

Determination of zinc, nickel and cadmium in natural water samples by flame atomic absorption spectrometry after preconcentration with ion exchange and flotation techniques

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Abstract

Two preconcentration techniques, ion exchange and flotation, were used for the determination of zinc (Zn), nickel (Ni) and cadmium (Cd) in natural water samples. In the first part of our work, the adsorption of zinc(II), nickel(II) and cadmium(II) on Lewatit TP 207 chelating resin containing iminodiacetate groups was studied at different pH values by a batch process. The effects of parameters such as amount of resin, contact time, pH and initial metal concentration on the ion exchange separation were investigated. For the determination of the adsorption behavior of the resin, the adsorption isotherms of metal ions were also studied. The concentrations of metal ions were measured by batch techniques and with atomic absorption spectrometry analysis. Adsorption analysis results obtained at various concentrations showed that the adsorption pattern on the resin followed Langmuir and Freundlich isotherms. The efficiency of removal is higher for Ni and Zn than Cd ions. Here, we report the method that is applied for the sorption and separation of some toxic metals from the solutions. In the second part of our work, the flotation technique was used for preconcentration. The ability of Co(III) hexamethylenedithiocarbamate, Co(HMDTC)₃, as a flotation collector for metals from natural waters was investigated. The flotation method was compared with the ion exchange method. The recoveries of Zn, Cd and Ni from natural water samples were approximately 99%. Our results showed that the two methods were very effective, but the flotation results were higher than the ion exchange results. In the present study, a method was described for the determination of Zn, Ni and Cd by flame atomic absorption spectrometry (FAAS) after preconcentration and separation in water by ion exchange resin and flotation. Results of these two methods are compared. Analytical parameters such as precision and accuracy of methods were also studied. The equilibrium experimental results of Zn, Ni and Cd ions exchanged were fitted by Langmuir-Freundlich adsorption isotherm models.

Keywords: Cd(II); flotation; Freundlich isotherm; Langmuir isotherm; Lewatit TP 207; Ni(II); Zn(II).

Introduction

Heavy metals such as zinc (Zn), cadmium (Cd) and nickel (Ni) are pollutants in waters. Sensitive determination of heavy metal ions at the trace levels is a very important part of environmental and public health studies (Elik 2003, Narin and Soylak 2003, Yunes et al. 2003).

The flame atomic absorption spectrophotometer (FAAS) has been widely used for the determination of heavy metal ions in water samples because of its high specificity. However, the direct determination of trace concentrations of these elements by FAAS is generally difficult because of matrix interference problems and concentrations below the detection limit of FAAS. These problems can be overcome by using preconcentration techniques.

For this purpose, various preconcentration methods such as precipitation, solvent extraction, flotation, ion exchange, solid phase extraction have been widely used (Misaelides et al. 1994, Shanableh and Kharabsheh 1996, Peric et al. 2004).

The ion exchange technique has had many applications for the preconcentration of trace metal ions (Cespon-Romero et al. 1996, Dapaah and Ayame 1998, Cessela et al. 1999, Zhang et al. 1999, Mahmoud and Al Saadi 2001, Qian et al. 2001, Tewari and Singh 2001, Kendüzler and Türker 2002). Koivula et al. studied chelating ion exchangers that were tested for their abilities to remove Zn, Ni, copper (Cu) and Cd from solutions simulating waste effluents from the metal-plating industry (Koivula et al. 2000). Abou-Mesalam studied sorption kinetics of Cu, Zn, Cd and Ni ions on a silico-antimonate ion exchanger (Abou-Mesalam 2003). Simpson and Laurie studied ion exchange resins for recovery of Zn (Simpson and Laurie 1999). Kurama and Çatalarik used Lewatit MP62 for the treatment of excess Zn cyanide from alkaline leach solutions (Kurama and Çatalarik 2000).

The flotation technique is much simpler than conventional preconcentration and separation techniques such as liquid-liquid extraction, sorption, etc. (Stafilov et al. 1998). Flotation is an accurate, fast and inexpensive procedure (Koyuncu et al. 2004).

In the first part of this work, we studied Lewatit TP 207 chelating resin containing iminodiacetate groups as active sites for its use for the separation and preconcentration of Zn, Cd and Ni in water samples. We studied the batch system and for measurement we used FAAS. After designated optimum conditions we applied water samples which were collected from ISKI (Water Authority for İstanbul) at different seasons. The equilibrium experimental results of Zn, Cd and Ni ions

exchanged have been fitted by Langmuir-Freundlich adsorption isotherm models.

