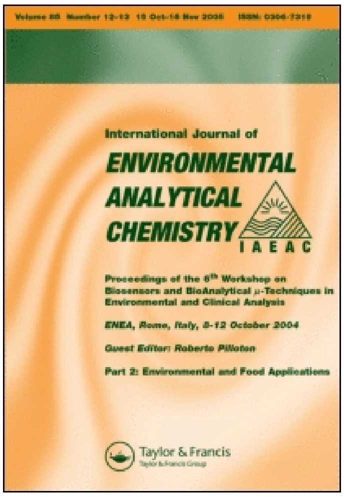

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SILVER COFLOTATION WITH IRON(III) AND COBALT(III) HEXAMETHYLENEDITHIOCARBAMATE SALTS PRIOR TO ITS DETERMINATION BY ELECTROTHERMAL ATOMIC ABSORPTION SPECTROMETRY

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Two coflotation methods for separation of silver in traces from water matrices using iron(III) hexamethylenedithiocarbamate, $Fe(HMDTC)_3$, and cobalt(III) hexamethylenedithiocarbamate, $Co(HMDTC)_3$, as collectors were proposed. After coflotation silver was determined by electrothermal atomic absorption spectrometry (ETAAS). The optimal conditions for effective silver coflotation performed separately by each collector were established. The results of ETAAS analyses are compared with those obtained by inductively coupled plasma-atomic emission spectrometry (ICP-AES). The limit of detection of ETAAS using both $Fe(HMDTC)_3$ and $Co(HMDTC)_2$ as collectors is 0.003 μg/L Ag.

Keywords: Silver; water; coflotation; iron(III) hexamethylenedithiocarbamate; cobalt(III) hexamethylenedithiocarbamate; electrothermal atomic absorption spectrometry

INTRODUCTION

Because the level of silver in uncontaminated fresh water is very low, its determination has to be performed by analytical methods with very low detection limits. Atomic absorption spectrometry (AAS) is very useful for this purpose, however, when the silver concentrations are extremely low, a previous preconcentration step is neccessary. Today there is on the market very modern expensive apparatus suitable for preconcentration of trace elements. Nevertheless, many labs around the

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world which can not provide them, may apply the classical preconcentration methods as extraction, coprecipitation, evaporation, ion exchange, sorption *etc.*[1,2]. Consequently, improvements, modifications, as well as developments of new preconcentration methods for trace element analysis are still actual and useful.

Recently much attention has been paid to the preconcentration of heavy metals from water matrices by flotation techniques based on adsorptive bubbles [1–4]. Among them the method of colloid precipitate flotation, called coflotation, has been shown as the most advantageous and helpful one due to its rapidity and excellent recoveries of analytes. Many factors influence to perform a proper coflotation, but an important role has the collector with its colloidal nature. The most frequently applied collectors for these purposes are the hydrated metal oxides, as hydrated iron(III) oxide, $Fe_2O_3 \cdot xH_2O$ [1–9], hydrated aluminium(III) oxide, $Al_2O_3 \cdot xH_2O$ [1–4,7,10], hydrated indium(III) oxide, $In_2O_3 \cdot xH_2O$ [1–4,11] *etc.* Although all these have been shown as suitable for flotation of many heavy metals, they were inappropriate for flotation of silver.

Our experience showed that silver flotation with $Fe_2O_3 \cdot xH_2O$ could be possible, if tetramethylenedithiocarbamate anions, $TMDTC^-$, were introduced into the floating system [12]. These anions reacted with iron(III) present in the solution, a mixture of $Fe_2O_3 \cdot xH_2O$ and $Fe(TMDTC)_3$ was formed and silver floated quickly and easily. In this work, we present two other dithiocarbamate salts, $Fe(HMDTC)_3$ and $Co(HMDTC)_3$, as new possible reagents for coflotation of silver traces prior to ETAAS. The employment of $Fe(HMDTC)_3$ for coflotation of lead, zinc and chromium was reported in our earlier papers [13–17], while $Co(HMDTC)_3$ is applied for silver firstly. The advantages of application of $Fe(HMDTC)_3$, as well as of $Co(HMDTC)_3$ for silver preconcentration and separation from fresh water samples are discussed.

