

**APPLICABILITY OF IRON(III)  
HEXAMETHYLENEDITHIOCARBAMATE AS COLLOID COLLECTOR FOR  
FLOTATION PRECONCENTRATION AND SEPARATION OF SOME TRACE  
ELEMENTS IN ARAGONITE BEFORE THEIR AAS DETERMINATION**

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### **Abstract**

The applicability of iron(III) hexamethylenedithiocarbamate,  $\text{Fe}(\text{HMDTC})_3$ , as collector for colloid flotation separation of Ag, Cd, Cr, Mn, Tl and Zn in traces from aragonite and their determination by flame (FAAS) or electrothermal atomic absorption spectrometric (ETAAS) is presented. The interference of Ca as matrix element on Ag, Cd, Cr, Mn, Tl and Zn atomic absorption spectrometric (AAS) determination was investigated. The results show that Ca does not interfere on absorbance of Zn and Mn, but tends to decrease absorbance of Ag, Cd, Cr, and Tl. Accordingly, a flotation separation method for investigated elements from the aqueous solution of aragonite obtained by dissolution the mineral in HCl and  $\text{HNO}_3$  was suggested.

**Key words:** *Aragonite, trace elements, flotation separation, determination, AAS*

### **1. Introduction**

More than hundred years the adsorptive bubble 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. Although this kind of separation has received a great deal of attention in chemical engineering, it has awakened less interest in analytical chemistry [1-3]. Today there are many flotation methods developed for separation and preconcentration of trace elements from sea and fresh water [1-9], but there is no successful application for other type of samples. Besides, the developments 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 this adsorptive bubbles technique. Using dithiocarbamates as very suitable colloid precipitate collectors for trace element separations 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 [4-9]. Thus the aim of this study is to use a flotation by the chelate  $\text{Fe}(\text{HMDTC})_3$  as precipitate collector for separation of Ag, Cd, Cr, Mn, Tl and Zn from aragonite aqueous solutions before their AAS determination.

### **2. Experimental**

*Apparatus and chemical.* The AAS apparatus, the flotation cell and the preparation of all chemical used in this work are described previously [4-9]. Aragonite solution for flotation was prepared by dissolving 1 g of powdered sample of mineral with 20 ml of conc. HCl and 5 ml of conc.  $\text{HNO}_3$ . A few drops of  $\text{H}_2\text{O}_2$  (30 %) were added and the mixture was evaporated near dryness. Later, the residue was dissolved in 5 ml concentrated HCl and diluted with redistilled water to 1 l.

**Flotation procedure.** After adding 6 ml of saturated  $\text{KNO}_3$  solution into 1 l of aragonite solution, 10 mg of Fe(III) was put into the beaker and pH is adjusted to 6.0 by KOH solutions (10 % and 2.5 %). The red-brown precipitate of hydrated iron(III) oxide was stirred about 5 min by a magnetic stirrer. Next, 6 ml of 0.1 mol/l solution of hexamethylenedithiocarbamate,  $\text{HMDTC}^-$  [10], was introduced. After stirring for 15 min 1 ml solution of the surfactant sodium dodecylsulfate, NaDDS, is added. Then, the content of the beaker is transferred quantitatively into the flotation cell using small portions of 0.1 mol/L  $\text{NH}_4\text{NO}_3$ . The further procedure is the same as previously described [4-9].

### 3. Results and discussion

**Calcium matrix interferences.** Because aragonite is calcium mineral, it was necessary to check Ca matrix interferences on absorbance of analytes during their electrothermal atomic absorption spectrometric (ETAAS) determination. For this purpose, series of solutions with the constant concentration of Ag, Cd, Cr, Mn, Tl and Zn and different concentration of Ca were prepared. The mass ratios calcium/ analyte,  $m(\text{Ca})/m(\text{M})$ , were similar to those in the aqueous solutions of aragonite. Then, analytes were tested by AAS. The results show that Ca does not interfere on absorbance of Zn and Mn, which can be tested by flame AAS (FAAS), but tends to decrease absorbance of Ag, Cd, Cr and Tl (Fig. 1). These trace elements have to be determined by ETAAS. To overcome Ca interferences on Ag, Cd, Cr and Tl absorbance a method of flotation was proposed as a mode for their separation from the aqueous solutions of aragonite.