In the second part of this work, Co(HMDTC)₃ as a flotation collector for metals was used and the flotation technique was applied to the natural water samples which were collected from ISKI at different seasons.

Materials and methods

Reagents

All chemicals used were of the highest grade available except for surfactants sodium dodecylbenzenesulfonate. All solutions were prepared with deionized water. Unless stated, analytical grade acids and other chemicals used in this study were obtained from Merck, Darmstadt, Germany. Synthetic Lewatit TP 207 hydrogen form (16–45 mesh size) was obtained from Fluka Co. (İstanbul, Turkey). The properties of Lewatit TP 207 are given in Table 1. Stock solutions 1000 mg/l of Zn(II), Ni(II) and Cd(II) were prepared by dissolving appropriate amounts of ZnO, CdCl₂·H₂O and NiCl₂·2H₂O. Working standard solutions of the metal ions were prepared by a suitable dilution with a stock solution with double distilled water.

Stock solution of Co(II) (10 mg/ml) was prepared by dissolving an appropriate amount of Co(NO₃)₂·6H₂O (Merck) in deionized redistilled water. The 0.1 mol/l solution of HMDTC was prepared by dissolving an appropriate amount of home-synthesized crystalline hexamethylenammonium hexamethylenedithiocarbamate (Simpson and Laurie 1999, Koivula et al. 2000, Abou-Mesalam 2003) in 96% ethanol (Busev et al. 1970, 1973).

The pH was adjusted by solutions of KOH (1.25%, 2.5% and 10%) and HNO₃ (0.1 mol/l). Ionic strength (Ic) was regulated with saturated solution of KNO₃. A 0.1-mol/l NH₄NO₃ solution served to transfer the contents of the beaker into the flotation cell. The pH values of the solutions were adjusted with the buffer solutions. The pH 2 buffer solution was prepared by mixing appropriate volume of 1 M sodium sulfate and 1 M sodium hydrogen sulfate solutions. Acetate buffers were prepared by mixing different amounts of 1 M sodium acetate and 1 M acetic acid was used to maintain the pH between 4 and 6. Potassium dihydrogen phosphate (0.1 M) and disodium hydrogen phosphate (0.1 M) were used for pH 7.

Table 1 Characteristic data of tested Lewatit TP 207.

Resin type	Weak acidic cation exchange resin Lewatit TP 207
Active group	Iminodiacetic acid
Matrix	Crosslinked polystyrene
Ionic forms as shipped	H ⁺
Physical form	Macroporous
Mean particle size (mm) (90%)	0.4–1.25
pH range	0–14
Total exchange capacity	2.4 mmol/g of resin

Apparatus

A Varian Spectra AA-20 Model (İstanbul, Turkey) atomic absorption spectrometer (AAS) equipped with deuterium lamp, background correction, a hollow cathode lamp and an air-acetylene burner was used for quantitative determination of Zn(II), Ni(II) and Cd(II) under the following conditions: wavelength 213.9 nm, 232 nm and 228.8 nm; spectral bandwidth 0.5 nm, 0.2 nm and 1.2 nm. All pH measurements were performed with a Metrohm Herisau E 510 Model (İstanbul, Turkey) pH meter. An electrical temperature-controlled shaker was used for shaking.

The flotation cell was a glass cylinder (4×105 cm) with a sintered glass bottom (porosity no. 4) to produce air bubbles as described previously (Koyuncu et al. 2004).

Ion exchange procedure

Water washing of resin The hydrogen form of the ion exchange resin was washed with double distilled water and dried at 110°C for 1 h and stored in a desiccator until use.

General studying procedure The metal ions were preconcentrated by the batch method.

Batch method The effects of concentration, pH, stirring time and resin amount were investigated for determination of optimum conditions. An amount of 0.1 g of resin samples was put into contact with 50 ml of solution containing Zn(II), Ni(II) and Cd(II) for 60 min (pH 4). All experiments were conducted at room temperature. Stirring speed was 2000 rpm during the batch experiments. The resin was filtered through quantitative filter paper and washed with double distilled water. After filtration, the concentration of the metal ions in the eluate was determined by AAS and if dilution was necessary it was diluted.

