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Atomic Absorption Spectrometry Determination of Cd, Cu, Fe, Ni, Pb, Zn, and Tl Traces in Seawater Following Flotation Separation

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ABSTRACT

A fast method for separation of Cd, Cu, Fe, Ni, Pb, Zn, and Tl from seawater before their determination by atomic absorption spectrometry (AAS) is described. The ability of Co(III) hexamethylenedithiocarbamate, $Co(HMDTC)_3$, as a flotation collector for metals from seawater was investigated. The influence of pH of the media, as one of the crucial parameters for effective flotation, as well as mass of cobalt as one of the

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constituents of a chelatometric collector was optimized. The used mode of atomization flame (FAAS) or electrothermal (ETAAS) depends on the concentration level of analyte present in the seawater sample investigated. The AAS method following flotation was compared with the method of inductively coupled plasma–atomic emission spectrometry (ICP–AES). The limit of detection (LOD) of each analyte obtained by FAAS or ETAAS is determined: flotation/ETAAS for Cd is 0.010 μg/L, for Cu 0.034 μg/L, for Ni 0.305 μg/L, for Pb 0.290 μg/L, and for Tl 0.032 μg/L, whereas flotation/FAAS for Fe is 0.890 μg/L and for Zn 0.994 mg/L.

Key Words: Heavy metals; Seawater; Determination; Matrix interferences; Flotation; Cobalt(III) hexamethylenedithiocarbamate; AAS; ICP–AES.

INTRODUCTION

The study of seawater and ocean water has great importance. All streams and rivers from the beginning of their sources pass through many kinds of natural and artificial water systems and finish in sea and ocean basins. Therefore, the freshwaters, with all their physical, chemical, and biological damages, condition the quality of seawater and ocean waters and, consequently, influence the life in these very important ecological systems.

Heavy metals are widespread pollutants of water. They originate primarily from industrialized regions where streams and rivers flow. Microconcentrations of heavy metals in water influence harmfully on the environment gradually by the time they accumulate in certain parts of the animal and plant organism, causing the change in their biochemical balances. In this way, some biochemical reactions can be blockaded or catalytically routed to some undesired directions. Consequently, many organisms can essentially damage and change the natural environment. Therefore, accurate information about the presence of heavy metals in seawater is of great biological and environmental significance.[1]

Atomic absorption spectrometric (AAS) methods are very suitable methods for monitoring the levels of heavy metals in natural waters. They provide accurate and rapid determinations, but for the extremely low concentration of these pollutant, a direct apply of AAS is impossible without any previous concentration and separation of analytes from the sample. Today this problem can be solved by very modern expensive instrumentation for preconcentration and separation of trace metals. However, many laboratories around the world, which cannot provide them, can yet apply the methods as solvent–solvent extraction, solid-phase extraction, evaporation, coprecipitation, etc., which do not require expensive equipment.[2–5]

Some of these common methods are rapid, but others are slower. Some of them do not need expensive reagents; others do. So the development of accurate, rapid, and low-cost methods that help to monitor heavy metals in seawater is very actual and essential today.

Among accurate, fast, and inexpensive procedures that can solve the separation of heavy metals from freshwater matrix immediately before their instrumental analysis is the method of colloid precipitate flotation.[2,3,5–16] Considering the similarity between physicochemical properties of seawater and those of freshwater with higher hardness, a flotation method is proposed as a way to avoid the matrix effect resulting from high concentrations of alkali- and alkaline-earth metals in seawater on AAS determination of microelements. In our earlier works Co(III) hexamethylenedithiocarbamate, Co(HMDTC)$_3$, was validated as an effective flotation collector.[13–15] The idea of these investigations is to apply it for a flotation separation of Cd, Cr, Cu, Fe, Ni, Pb, Zn, and Tl from seawater. The proposed flotation method coupled with AAS (flotation/AAS) for seawater analysis was compared with the ICP–AES method.