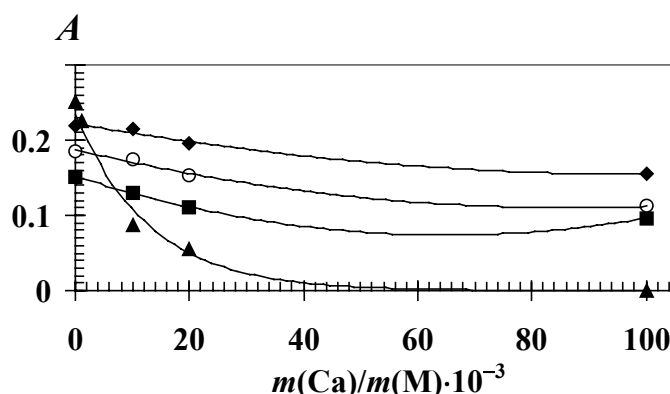


Fig. 1. Influence of Ca as matrix element on Ag (◆), Cd (■), Cr (○) and Tl (▲) absorbance

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**Selection of pH, ionic strength and foaming reagent.** To perform the flotation of aragonite solutions, pH, ionic strength ( $I_c$ ) and the type of surfactant were applied from the previous papers [4-9]. Therefore, the flotation of tested elements was performed at pH 6.0,  $I_c$  0.02 mol/L, regulating by  $\text{KNO}_3$  and NaDDS as surfactant.

**Effect of  $\text{HMDTC}^-$ .** The influence of  $\text{HMDTC}^-$  on flotation recoveries of trace elements present in aragonite was studied by flotation four series of 1-l solutions of aragonite by 10 mg Fe(III) at pH 6.0 and  $I_c$  0.02 mol/L. The amount of  $\text{HMDTC}^-$  was changed from 0.13 to 0.6 mmol to 1 l of solution. The data evidence that the larger quantity of  $\text{HMDTC}^-$  rises the recoveries of all analytes. If larger quantities of  $\text{HMDTC}^-$  (0.6 mmol) were used, trace elements present in aragonite float quantitatively reaching significant recovery values of 90.9 % to 100.0 % (Table 1). Thus 0.6 mmol of  $\text{HMDTC}^-$  was chosen for further investigations.

**Influence of large mass of calcium on flotation process:** During the flotation the ions present in the system with high hardness can react with surfactant and suppress the flotation. So it was necessary to find the most appropriate concentration of aragonite in solution for flotation. Series of 1-l solutions containing different aragonite mass (5.0, 4.0, 3.0, 2.0 and 1.0 g) were floated at pH 6.0 and  $I_c$  0.02 mol/l using 10 mg/l Fe, 0.6 mmol/l  $\text{HMDTC}^-$  and 1 ml of 0.5 % alcoholic solution of NaDDS. The experiments showed that the presence of high concentrations of  $\text{Ca}^{2+}$  had no significant influence on the formation of the precipitate of the collector iron(III) hexamethylenedithiocarbamate,  $\text{Fe}(\text{HMDTC})_3$ , during the step of

coprecipitation, but had a negative effect during the process of flotation. The solutions with  $\text{Ca}^{2+}$  concentration of 2.0 to 0.8 g/l could not be floated. The increasing of the amount of NaDDS and HMDTC<sup>-</sup> did not show any positive effect on flotation separation of solid phase from the processed aqueous solution in the flotation cell. Therefore, it is ascertained that the suitable concentration of aragonite for flotation has to be 1 g/l.

Table 1. Effect of HMDTC<sup>-</sup> on flotation recoveries, R, of trace element present in aragonite.

$n(\text{HMDTC}^-)$ mmol	R (%)					
	Ag	Cd	Cr	Mn	Tl	Zn
0.13	83.1	81.2	93.7	32.5	61.0	89.9
0.20	86.1	94.5	94.7	51.3	94.1	93.5
0.30	95.0	94.8	95.7	62.5	94.7	95.5
0.60	100.0	100.0	100.0	90.9	98.7	98.0

*Elimination of calcium matrix interference on absorbance of analytes.* Because during the flotation the solutes was 40-fold concentrated, it was possible to expect a very complex matrix in the final solution and significant interferences on trace elements 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 not separated from the aqueous solution of aragonite under conditions recommended for the other analytes. The recovery values (0.28-1.19 %) evidence that Ca remains in the water phase. In this way the possible interferences of Ca matrix on investigate trace elements in aragonite by ETAAS were avoided.

