation methods for analysis of trace elements in water systems provides a lot of valuable knowledge and experience and thus new ideas about further applications of these adsorptive bubble techniques for other type of samples.[17] Considering the similar physical and chemical properties of natural waters with higher water hardness and those of diluted aqueous solutions of calcium mineral, the idea of this study is to use a flotation method for separation of Ag, Cd, Cr, Mn, Tl, and Zn from mineral aragonite ($CaCO_3$) before their atomic absorption spectrometric (AAS) determination. In that way the possible interferences of calcium matrix on analyte absorbances could be eliminated.

EXPERIMENTAL METHODS

Apparatus

The AAS measurements of Ag, Ca, Cd, Cr, Mg, Mn, Tl, and Zn concentrations were carried out by the Perkin–Elmer 1100 B spectrometer supplied by graphite furnace HGA-700 and hollow cathode lamps. Standard pyrolytically coated graphite tubes and platforms were used. The parameters for AAS are presented in Table 1. The pH measurements were performed by Iskra pH Meter (M 5705) with the combined glass electrode (Iskra, M 0101). The specification and scheme of cell necessary for flotation separation were presented in previous paper.[18]

Reagents

The highest-grade pure chemicals (Merck) served to prepare the stock solutions (1 g/l) of all analytes (Ag, Ca, Cd, Cr, Mn, Tl, and Zn) as nitrates in deionized redistilled water (with a purity of $<1\ \mu$S/cm). Before each

Table 1. Instrumental parameters for AAS determination.

ETAAS	Ag	Cd	Cr	Tl
Wavelength	328.1 nm	228.8 nm	357.9 nm	276.8 nm
Spectral slit	0.7 nm	0.7 nm	0.7 nm	2.0 nm
Lamp current	10 mA	4 mA	25 mA	20 mA
Calibration mode	Peak height			
Background correction	Deuterium			
Drying	100°C, 30 s	100°C, 25 s	100°C, 25 s	100°C, 25 s
Pyrolysis	500°C, 25 s	300°C, 20 s	1100°C, 20 s	400°C, 30 s
Atomizing	2000°C, 6 s	1800°C, 6 s	2500°C, 6 s	2200°C, 6 s
Cleaning	2650°C, 5 s	2650°C, 5 s	2650°C, 5 s	2650°C, 5 s
Sheath gas	Argon			
FAAS	Ca	Mn	Zn	
Wavelength	422.8 nm	279.5 nm	213.7 nm	
Spectral slit	2.0 nm	0.7 nm	0.7 nm	
Lamp current	7 mA	10 mA	15 mA	
Oxidant/Fuel gas mixture	Air/acetylene			

investigation, series of metal standard solutions were made by diluting these stock solutions. Iron(III) stock solution (30 mg/ml) was prepared as $Fe(NO_3)_3$ by dissolving high-purity iron metal (Merck) in conc. HNO_3. Diluting this stock solution, series of standards with a concentration of Fe(III) from 2.5 to 100 mg/ml were obtained. The solution of hexamethyleneammonium hexamethylenedithiocarbamate (HMA–HMDTC) was prepared as 0.1 mol/l in 95% ethanol.[19,20] The surfactants used for this study were made as 0.5% in 96% ethanol (sodium dodecylsulfate, NaDDS, sodium oleate, NaOL, benzethonium chloride, BTC, cetyltrimethylammonium bromide, CTAB), 99.7% propan-2-ol (sodium palmitate, NaPL, sodium stearate, NaST), and water (triton X-100, TX-100). The pH was adjusted by addition of aqueous solutions of HNO_3 (0.1 mol/l) and KOH (2.5% and 10%). The ionic strength (I_c) was regulated by adding saturated solution of KNO_3. A 0.1 mol/l NH_4NO_3 solution served to quantitatively transfer the contents of the beaker into the flotation cell.

Separation Procedure

The solution appropriated for flotation was obtained by dissolving 1.0 g of powdered aragonite sample in 20-ml mixture of conc. HCl and 5 ml of conc. HNO_3. After addition of 0.5–1 ml of H_2O_2 (30%) the liquid was evaporated. Then, the residue was dissolved in 5 ml of conc. HCl and diluted with redistilled water to 1000 ml.