EXPERIMENTAL

Apparatus

A Perkin-Elmer 1100 B spectrophotometer provided with a graphite furnace HGA-700 was used for AAS. Instrumental parameters for ETAAS of silver were established by extensive testing (Table I). ICP-AES measurements were performed by Varian Liberty 110. The flotation cell was a glass cylinder (4 × 105 cm) with a sintered glass disc (porosity No. 4) at the bottom to generate air bubbling. A pH Meter (Iskra, M 5705) with a combined glass electrode (Iskra, M 0101) were used for all pH measurements.

TABLE I Optimal instrumental parameters for silver ETAAS

Wavelength	328.1 nm
Spectral width slit	0.7 nm
Hollow cathode lamp current	10 mA
Background correction	D_2
Drying temperature	100 °C
Time of drying	30 s
Pyrolysis temperature	600 °C
Time of pyrolysis	20 s
Atomisation temperature	2000 °C
Time of drying	5 s
Cleaning temperature	2650 °C
Time of cleaning	3 s
Carrier gas	Argon

Reagents and standards

All chemicals used were of the highest grade available except for surfactants sodium dodecylsulfate (NaDDS), sodium oleate (NaOL), sodium palmitate (NaPL), sodium stearate (NaST), benzethonium chloride (BTC) and cetyltrimethylammonium bromide (CTAB). Deionized redistilled water was used throughout. The iron(III) stock solution (10 mg/mL) was prepared by dissolving high purity iron metal (Merck) in conc. HNO_3 by heating. Thus all iron was converted into iron(III). Stock solutions of silver and cobalt(II) were prepared as nitrates (Merck) with a concentration of 1 mg/mL. They were suitably diluted daily before each investigation. The 0.1 mol/L solution of $HMDTC^-$ was prepared by dissolving appropriate amount of home-synthesised crystalline hexamethyleneammonium hexamethylenedithiocarbamate [18] in 96 % ethanol. The solutions of surfactants were prepared as 0.5 % solutions in 95 % ethanol (NaDDS, NaOL, BTC, CTAB) and in 99.7 % propan-2-ol (NaPL, NaST). The pH was adjusted by KOH (2.5 % and 10 %) and HNO_3 (0.1 mol/L). Ionic strength (I_c) was regulated with saturated solution of KNO_3. A 0.1 mol/L NH_4NO_3 solution served to transfer the contents of the beaker into the flotation cell.

General procedure

Without previous filtration immediately after sampling, fresh water samples were conserved with a few millilitres of conc. HNO_3 ($pH < 3$). The flotation procedures by the two collectors recommended are different in some details.

Flotation using Fe(HMDTC)$_3$

A combined glass electrode was immersed into 1-L aliquot of acidified water sample. The saturated solution of KNO_3 (6 mL) and 1 mL of stock solution of Fe(III), with a concentration of 10 mg/mL, were added. The pH was adjusted to 6.0 by KOH solutions. After 5 min of stirring (first induction time), 3 mL 0.01 mol/L solution of $HMDTC^-$ were introduced. After further 15 minutes of stirring (second induction time), 1 mL NaDDS was added and the contents of the beaker was transferred quantitatively into the flotation cell. A stream of air bubbles (50 mL/min), was passed through from the perforated bottom of the cell for 1 min raising the precipitate flakes of the system to the water surface. The glass pipette-tube was immersed into the cell through the froth layer and the liquid phase was sucked off. Solid phase in the cell was decomposed by 2.5 mL of hot 65 % HNO_3. The clear yellow solution was drawn out through the bottom of the cell into a 25-mL volumetric flask. The flask was filled up with 4 mol/L HNO_3 and the sample was ready for AAS.

Flotation using Co(HMDTC)$_3$

After adding 6 mL of saturated KNO_3 solution, 1.5 mL of stock solution of Co(II), with a concentration of 1.0 mg/mL, was put into the beaker. The pH was carefully adjusted to 6.0 by KOH solutions and 3 mL 0.01 mol/L solution of $HMDTC^-$ was introduced. After 10 minutes of stirring, Co(II) oxidized to Co(III) and a green precipitate of Co(HMDTC)$_3$ was formed [18–21]. After the addition of 1 mL NaDDS, the contents of the beaker was transferred quantitatively into the flotation cell. Air (50 mL/min) was passed through the solution for 1 min. The water phase was drawn out by pipetting and 5 mL of hot 65 % HNO_3 was added. The clear red solution was collected in a flask of 25 mL. The flask was filled up with 4 mol/L HNO_3 and the sample was ready for AAS.