*Detection limits.* To determine the standard deviations of the recommended method, ten blanks were floated by the flotation procedure. Then the concentration of Mn and Zn were determined by FAAS, while the concentrations of trace elements by ETAAS. The detection limit ( $L_d$ ) of the method for each element were estimated as three values of the standard deviation ( $s$ ) of the blank. The precision were expressed by means of the relative standard deviation ( $s_r$ ) (Table 2).

Table 2. Standard deviation ( $s$ ), relative standard deviation ( $s_r$ ) and detection limit ( $L_d$ ) of AAS method followed by flotation for elements present in aragonite.

Element	$s / \mu\text{g}\cdot\text{g}^{-1}$	$s_r$ (%)	$L_d / \mu\text{g}\cdot\text{g}^{-1}$
Ag	0.007	1.95	0.021
Cd	0.006	4.73	0.019
Cr	0.005	4.56	0.014
Tl	0.037	6.32	0.110
Mn	0.500	4.52	1.500
Zn	0.270	3.93	0.800

*Analysis of trace elements.* To evaluate the method, 1-l aliquots of aqueous solutions containing 1 g of aragonite and known amounts of elements investigated were floated in accordance with the proposed procedure. Then AAS determination of each analyte was performed using a method of standard additions. The recoveries of 98.7 - 102.4 % show that the separation of tested elements using the recommended method is satisfactory (Table 3).

#### 4. Conclusion

This study has proved that flotation can be used to overcome the problem with Ca matrix interferences on Ag, Cd, Cr and Tl present in traces in aragonite during their ETAAS analysis. This paper is the first attempt to apply flotation as an analytical method for selective separation of Ag, Cd, Cr, and Tl in traces from Ca mineral. Considering the similar physical and chemical properties of natural waters with higher water hardness and those of diluted aqueous solutions of aragonite, colloid precipitate flotation, as a method suitable for analysis

of trace elements in water matrices, was chosen as procedure. After incorporation of Ag, Cd, Cr, Mn, Tl and Zn traces in the structure of Fe(HMDTC)<sub>3</sub> particles and addition of NaDDS, the collector containing these analytes were separated from the processed water phase by air bubbles. The investigation proves that under the conditions appropriate for flotation for these elements, the mostly of Ca amount can not float and remains in the processed aqueous solution of aragonite. Therefore, amount of Ca in the final solutions tested by ETAAS has a concentration, which can not interfere on Ag, Cd, Cr, and Tl absorbances. The major advantages of this separation and preconcentration method is the rapidity of procedure, the use of inexpensive devices and the possibility to obtained low detection limits for the all investigated elements.

Table 3. ETAAS determination of elements investigated in aragonite by the method of standard addition after separation and preconcentration by flotation

Ag				Cd			
Added <i>m/μg</i>	Estimated <i>μg·g<sup>-1</sup></i>	Found <i>μ</i> <i>g·g<sup>-1</sup></i>	R (%)	Added <i>m/μg</i>	Estimated <i>μg·g<sup>-1</sup></i>	Found <i>μ</i> <i>g·g<sup>-1</sup></i>	R (%)
-	-	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			
Added <i>m/μg</i>	Estimated <i>μg·g<sup>-1</sup></i>	Found <i>μ</i> <i>g·g<sup>-1</sup></i>	R (%)	Added <i>m/μg</i>	Estimated <i>μg·g<sup>-1</sup></i>	Found <i>μ</i> <i>g·g<sup>-1</sup></i>	R (%)
-	-	3.95	-	-	-	170.33	-
0.50	4.45	4.44	99.8	12.5	182.73	182.78	100.0
1.00	4.95	4.93	99.6	25.0	195.20	194.20	99.4
Tl				Zn			
Added <i>m/μg</i>	Estimated <i>μg·g<sup>-1</sup></i>	Found <i>μ</i> <i>g·g<sup>-1</sup></i>	R (%)	Added <i>m/μg</i>	Estimated <i>μg·g<sup>-1</sup></i>	Found <i>μ</i> <i>g·g<sup>-1</sup></i>	R (%)
-	-	< 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

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