Analysis of the water samples The water samples analyzed were drinking waters, treated waters and filtered raw waters. Water samples collected from Istanbul Buyukcekmece and Kagithane were immediately filtered through cellulose nitrate [0.45 µm pore size, 47 mm diameter; Whatman (İstanbul, Turkey)] and acidified to pH 3 with nitric acid and stored in precleaned polyethylene bottles. The pH values of the samples were adjusted 4 with acetate buffer solution. Then, the separation and preconcentration method was applied. The concentration of the investigated analyte ions in final solution was determined by AAS. Results are shown in Table 2.

Flotation procedure

The flotation procedure was applied as previously described (Koyuncu et al. 2004). The flotation procedure consisted of two steps: coprecipitation and air bubble separation.

Coprecipitation A combined glass pH electrode was immersed into the water sample. A 6-ml solution of saturated KNO₃ and 1.5 mg of Co(II) as nitrate solution were introduced.

Table 2 Metal determination in natural water samples.

Water sample	Adsorption % for Zn			Adsorption % for Cd			Adsorption % for Ni					
	Raw water		Treated water ^a	Raw water		Treated water ^a	Raw water		Treated water ^a			
	Ion exchange	Flotation	Flotation	Ion exchange	Flotation	Flotation	Ion exchange	Flotation	Flotation			
K.H. Spring	97.1±1.5	105.2±1.3	97.5±1.0	105.3±0.6	95.0±1.0	98.1±1.5	95.4±2.1	102.3±1.4	97.7±1.5	102.1±0.9	99.4±1.8	107.2±0.7
K.H. Summer	95.3±0.6	99.1±1.0	97.3±0.5	102.6±1.0	95.4±2.3	101.2±0.5	95.5±1.0	105.5±0.6	98.8±2.2	105.3±0.7	99.6±0.6	105.8±1.5
B.Ç. Spring	96.0±1.2	102.0±1.1	97.6±2.0	102.5±1.0	96.0±1.2	100.0±1.7	96.2±1.5	103.2±1.0	99.0±0.5	106.2±1.0	99.8±1.3	106.7±1.0
B.Ç. Summer	95.5±1.1	99.5±0.5	95.6±1.1	101.1±1.5	95.3±1.1	104.2±0.5	95.5±2.0	104.7±1.1	98.8±1.4	105.5±0.5	99.9±1.5	106.4±0.5

^aTreated with chlorination and with ozone.
K.H., Kağıthane; B.Ç., Büyükçekmece.

The pH was carefully increased to 6.0 by KOH solutions and adjusted by HNO₃ solution (0.1 mol/l). When 3 ml of 0.1 mol/l solution of HMDTC is introduced, the desired pH was established again with a few milliliters of 0.1 mol/l HNO₃. During 15 min of stirring, Co(II) oxidized to Co(III), and a green precipitate of Co(HMDTC)₃ occurs that acts as collector for our metals (Glen 1950, Krishnamurty 1977, Byr'ko 1984, Cundeva et al. 2000). During this process, analytes were taken up in this collector. At the end of stirring, 1 ml of sodium dodecylbenzenesulfonate solution was added. The combined glass electrode was washed by the electrolyte NH₄NO₃ (0.1 mol/l), which serves to transfer the contents of the beaker into the flotation cell so that the medium Ic was not changed.

Separation by air bubbles A stream of air bubbles (50 ml/min) was passed from the bottom of the cell for 1 min, increasing 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. The water phase was drawn out and the solid phase left in the cell was decomposed by 5 ml of hot (40°C) 65% HNO₃. The clear red solution was sucked off through the sintered bottom of the cell and collected in a 25-ml flask. The flotation cell and a glass pipette tube were washed two times with 5 ml of hot 4 mol/l HNO₃ solution. At the end, the flask was filled up to the mark by redistilled water and the sample was ready for AAS (Koyuncu et al. 2004).

Results and discussion

Ion exchange results

The effects of pH, iminodiacetate resin Lewatit TP 207 dosage, initial metal concentration and contact time were investigated for the determination of optimum conditions and adsorption isotherms.