RESULTS AND DISCUSSION

Optimisation of pH

The optimisation of pH for flotation of silver using Fe(HMDTC)$_3$was carried out by floating series of 1-L solutions, containing 25 and 50 μg silver. The pH values were varied from 3.0 to 6.5, while I_c (0.02 mol/L), iron mass (20 mg) and amount of $HMDTC^-$ ($2 \cdot 10^{-4}$ mol) were kept constant. NaDDS was applied as surfactant. The investigations at pH higher than 6.5 were not performed because the collector hydrolysed. At pH > 6.5 the solid phase in the cell changed its colour from black into red-brown, and it was a sure sign that Fe(HMDTC)$_3$ transformed into $Fe_2O_3 \cdot xH_2O$. The R/pH curves in Figure 1 show that an optimal pH range for silver flotation using Fe(HMDTC)$_3$is 6.0–6.5, where the recoveries are 100.0 %. Therefore, pH 6 was selected for further investigations.

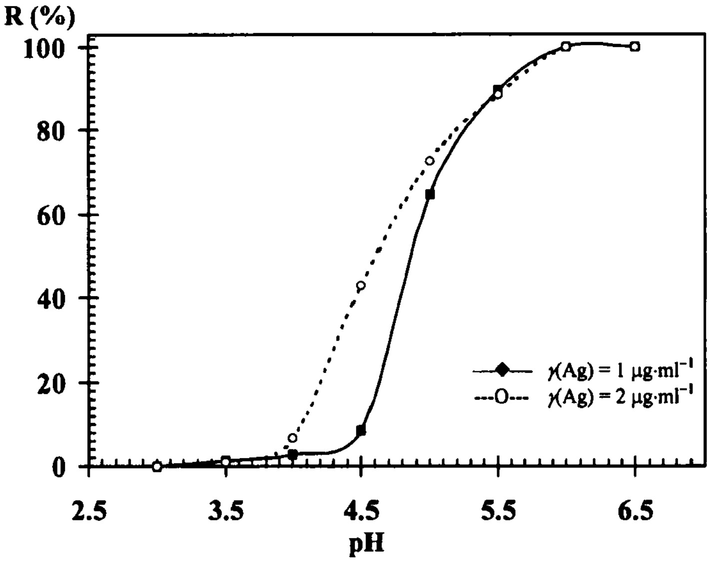

FIGURE 1 Dependence of silver recovery (R) on medium pH during flotation by Fe(HMDTC)$_3$ (20 mg Fe, $2 \cdot 10^{-4}$ mol HMDTC$^-$, I_c = 0.02 mol/L by KNO_3, NaDDS as surfactant)

To find the optimal pH for flotation of silver with Co(HMDTC)$_3$, series of 1-L solutions, containing 25 and 50 μg silver, were floated within pH range of 3.0 – 10.0 by 2 mg cobalt and $3 \cdot 10^{-4}$ mol HMDTC$^-$ at constant I_c (0.02 mol/L). The R/pH curves (Figure 2) evidence that the highest silver recoveries (95.0 – 100.0 %) are reached within the pH range of 6.0–8.0. At pH's higher than 8.0, hydrolysis of Co(HMDTC)$_3$ takes place present and the silver recoveries decrease. pH 6 was selected as the most convenient.