A combined glass electrode is immersed into 1 l of aragonite solution. After adding 6 ml of saturated KNO_3 solution, 10 mg of Fe as $Fe(NO_3)_3$ solution were introduced and the pH of the medium was carefully adjusted to 6.0 with KOH solutions. The red-brown precipitate of $Fe_2O_3 \cdot xH_2O$ was stirred about 5 min by means of a magnetic stirrer. Subsequently, 6 ml of $0.1\ \mathrm{mol\,l^{-1}}$ solution of HMA–HMDTC were added to the system and black precipitate of $Fe(HMDTC)_3$ was formed. After 15 min of stirring, 1 ml of NaDDS solution was introduced. The content of the beaker was removed quantitatively into the flotation cell by 5–6 ml of NH_4NO_3 solution. Numerous air bubbles effluxing from the bottom of the cell were passed through the solution for 1 min by the speed of 50 ml/min and separated the solid from the liquid phase. A glass pipette was immersed into the system through the scum collected at the top of the water column and the processed solution was suctioned off. Five ml hot conc. HNO_3 was enough to decompose the solid phase left in the cell. The strong acidic solution was suctioned off by vacuum through the bottom of the cell and collected in a volumetric bottle of 25 ml. The cell and the pipette were washed with 4 mol/l HNO_3 solution. The bottle was filled to the mark with 4 mol/l HNO_3, and the sample was ready for AAS determinations.

RESULTS AND DISCUSSION

Interference of Calcium on the Absorbance of Analytes

Because aragonite is calcium mineral, Ca matrix interferences on absorbance of analytes during their AAS determinations may be expected.[21,22] So, series of solutions with the constant concentrations of Ag, Cd, Cr, Mn, Tl, and Zn (similar to those in the aqueous solutions of aragonite) and different concentrations of Ca were prepared. After AAS testing it was obvious that Zn and Mn absorbances do not undergo any interference of Ca matrix (Fig. 1). Their concentration in natural aragonite is such that they can be tested by flame AAS (FAAS). Nevertheless, the analytes

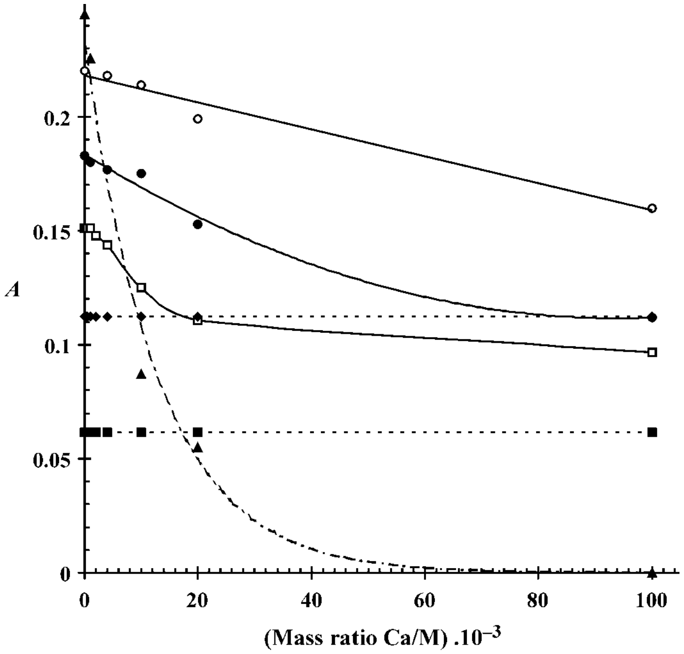

Figure 1. Influence of Ca as matrix element on Ag (–○–), Cd (——), Cr (–●–), Mn (– –■– –), Tl (–·–▲–·–), and Zn (– –◆– –) absorbance (M—trace element).

present in aragonite in trace amounts, which have to be tested by ETAAS, suffer due to the large mass of Ca. Among them Tl absorbance undergoes the greatest decrease. To overcome these matrix interferences a method of flotation separation from aqueous solution of mineral was proposed.

pH and I_c of the System

Our previous investigation established that pH 6.0 and ionic strength (I_c) 0.02 mol/l are optimal for flotation of many metals from waters.[11,12,15,23–25] Considering the very similar physical and chemical properties of aqueous solution of aragonite with those of fresh waters with higher water hardness, pH 6.0 and ionic strength of 0.02 mol/l were selected to be working parameters for trace metal (Ag, Cd, Cr, Mn, Tl, and Zn) flotation from aragonite solution.