EXPERIMENTAL

Apparatus

The ETAAS determinations of metal in traces were performed by Varian SpectraAA 640 Z (Table 1). The FAAS measurements of analytes in higher concentration were carried out by Thermo Elemental Solar S4 (Table 2). Thermo Solar S4 served also for flame atomic emission spectrometry (FAES) of sodium and potassium (Table 3). The determination of heavy metals by ICP–AES was performed by Varian Liberty 110 (Table 4). The flotation cell, as a necessary advice for this kind of investigations, was a glass cylinder (4 × 105 cm) with a sintered glass bottom (porosity no. 4) to produce air bubbles.[11] The pH Meter Iskra, M 5705 with a combined glass electrode Iskra, M 0101 serves to monitor the pH of the medium.

Reagents and Standards

All chemicals used were of the highest grade available except for surfactants sodium dodecyl sulfate (NaDDS), sodium oleate (NaOL), sodium palmitate (NaPL), and sodium stearate (NaST). Stock solutions (1 mg/mL) of Ca, Cd, Cr, Cu, Fe, K, Mg, Na, Ni, Pb, Zn, and Tl (Solution Plus Inc.) served for preparation of standards by a suitable daily dilution before each

Table 1. Optimal instrumental parameters for ETAAS determination of metal in traces.

	Analyte					
Parameter	Cd	Cr	Cu	Ni	Pb	Tl
Wavelength (nm)	228.8	357.9	327.4	232.0	283.3	276.8
Spectral width slit (nm)	0.5	0.5	0.5	0.2	0.5	0.5
Lamp current (mA)	4.0	7.0	4.0	4.0	5.0	10.0
Background correction	Zeeman					
Drying temperature (°C)	85; 95; 120	85; 95; 120	85; 95; 120	85; 95; 120	85; 95; 120	85; 95; 120
Time of drying (sec)	5; 40; 10	5; 40; 10	5; 40; 10	5; 40; 10	5; 40; 10	5; 40; 10
Pyrolysis (°C)	250	1,000	800	800	400	250
Time of pyrolysis (sec)	5; 1; 2	5; 1; 2	5; 1; 2	5; 1; 2	5; 1; 2	5; 1; 2
Atomization (°C)	1,800	2,600	2,300	2,400	2,100	2,200
Time of atomization (sec)	0.8; 2	1.2; 2	1.1; 2	1.1; 2	1; 2	1; 2
Cleaning (°C)	1,800	2,600	2,300	2,400	2,100	2,200
Time of cleaning (sec)	2	2	2	2	2	2
Sheath gas	Argon					

Table 2. Optimal instrumental parameters for FAAS determination of metals.

	Analyte			
Parameter	Fe	Zn	Ca	Mg
Time of measurement (sec)	4.0	4.0	4.0	4.0
Wavelength (nm)	248.3	213.9	422.7	285.2
Lamp current (%)	75	75	100	75
Spectral width slit (nm)	0.2	0.5	0.5	0.5
Flame	Air/acetylene			
Acetylene flow rate (L/min)	0.9	0.9	1.2	1.1
Background correction	On	On	Off	On

investigation. Stock solution of Co(II) (10 mg/mL) was prepared by dissolving an appropriate amount of $Co(NO_3)_2 \cdot 6H_2O$ (Merck) in deionized redistilled water. The 0.1 mol/L solution of $HMDTC^-$ was prepared by dissolving appropriate amount of home-synthesized crystalline hexamethyleneammonium hexamethylenedithiocarbamate[17,18] in 96% ethanol. Because aqueous or nonaqueous solutions of dithiocarbamates are decomposable of light or warmth, $HMDTC^-$ solution was prepared immediately before each investigation. The surfactant solutions were prepared as 0.5% (w/w). Crystalline NaDDS and NaOL were dissolved by 95% ethanol, whereas NaPL and NaST were dissolved by 99.7% propane-2-ol. The pH was adjusted by solutions of KOH (1.25%, 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.

To optimize the experimental conditions for flotation of seawater (optimal pH, effect of cobalt mass and type of surfactant), a series of model seawater

Table 3. Instrumental parameters for FAES measurements.