Influence of iron and cobalt amounts on silver flotation recoveries

To investigate the dependence of silver flotation on iron mass, 1-L solutions containing 25 and 50 μg of silver were floated. To each solution different iron quantities (2.5–100 mg) were added. During the flotations pH (6.0), I_c (0.02 mol/L) and HMDTC$^-$ amounts ($2 \cdot 10^{-4}$ mol) were kept constant. The data from these

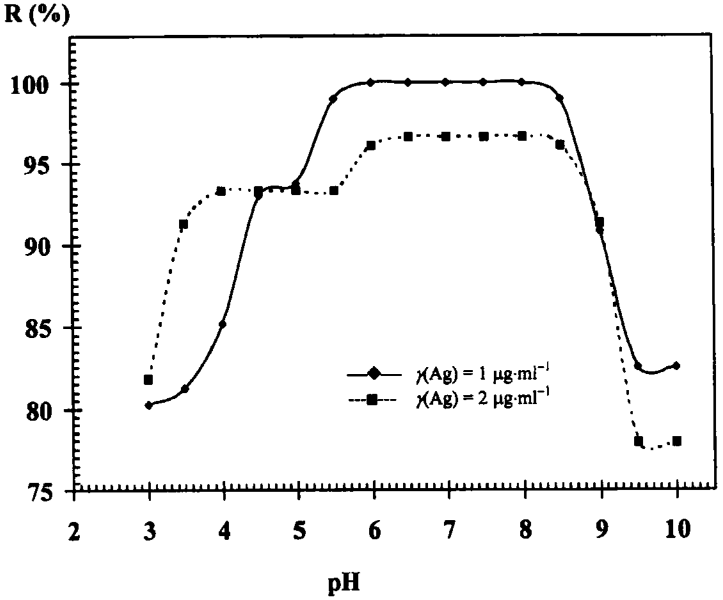

FIGURE 2 Dependence of silver recovery (R) on medium pH during flotation by $Co(HMDTC)_3$ (2 mg Co, $3\cdot10^{-4}$ mol $HMDTC^-$, $I_c = 0.02$ mol/L by KNO_3, NaDDS as surfactant)

investigations (Table II) show that silver flotation recoveries reach a maximum, if the iron amount is kept between 20 to 30 mg (89.2–90.9%).

TABLE II Influence of iron amount on silver recovery (R) (pH = 5.5, $I_c = 0.02$ mol/L, $2\cdot10^{-4}$ mol $HMDTC^-$ per 1 L, NaDDS as surfactant)

γ(Fe) mg/L	*R (%)*	
	γ(Ag) = 1 μg/mL	*γ(Ag) = 2 μg/mL*
2.5	50.3	54.4
5	50.8	54.8
10	88.0	86.1
20	90.6	89.2
30	90.9	89.4
40	89.7	88.0
60	73.4	71.8
80	69.2	68.5
100	69.2	68.3

γ(Fe) – concentration of iron in initial solutions prior to flotation
γ(Ag) – concentration of silver in final solutions after flotation

The influence of cobalt amount on silver flotation recoveries was performed by flotation of series 1-L solutions, containing 25 and 50 μg silver at a constant pH (6.0), I_c (0.02 mol/L) and HMDTC$^-$ amount (2·10^{-4}mol). Solutions contained different cobalt mass ranging from 0.5 to 10 mg. The data show that near-quantitative recoveries of silver (95.2–96.0 %) can be reached by using a minimal cobalt amount of 1.5 mg Co added to 1 L of solution (Table III).

TABLE III Influence of cobalt amount on silver recovery (R) (pH = 6.0, I_c = 0.02 mol/L, c(HMDTC$^-$)= 2·10^{-4} mol/L

γ(Co) mg/L	*R (%)*	
	γ(Ag) = 1 μg/mL	*γ(Ag) = 2 μg/mL*
0.5	85.1	84.2
1.0	88.9	86.7
1.5	95.2	96.0
2.0	95.5	96.4
5.0	96.2	100.0
10.0	100.0	100.0

γ(Co) – amounts of cobalt in initial solutions prior to flotation
γ(Ag) – amounts of silver in final solutions after flotation

Effect of *n*(HMDTC$^-$)

To investigate the effect of *n*(HMDTC$^-$), series of 1-L solutions, containing 25 μg silver were floated by addition of different amounts of HMDTC$^-$ (1.3·10^{-4} – 6· 10^{-4} mol) at a constant pH (6.0) and I_c (0.02 mol/L). Each solution contained constant amounts of iron (5.0, 10.0, 20.0, 30.0 mg) and cobalt (0,5, 1.0, 1.5, 2.0 mg), respectively. The results of these investigations are presented in Figure 3 and 4.