Amount of $HMDTC^-$ and the Flotation Process

During the flotation process the metal ions are removed from the aqueous solution of aragonite by incorporation in collector precipitate mass. There are two mechanisms of incorporation of trace metal ions into precipitate. The first is their adsorption on the surface of the particles, including ion exchange, and the second is the occlusion into the structure of the precipitate particles. Because this flotation process uses collector mixture of hydrated iron(III) oxide, $Fe_2O_3 \cdot xH_2O$, and iron(III) hexamethylenedithiocarbamate, $Fe(HMDTC)_3$, the first collection occurs in the mass of $Fe_2O_3 \cdot xH_2O$ and then in the mass of $Fe(HMDTC)_3$. In previous papers we found that removing the trace metals from aqueous systems only by $Fe_2O_3 \cdot xH_2O$ at pH 6.0 is not satisfactorily; to reach quantitative metal recovery it is necessary to add dithiocarbamate.[9–13]

Experience has shown that addition of hexamethyleneammonium hexamethylenedithiocarbamate, HMA–HMDTC, into the reaction system improves the flotation.[15,23–26] The cation hexamethyleneammonium (HMA^+) doesn't participate in the reaction with Fe^{3+}. It is left in the processed water solution. However, the hexamethylenedithiocarbamate anion, $HMDTC^-$, reacts with Fe^{3+} and forms $Fe(HMDTC)_3$. The hydrophobility of $Fe(HMDTC)_3$ is significant, and consequently the analyte flotation recoveries become higher than the recoveries obtained only by $Fe_2O_3 \cdot xH_2O$.[11–13,15]

It was very useful to examine the influence of $HMDTC^-$ on the recovery of elements (R) present in aragonite and find the optimal concentration of this reagent for the system. For that reason, series of solutions of 1 l containing 0.4 g Ca and amounts of Ag, Cd, Cr, Mn, Tl, and Zn similar to those in aqueous solution of aragonite were floated by 10 mg Fe(III) at pH 6.0 and I_c 0.02 mol/l. The amount of $HMDTC^-$ was changed from 0.13 to 0.6 mmol per 1 l of solution. The results show that the increase of $n(HMDTC^-)$ increases the recoveries of all analytes. As can be seen from the Fig. 2, the curve $R/n(HMDTC^-)$ for Mn is a bit distant. The maximal recovery values for Mn are lower (91.9%) than those for Ag, Cd, Cr, Tl, and Zn (96.6–100.0%). The explanation is the nature of Mn, which behaves differently of all other heavy metals during the flotation by dithiocarbamates.[15] However, its recoveries, as the recoveries of all other analytes, could be improved, if greater amounts of dithiocarbamate were added. Therefore, amount of 0.6 mmol of $HMDTC^-$ was selected for further investigations.

Selection of Surfactant

A foaming reagent selected properly is a very important criterion for a successful flotation separation. The role of surfactant is to convert