	Analyte	
Parameter	K	Na
Time of measurement (sec)	4.0	4.0
Wavelength (nm)	766.5	589.0
Spectral width slit (nm)	0.5	0.5
Flame	Air/acetylene	
Acetylene flow rate (L/min)	0.9	0.9
Background correction	Off	Off

Table 4. Instrumental parameters for ICP–AES determination of heavy metals.

Introduction area			
Nebulizer type	V-groove		
Spray chamber	Inert Sturman-Masters		
Peristaltic pump	10 rollers, dual channel		
Conditions for program			
Plasma power	1.0 kW	Pump rate	25 rpm
Plasma flow rate	15 L/min	Stabilization time	30 sec
Auxiliary flow rate	1.5 L/min	Rinse time	30 sec
Nebulizer pressure	150 kPa	Sample delay	30 sec
Background correction	Dynamic	PMT/V	650

Conditions for line

Analyte	Wavelengths (nm)	Search window (nm)	Filter	Grating order	Integration time (sec)	Viewing high (mm)
Ni	231.604	0.01	6	2	5	5
Fe	259.940	0.01	6	2	3	5
Zn	213.856	0.007	1	3	5	5
Cu	324.754	0.01	6	2	5	5
Pb	220.353	0.007	1	3	7	5
Cd	228.802	0.007	1	3	5	5
Tl	190.790	0.02	1	1	10	5

solutions were prepared according to German standard DIN 50 900. For that purpose, 28 g NaCl, 7 g $MgSO_4 \cdot 7H_2O$, 5 g $MgCl_2 \cdot 6H_2O$, 0.2 g $NaHCO_3$, and 1.6 g $CaCl_2 \cdot 2H_2O$ were dissolved in 1 L of redistilled water.

Seawater Sampling

Water samples, from Marmara Sea (Harem, Turkey) and Aegean Sea (Platamona, Greece) were filtrated immediately after sampling. Then they were conserved by the addition of 1 mL concentrated HNO_3 to 1 L seawater until pH of 2.7–3.

Seawater Flotation

The basic procedure of seawater flotation consisted of two steps: coprecipitation of heavy metals in collector mass (occurring in a beaker) and air bubble separation (in a flotation cell).

Coprecipitation

The procedure begins by immersing a combined glass electrode 1 L of acidified seawater sample and by adding 6 mL of saturated KNO_3 solution. Then, 1.5 mg of Co(II) as nitrate solution is introduced. The pH is carefully raised to 6.0 by KOH solutions (beginning by 10% and finishing with 1.25%) and adjusted by HNO_3 solution (0.1 mol/L). When 3 mL 0.1 mol/L solution of $HMDTC^-$ are introduced, the desired pH was established again with a few milliliters of 0.1 mol/L HNO_3. During 15 min of stirring, Co(II) oxidized to Co(III), and a green collector precipitate of $Co(HMDTC)_3$ occurs.[4,19,20] During this process, analytes are incorporated in a collector mass. At the end of stirring, 1 mL of NaDDS solution and 1 mL of NaOL solution are added. To not change the medium I_c the combined glass electrode is washed by the electrolyte NH_4NO_3 (0.1 mol/L), which also serves to transfer the contents of the beaker into the flotation cell.

Separation by Air Bubbles

A stream of air bubbles (50 mL/min) is passed from the bottom of the cell for 1 min, raising the precipitate flakes of the system to the water surface. The glass pipette tube is immersed into the cell through the froth layer and the liquid phase was sucked off. The water phase is drawn out and the solid phase left in the cell is decomposed by 5 mL hot 65% HNO_3. The clear red solution is sucked off through the sintered bottom of the cell and collected in a 25-mL flask. The flotation cell and a glass pipette tube are washed two times by 5 mL of hot 4 mol/L HNO_3 solution. At the end, the flask is filled up to the mark by redistilled water and the sample is ready for AAS.

RESULTS AND DISCUSSION

pH of Seawater Sample and Flotation Separation of Heavy Metals

The pH is always one of the most important parameters that condition effectiveness of an analytical method. During the coprecipitation step, the pH value determines the sign and magnitude of the charge on the surface of the collector particles. In that way, pH directly influences the formation of complexes between the analytes and all species present in the system and their incorporation into the mass of collector. During the flotation step, pH influences the stability of the foam and, consequently, the successful separation of solid from liquid phase in the cell.