Effect of pH The sorption of metal ion on the iminodiacetate resin Lewatit TP 207 was studied at pH range of 2.0–7.0. Buffer solutions were used for pH adjustment. As seen in Figure 1, quantitative retention was obtained for Zn at pH 3.0 for Cd and Ni at pH 4.0. Experimental conditions studied included concentration of metals (10 mg/l), resin amount (500 mg) and contact time (60 min). pH 3 was suggested for highest retention of Zn, Cd and Ni at pH 4.

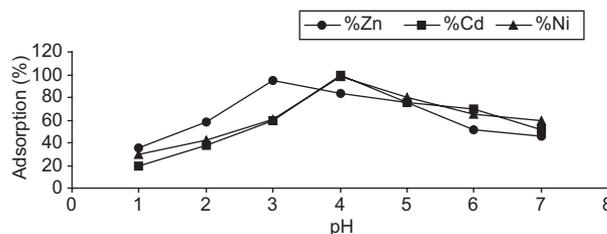


Figure 1 The effect of pH on the retention of metals on Lewatit TP 207.

Effect of resin amount on metal adsorption The resin amount is the other important parameter for obtaining quantitative recovery. Thus, the effect of amount of resin on the sorption concentration of metals 10 mg/l, contact time 60 min, at pH 3 for Zn and pH 4 for Cd and Ni were examined in the range 5–1000 mg of resin. The effect of resin amount on the retention of metals is given in Figure 2. The results demonstrated that metals were quantitatively recovered by 400–600 mg. Therefore, in subsequent experiments, 500 mg of resin was used.

Effect of contact time The effect of time on the adsorption of metal ions by the resin was studied by taking 0.5 g Lewatit TP 207 iminodiacetate resin with 10.0 ml of a metal salt solution of a metal ion in different stoppered flasks. The flasks were shaken for different time intervals. The effect of contact time on adsorption of Cd(II), Ni(II) and Zn(II) using Lewatit TP 207 iminodiacetate resin are shown in Figure 3. The results show that the percentage of metal ions and Lewatit TP 207 iminodiacetate resin sorption increased with increasing time of equilibration and it reached the plateau value at 60 min for Ni(II), Cd(II) and Zn(II).

Effect of initial metal concentration The effect of initial concentration on the capacity of adsorption is shown in Figure 4 where the data obtained at the end of the experiment are given. Percent removal of Ni(II), Zn(II) and Cd(II) ions

were determined at given contact times in the range between 5 and 1000 mg/l concentrations of metals. The pH values of the solutions were adjusted to 4 and 3 with buffer solution for Ni, Cd and Zn, respectively. The adsorption of metal ions with 500 mg resin was not affected by amount of sample until 50 mg/l.

Eluent type and eluent volume for desorption of Ni, Cd and Zn ions Desorption of Ni, Cd and Zn ions from resin were investigated by using various eluting agents. The effects of 10 ml of various eluents on the recoveries of Ni, Zn and Cd on Lewatit TP 207 resin were studied. The recovery values for metal ions by using 1 M HCl, 1 M HNO₃, 2 M HNO₃, 3 M HNO₃ and 4 M HNO₃ were 92±1, 94±2, 97±2, 99±2 and 101±1, respectively. The quantitative recoveries of metals were obtained by using 4 M HNO₃ as an eluent. Quantitative recovery values for analytes were obtained by using 10.0 ml of 4 M HNO₃.

Adsorption isotherms The Langmuir model is illustrated as follows (Turhan et al. 2005):

$$q = (q_{\max} \times b \times C_e) / (1 + b \times C_e)^{-1}, \quad (1)$$

where q is milligrams of metal accumulated per gram of the adsorbent material; C_e (mg/l) is the metal residual concentration in solution; q_{\max} (mg/g) is the maximum specific

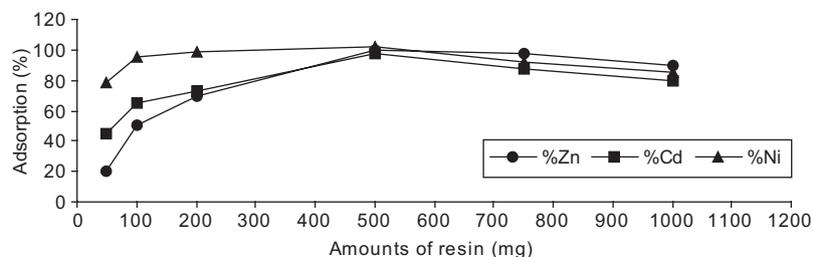


Figure 2 The effect of resin amount on the retention of metals.