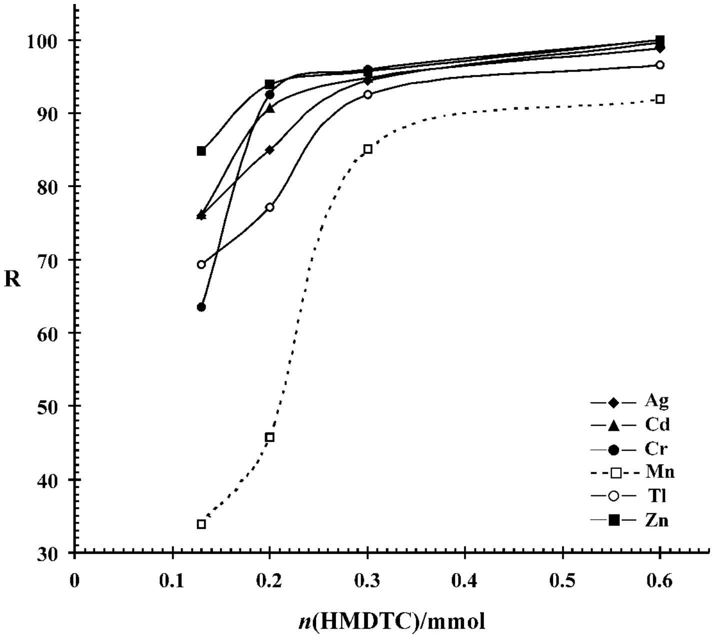

Figure 2. Effect of $n(HMDTC^-)$ on flotation recoveries of Ag, Cd, Cr, Mn, Tl, and Zn.

the hydrophilic surface of the species floated in hydrophobic, and in that way to facilitate the separation of the solid from the liquid phase of the system.

For flotation of aragonite aqueous solutions, several surfactants were investigated at pH 6.0 and I_c 0.02 mol/l. The concentrations of analytes in the solutions studied were similar to those in the aqueous solutions of natural aragonite. The flotation experiments were made for 10 mg of iron and 0.6 mmol of $HMDTC^-$. A volume of 1 ml surfactant solution (0.5%) was added into the reaction mixtures.

The cationic surfactants, BTC and CTAB, as well as nonionic TX-100, foamed well, but they were unable to separate the solid phase from the liquid system. The ineffectiveness of cationic as well as nonionic surfactant is the consequence of the positive charge of the particle surface of two collectors used.[11,12,15] Among anionic surfactants, tested singly or in pairs, NaDDS was the most useful (Table 2). This anionic surfactant, with its negative-charged part (a head group), adsorbs onto the precipitate particles while its hydrocarbon tail (chain) amplifies hydrophobic character of the precipitate. As the result of that interaction, the gas bubbles passing through the system attached very well onto the hydrocarbon tail, and the separation of the solid from the liquid phase

Table 2. Various surfactants tested for flotation separation of Ag, Cd, Cr, Mn, Tl, and Zn from aragonite solutions ($pH = 6.0$, $I_c = 0.02\,mol/L$, 10 mg/l iron, 0.6 mmol/l $HMDTC^-$ and 1 mL 0.5% surfactant solution).

	Ag	Cd	Cr	Mn	Tl	Zn
Cationic surfactants			R (%)			
BTC			Foam, no flotation			
CTAB			Foam, no flotation			
Anionic surfactants			R (%)			
NaDDS	95.1	97.9	95.2	91.7	94.9	100.0
NaOL	94.2	94.2	89.7	90.7	94.2	93.7
NaPL	93.7	93.7	76.7	67.0	90.2	91.0
NaST	77.5	83.7	87.7	70.0	89.8	86.9
Nonionic surfactants			R (%)			
TX-100			Foam, no flotation			
Equimolar mixture of anionic surfactants			R (%)			
NaDDS/NaOL	94.2	94.6	95.1	90.6	94.9	97.8
NaST/NaOL	77.7	94.3	94.2	91.3	93.6	86.9
NaPL/NaOL	82.9	94.4	83.8	92.3	94.1	84.9

occured more easily. The highest recovery values achieved by this reagent were 95.1–100.0% for Ag, Cd, Cr, Tl, and Zn as well as 91.7% for Mn, respectively.

Suitable Concentration of Aragonite for Flotation

There are too many Ca^{2+} cations in the aqueous solution of aragonite. So, it was necessary to find the suitable concentration of aragonite to perform a successful flotation.

For that purpose, series of solutions (1 l) containing different mass of aragonite (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, 1 ml of NaDDS solution). After that, it was clear that higher concentration of Ca did not restrain the formation of precipitates $F_2O_3{\cdot}xH_2O$ and $Fe(HMDTC)_3$, but suppressed the process of flotation. Because of very high Ca^{2+} concentration, the reaction among this cation and dodecylsulfate anion, DDS^-, occurs, and that inhibits the flotation. The solutions of aragonite at concentrations of 5.0 to 2.0 g/l could not be floated. The increase of amounts of NaDDS and $HMDTC^-$ could not improve the flotation efficiency. Therefore, it was concluded that the concentration of 1 g/l aragonite was the most suitable for flotation.