The effect of pH on separation of each element investigated was studied by floating series of seawater model standard solutions. Each standard (1 L) contained 25 μg of analyte. Flotations were performed within the pH range of 4.0–7.5. All other parameters are kept constant: 1.5 mg cobalt, 3 mmol $HMDTC^-$, 1 mL 0.5% alcoholic solution of NaDDS, as well as NaOL. I_c was 0.02 mol/L. After flotation, the concentration of each analyte was measured by FAAS, and recoveries (*R*%) were estimated.

The *R*/pH curves of Fig. 1 show that all analytes, excluding chromium, reached the highest recoveries (95.0–100.0%) within a pH range of 5.2–6.3. At pHs higher than 6.5, the hydrolysis of $Co(HMDTC)_3$ is present and the recoveries of analytes decrease. Therefore, pH 6 was selected as the most appropriate for further investigations.

Effect of Cobalt Mass on Separation Process

To investigate this effect, series solutions (1 L) containing 25 μg investigating element were floated by additions of different mass of Co (0.1–2 mg) at a constant pH (6.0). I_c (0.02 mol/L) and amount of $HMDTC^-$ (0.3 mmol). The data show that quantitative recoveries of each element (96.0–100.0%) were obtained by 1.5 mg Co (Fig. 2).

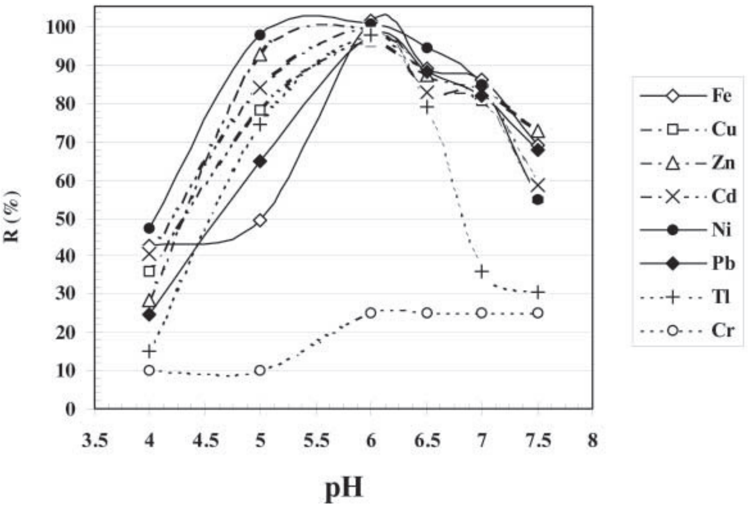

Figure 1. Effect of pH on flotation separation of heavy metal from seawater matrix.

Consequently, the addition of 1.5 mg Co with 0.3 mmol of $HMDTC^-$ to 1 L of seawater sample is the most convenient for flotation of all heavy metals investigated, excluding chromium. Low flotation recovery of chromium is probably due to anionic form of Cr(VI) in the samples.

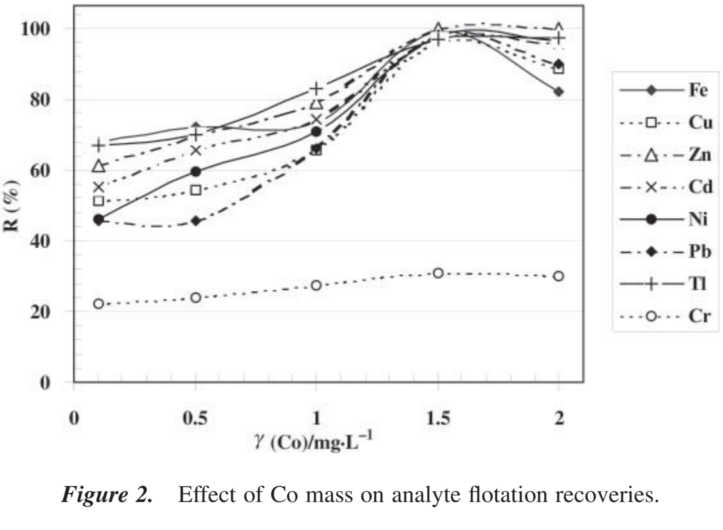

Figure 2. Effect of Co mass on analyte flotation recoveries.