As depicted by Figure 3 silver recoveries increase with *n*(HMDTC$^-$). Quantitative recoveries of 100.0 % can be obtained with 10, 20, and 30 mg iron and 3·10^{-4} or 6·10^{-4} mol HMDTC$^-$per litter. For the procedure 10 mg Fe and 3·10^{-4}mol HMDTC$^-$ were chosen as the most appropriate.

The flotations by Co(HMDTC)$_3$ attain near-quantitative silver recoveries (96.0 %) with 1.5 and 2.0 mg cobalt and *n*(HMDTC$^-$) of 3·10^{-4} or 6·10^{-4} mol per litter (Figure 4). 1.5 mg cobalt and 3·10^{-4} mol HMDTC$^-$ were selected as suitable for the procedure.

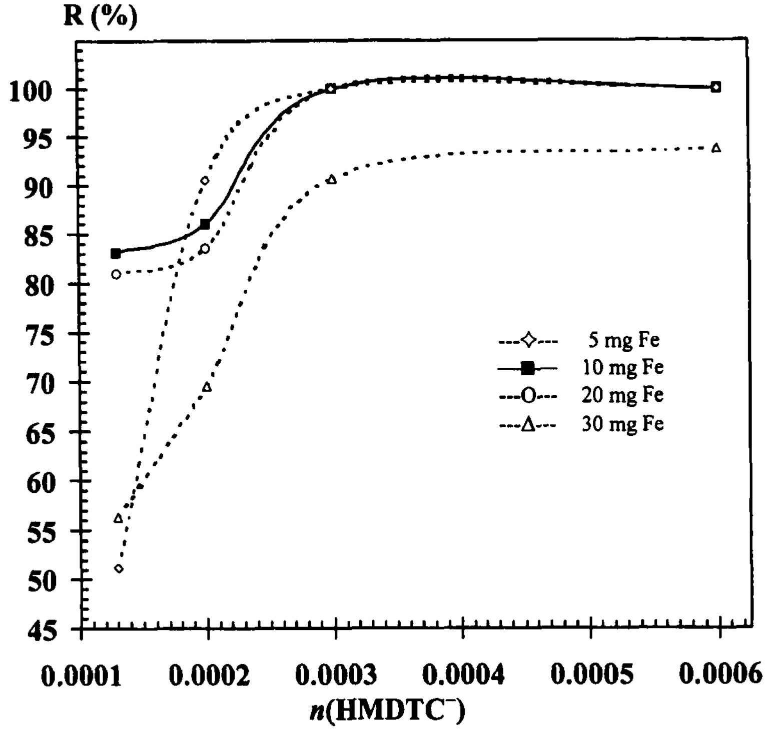

FIGURE 3 Influence of *n*($HMDTC^-$) on silver flotation recoveries during flotation by $Fe(HMDTC)_3$ (pH = 6.0, I_c= 0.02 mol/L, *m*(Fe) = 5, 10, 20 and 30 mg)

Selection of surfactant

Different foaming reagents were tested under the conditions optimised in previous sections. The cationic surfactants (BCT and CTAB) foam very well, but no flotation occurred. The anionic surfactants, having the opposite charge of $Fe(HMDTC)_3$ and $Co(HMDTC)_3$ particles, were shown more effective (Table IV). Since the recoveries obtained by NaDDS were the highest with both collectors, it was selected as the most appropriate surfactant for the procedures.

Induction time

The flotation with $Fe(HMDTC)_3$ needs two induction times: the first of 5 minutes and the second of 15 minutes. The flotation by $Co(HMDTC)_3$ needs only one induction time of 10 minutes.