Flotation Preconcentration and Interferences

The final solution ready for AAS measurements have 40 times higher concentrations of Ag, Cd, Cr, Mn, Tl, and Zn. If the concentration of Ca as matrix element increased 40 times, a very complex matrix should be expected in the final solutions, and consequently very significant interferences on trace elements occurred during their ETAAS determination. So, the concentration of Ca was determined by FAAS in the final solutions and its flotation recoveries were estimated. The results show that Ca was floated from the aqueous solution of aragonite only 0.28–1.19%. These recovery values show that Ca, under conditions recommended for flotation of all other analytes, could not be separated and remained in the water phase. This fact confirms that the possible interferences of Ca matrix on absorbances of investigate trace elements in aragonite during their ETAAS were eliminated.

Table 3. Standard deviation (s), relative standard deviation (s_r), and detection limit (L_d) of AAS method.[a]

Element	$s/\mu g\,g^{-1}$	s_r (%)	$L_d/\mu g\,g^{-1}$
Ag	0.008	1.55	0.024
Cd	0.064	4.56	0.019
Cr	0.005	3.96	0.016
Mn	0.532	4.33	1.596
Tl	0.039	5.99	0.117
Zn	0.264	4.09	0.792

[a] Concentration of analytes in 1 g of aragonite dissolved in aqueous solution.

Table 4. AAS determination of elements present in aragonite by the method of standard addition following flotation separation and preconcentration.

Added $m/\mu g$	Estimated $\mu g\,g^{-1}$	Found $\mu g\,g^{-1}$	R (%)	Added $m/\mu g$	Estimated $\mu g\,g^{-1}$	Found $\mu g\,g^{-1}$	R (%)
Ag				Cd			
—	—	0.33		—	—	0.05	
0.50	0.83	0.82	99.8	1.25	1.30	1.30	100.0
1.00	1.33	1.32	99.2	2.50	2.55	2.52	98.8
Cr				Mn			
—	—	3.95		—	—	170.33	
0.50	4.45	4.44	99.8	1.25	182.73	182.78	100.0
1.00	4.95	4.93	99.6	2.50	195.20	194.20	99.4
Tl				Zn			
—	—	<0.1		—	—	1.23	
1.25	1.25	1.25	100.0	5.00	6.23	6.20	99.5
2.50	2.50	2.56	102.4	10.0	11.23	11.08	98.7

Detection Limits

After flotations of ten blanks by the recommended flotation procedure, the concentrations of Mn and Zn were determined by FAAS, while the concentrations of trace elements were found by ETAAS. The detection limit (L_d) of the method for each element was estimated as three values of the standard deviation (s) of the blank. The precision was expressed by means of the relative standard deviation (s_r) (Table 3).

Analysis of Elements Enclosed in Aragonite

To evaluate the method, Ag, Cd, Cr, Mn, Tl, and Zn were determined in the final solutions of aragonite concentrated 40-fold by flotation. After AAS measurement their concentrations were estimated by calibration curves. To verify the method standard addition was used. To aliquots of 1 L of aqueous solutions of aragonite known amounts of Ag, Cd, Cr, Mn, Tl, and Zn were added. The recoveries of 98.7–102.4% show that their separation using the recommended method is satisfactory (Table 4).

CONCLUSION

This paper evidences the possibility of flotation applying a classical technique for removal of valuable substances from natural minerals as a separation method for very precise chemical analysis of impurities in mineral sample. The investigations in this work prove that flotation can solve very important problems characteristic of ETAAS analysis of trace element in minerals resulting of matrix interferences.

Although, the concentration of Ca in aragonite aqueous solutions is very high, at carefully optimized experimental conditions, there is no reaction between Ca and $HMDTC^-$, and practically the entire amount of matrix element remains in the processed solution. In that way, Ca can be eliminated from the system investigating. In the final solutions tested by ETAAS concentrations of Ca are so insignificant that it could not interfere with absorbances of analytes in traces.

Using the developed flotation procedure a 40-fold preconcentration of Ag, Cd, Cr, Mn, Tl, and Zn can be accomplished. Consequently very low detection limit of each tested element is obtained. The method of standard additions reveals that recoveries achieved for each analyte are higher than 98%, which confirms the recommended method.

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