Surfactants

Several anionic surfactants (NaDDS, NaOL, NaST, and NaPL) were tested under conditions optimized previously. After the step of coprecipitation, 1 mL of 0.5% ethanolic solution of the surfactant was added to the reaction mixture, and then the flotation by air bubbles followed. However, all surfactants used as a single reagent were ineffective. The high amounts of salts in seawater have suppressed the foaming and prevented the separation of solid from liquid phase by air bubbles in the flotation cell. The simultaneous addition of two reagents NaDDS/NaOL has solved the problem. The flotation separation performed by addition of 1 mL of 0.5% ethanolic solution of NaDDS and 1 mL of 0.5% ethanolic solution NaOL has been shown very successful for all analytes reaching flotation effectiveness of 94.4–99.0% (Table 5).

Alkali and Alkaline Earth Salts and 40-Fold Concentration

Using the proposed flotation procedure, seawater samples can be 40 times concentrated. To achieve this grade of concentration by evaporation of acidified seawater samples is impossible, because of precipitation of alkali and alkaline earth salts. So, it was necessary to clear up what happens with Na, K, Ca, and Mg during the flotation by $Co(HMDTC)_3$. For that purpose, Na, K, Ca, and Mg were determined in seawaters before flotation and in the final concentrated solutions. Next, the flotabilities of Na, K, Ca, and Mg were estimated (Table 6). The flotabilities of Na (0.80–1.42%), K (4.22–4.65%), Ca (0.20–0.87%), and Mg (0.11–0.30%) show their very poor flotation by means of $Co(HMDTC)_3$ and their lack in the final solutions measuring

Table 5. Flotation of heavy metals from seawater by $Co(HMDTC)_3$ at pH 6 using different surfactants.

Analyte	Single surfactant				Pair of surfactants NaDDS/NaOL
	NaDDS	NaOL	NaPL	NaST	
Cadmium	88.6	91.9	67.5	30.3	96.5
Copper	94.0	87.8	58.3	87.6	99.0
Iron	77.8	76.9	56.0	68.9	96.1
Nickel	80.0	40.0	89.6	79.1	96.6
Lead	80.2	60.0	91.1	68.8	94.7
Zinc	90.2	88.2	91.5	70.8	96.7
Thallium	72.0	60.5	86.7	61.6	94.4

Table 6. Flotability of alkali and alkaline earth metals achieved by flotation under conditions optimized for heavy metal tested (pH 6.0; I_c 0.02 mol/L; 1.5 mg/L Co; 0.3 mmol/L HMDTC$^-$; 1 mL 0.5% solution of NaDDS and 1 mL 0.5% solution of NaDDS).

Sample of seawater	Before flotation	After flotation	Flotability (%)
Harem	5,300 mg/L Na	42.5 mg/L Na	0.80
Platamona	11,000 mg/L Na	156.0 mg/L Na	1.42
Harem	225.3 mg/L K	9.5 mg/L K	4.22[a]
Platamona	471.0 mg/L K	21.9 mg/L K	4.65[a]
Harem	252.5 mg/L Ca	2.20 mg/L Ca	0.87
Platamona	304.0 mg/L Ca	0.60 mg/L a	0.20
Harem	608.0 mg/L Mg	0.70 mg/L Mg	0.11
Platamona	1143.0 mg/L Mg	3.47 mg/L Mg	0.30

[a] Added K from KNO_3 was not taken in the calculations.

by AAS. In that way, seawater matrix is separated from elements tested, and interferences of alkali and alkaline earth metals in 40 times concentrated solution are avoided.

Interferences of Cobalt Mass

The interferences resulting from the high cobalt quantity on analytes in AAS determination in the final 40-fold concentrated by flotation solutions were checked. For that purpose, a series of solutions with the constant concentration of Cd, Cu, Fe, Ni, Pb, Zn, and Tl, and different concentrations of Co

Table 7. Standard deviation (s), relative standard deviation (s_r), and limit of detection (LOD) for analytes investigated by flotation/AAS.