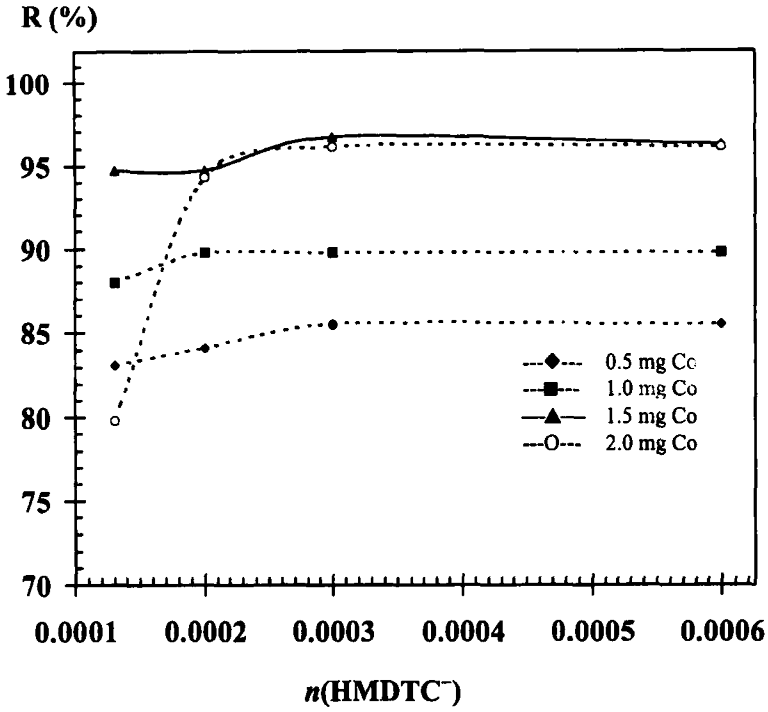

FIGURE 4 Influence of n(HMDTC$^-$) on silver flotation recoveries during flotation by Co(HMDTC)$_3$ (pH = 6.0, I_c= 0.02 mol/L, m(Co) = 0.5, 1.0, 1.5 and 2.0 mg)

TABLE IV Selection of surfactant

Flotation with Fe(HMDTC)$_3$ (pH = 6.0, I_c = 0.02 mol/L, 10 mg Fe, $3\cdot10^{-4}$ mol HMDTC$^-$)						
γ(Ag)	*Cationic surfactant*		*Anionic surfactant*			
	R (%)					
	BCT	*CTAB*	*NaDDS*	*NaOL*	*NaPL*	*NaST*
1 µg/mL	foam,	foam,	97.3	97.5	80.1	87.5
2 µg/mL	no flotation	no flotation	97.5	96.5	83.3	89.6
Flotation with Co(HMDTC)$_3$ (pH = 6.0, I_c = 0.02 mol/L, 1.5 mg Co, $3\cdot10^{-4}$ mol HMDTC$^-$)						
γ(Ag)	*Cationic surfactant*		*Anionic surfactant*			
	R (%)					
	BCT	*CTAB*	*NaDDS*	*NaOL*	*NaPL*	NaST
1 µg/mL	foam,	foam,	95.6	92.9	79.2	88.3
2 µg/mL	no flotation	no flotation	99.3	94.6	82.1	89.1

Interferences of matrix elements

It was important to examine the interferences resulting from high iron *e.i.* cobalt amounts present in the final concentrated by the flotation solution on silver absorbance during ETAAS. The investigations showed that 10 mg iron, added to 1 L of investigated water containing 0.125 mg silver, does not change the value of silver absorbance at all. As regards to the interferences resulting from cobalt quantity on silver absorbance, it was found that up to 15 mg of cobalt, added to 1 L of water containing 0.125 μg silver, do not influence on silver absorbance.

Application of the method

The flotation method with the new collectors $Fe(HMDTC)_3$ and $Co(HMDTC)_3$ were evaluated by examination the recovery of silver from seven samples of fresh waters. The analyses were performed using a calibration curve and a method of standard additions. For this purpose, known amounts of silver were added to 1-L water samples. Then they were floated, 40-fold concentrated and tested by ETAAS. The data are given in Table V. The data of the calibration and standard addition methods show that they are in good agreement. The silver recoveries of 96.9 to 104.8 % evidence that its preconcentration and separation by both procedures are satisfactory.

The detection limit of ETAAS was estimated as three values of the standard deviation of the blanks, while the precision of the methods was expressed by the relative standard deviation. The limit of detection for ETAAS followed by the flotation with $Fe(HMDTC)_3$ was found to be 0.003 μg/L silver, while the precision of the method was 2.0 %. The limit of detection for ETAAS followed by the flotation with $Co(HMDTC)_3$ was found to be 0.003 μg/L silver, and the precision of the method was 2.7 %. The ICP-AES was applied as an independent method to verify the proposed methods. It is evident that the ICP-AES results agree well with the ETAAS data (Table V).

CONCLUSION

The present paper proved that silver could be preconcentrated successfully by both coflotations for fresh water samples using $Fe(HMDTC)_3$, as well as $Co(HMDTC)_3$ prior to ETAAS. The experimental conditions for each collector are established. The method using $Fe(HMDTC)_3$ as collector needs two induction times. The first induction time for two methods is the time of coprecipitation of silver traces in the scum of hydrated iron(III) oxide ($Fe_2O_3 \cdot xH_2O$) as the first collector. The addition of $HMDTC^-$ anions is necessary to form the second collector $Fe(HMDTC)_3$. The coflotation by $Co(HMDTC)_3$ needs only one induction time. Amounts of iron, cobalt and $HMDTC^-$, as the constituents of the collectors investigated, have effect on silver flotation recoveries. The quantitative separation of silver from 1 L of water sample can be performed with 10 mg iron and $3 \cdot 10^{-4}$mol of $HMDTC^-$, *i.e.* 1.5 mg cobalt and $3 \cdot 10^{-4}$ mol of $HMDTC^-$. These amounts of iron and cobalt do not interfere on silver absorbance. $Fe(HMDTC)_3$ and $Co(HMDTC)_3$ were shown as collectors with a significant hydrophobility, which is an important criterion for a successful flotation. This can be evidenced by the excellent recoveries of silver obtained by means of each collector. The recommended preconcentration procedures are rapid (about 25 – 30 min). They extend the range of conventional AAS determination of silver. The necessary equipment for flotation is simple and inexpensive. The use of a little amount of surfactant and tiny air bubbles necessary to perform the proper flotation can not permit some serious contamination risks, which could result in high blank values.

TABLE V ETAAS determination of Ag in water samples compared with ICP-AES results

Sample of water	*ETAAS*							*ICP-AES*[a]
	µg/L Ag							*µg/L Ag Found*
	Added	*Estimated*		*Found*		*R (%)*		
		I[b]	*II*[c]	*I*	*II*	*I*	*II*	
Pantelejmon	0.00	–	–	0.140	0.125	–	–	0.12
15.05 DH°[d]	1.25	1.390	1.375	1.420	1.360	98.1	98.9	
pH = 7.84	2.50	2.640	2.625	2.652	2.609	100.4	99.4	
Sreden Izvor	0.00	–	–	0.045	0.040	–	–	0.04
17.65 DH°	1.25	1.295	1.290	1.322	1.250	102.1	96.9	
pH = 7.36	2.50	2.545	2.540	2.500	2.580	98.2	101.6	
Rašče	0.00	–	–	0.177	0.155	–	–	0.15
16.49 DH°	1.25	1.427	1.405	1.407	1.390	98.6	98.9	
pH = 7.18	2.50	2.677	2.655	2.702	2.660	100.9	100.2	
Raduša	0.00			0.026		–		0.05
25.57 DH°	1.25	1.276		1.337		104.8		
pH = 8.50	2.50	2.526		2.567		101.6		
Kavadarci	0.00	–	–	0.140		–	–	0.15
5.71 DH°	1.25	1.390		1.400		100.7		

Sample of water		*ETAAS*						*ICP-AES*[a]
		µg/L Ag						µg/L Ag Found
	Added	*Estimated*		*Found*		*R (%)*		
		I[b]	*II*[c]	*I*	*II*	*I*	*II*	
pH = 7.58	2.50	2.640		2.567		97.2		
Kapištec	0.00	–	–	0.145		–	–	0.125
23.36 DH°	1.25	1.395		1.430		102.5		
pH = 7.50	2.50	2.625		2.632		100.3		
Demir Kapija	0.00		–		0.069		–	0.07
5.60 DH°	1.25		1.319		1.320		101.1	
pH = 7.50	2.50		2.569		2.600		101.2	

a. The water samples for ICP-AES measurements were preconcentrated by evaporation of acidified water samples from 1000 mL to 25 mL.

b. I – Data obtained by coflotation using $Fe(HMDTC)_3$

c. II – Data obtained by coflotation using $Co(HMDTC)_3$

d. DH° (*Deutsche Härte*) German degree of water hardness

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