Analyte	s ($\mu g\,L^{-1}$)	s_r (%)	LOD ($\mu g\,L^{-1}$)
Cd	0.0035	2.22	0.010
Cu	0.0115	4.05	0.034
Fe	0.2966	7.5	0.890
Ni	0.1016	3.81	0.305
Pb	0.0953	4.00	0.290
Tl	0.0106	10.11	0.032
Zn	0.3312	4.7	0.994

Table 8. AAS determinations of heavy metal in seawaters compared by AES–ICP.

Seawater sample	ETAAS Added (μg/L)	ETAAS Estimated (μg/L)	ETAAS Found (μg/L)	ETAAS Recovery (%)	ICP–AES Found (μg/L)
Cadmium					
Harem	—	—	0.09	—	<0.1
	1.25	1.34	1.45	108.2	
Platamona	—	—	0.09	—	<0.1
Copper					
Harem	—	—	1.98	—	2.0
	2.00	3.98	4.07	102.2	
	4.00	5.98	5.75	96.1	
Platamona	—	—	3.60	—	3.0
	1.25	5.60	5.60	100.0	
	2.50	7.60	7.76	102.1	
Zinc					
Harem	—	—	2.00	—	—
	10.00	12.00	12.05	100.4	
	20.00	22.00	22.8	99.6	
Platamona	—	—	5.60	—	5.0
	10.00	15.60	15.53	99.6	
	20.00	25.60	25.70	100.3	
Nickel					
Harem	—	—	1.20	—	—
	4.00	5.20	5.33	102.5	
	8.00	9.20	9.45	102.7	
Platamona	—	—	4.40	—	—
	4.00	8.00	8.40	95.4	
	8.00	12.40	12.0	96.8	
Lead					
Harem	—	—	0.52	—	—
	2.50	3.02	2.90	96.0	
Platamona	—	—	0.90	—	1.1
	2.50	3.40	3.09	91.0	
	5.00	5.90	5.36	90.8	
Thallium					
Harem	—	—	0.07	—	<0.1
Platamona	—	—	0.06	—	<0.1
	1.25	1.32	1.40	106.0	
Iron					
Harem	—	—	2.96	—	2.5
Platamona	—	—	6.40	—	—

were prepared. The mass of these analytes, as well as the mass ratios cobalt/analyte, was similar to those in the natural seawater samples. Then, analytes were tested by AAS. The results show that a mass of 1.5 mg Co, added to working media, does not interfere on absorbances of all metal in traces investigated.

Accuracy and Precision of the Recommended Flotation Method

The limits of detection (LOD) for flotation/FAAS, as well as flotation/ETAAS methods for each analyte were estimated as three values of the standard deviation of the blank (Table 7).

Seawater Analysis

After the optimization of experimental conditions for flotation technique with Co(HMDTC)$_3$, the method was applied for heavy metal separation and analyses in seawater samples from Marmara Sea (Turkey) and Aegean Sea (Greece). The determinations of heavy metals were made by a calibration curve and the method of standard additions. Seawater samples were floated, 40-fold concentrated, and tested by FAAS or ETAAS depending on the concentration level of each analyte. The results are shown in Table 8. The recoveries of 108.2–90.8% show the successfulness of the preconcentration and separation of Cd, Cu, Fe, Ni, Pb, Zn, and Tl by the recommended procedure. The ICP–AES results correspond to ETAAS data, too.

CONCLUSION

The ability of Co(HMDTC)$_3$, as a new collector for flotation separation of seawater matrix from Cd, Cu, Fe, Ni, Pb, Zn, and Tl before their AAS is presented. The pH of the media, as well as amount of cobalt, has the effect on analyte flotation recoveries. The applied amount of cobalt does not interfere on trace element absorbances present in seawater samples investigated. The recommended preconcentration procedure is rapid (about 25 min) and extends the range of conventional AAS determination of heavy metals. 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 cannot permit some serious contamination risks, which could be manifested by the high blank values.

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