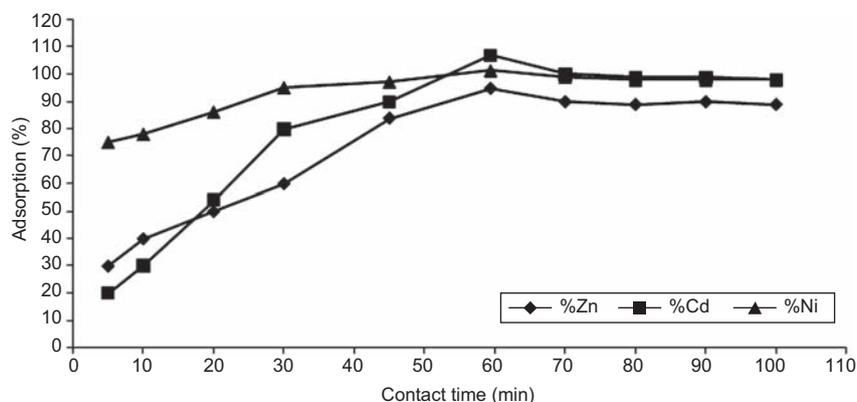


Figure 3 The effect of contact time on the recovery of metals.

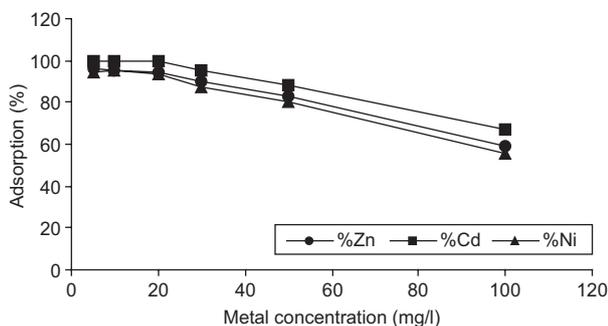


Figure 4 The effect of initial metal concentration.

uptake corresponding to the site saturation and b is the ratio of adsorption and desorption rates or related to the affinity between sorbent and sorbate. This is a theoretical model for monolayer adsorption. For the fitting of experimental data, the model was linearized as follows:

$$\frac{1}{q} = (q_{\max} \times b)^{-1} \times (C_e)^{-1} + (q_{\max})^{-1} \quad (2)$$

Another empirical model for monolayer adsorption is the Freundlich equation which deals with heterogeneous surface adsorption and is illustrated as follows:

$$q = K \times C_e^n, \quad (3)$$

where K and n are Freundlich constants. This equation is easily linearized by plotting it in a log-log format.

$$\log q = \log K + \frac{1}{n} \times \log C_e \quad (4)$$

The Ni, Zn and Cd, Langmuir and Freundlich adsorption isotherms equation parameters are shown in Table 3 and Figures 5–7.

The Langmuir model and the Freundlich model were applied to experimental data for Zn, Cd and Ni. The correlation coefficients (R^2) and q_{\max} and b constants for the Langmuir equation and K and n constants for the Freundlich equation were as follows: Langmuir R^2_{Zn} 0.9773, R^2_{Cd} 0.9881, R^2_{Ni} 0.9805, K_{Zn} 15.58, K_{Cd} 20.65, K_{Ni} 28.99, b_{Zn} 2.34, b_{Cd} 1.43, b_{Ni} 2.44; Freundlich R^2_{Zn} 0.9729, R^2_{Cd} 0.6334, R^2_{Ni} 0.9715, K_{Zn} 0.34, K_{Cd} 1.21, K_{Ni} 0.16, n_{Zn} 0.89, n_{Cd} 1.16, n_{Ni} 1.49.

Table 3 Values of constants of the Langmuir and Freundlich models.

Metals	Langmuir			Freundlich		
	K q_{\max} mg/g	b l/mg	R^2	K l/g	n	R^2
Zn	15.58	2.34	0.9773	0.34	0.89	0.9729
Cd	20.65	1.43	0.9881	1.21	1.16	0.6334
Ni	28.99	2.44	0.9805	0.16	1.49	0.9715

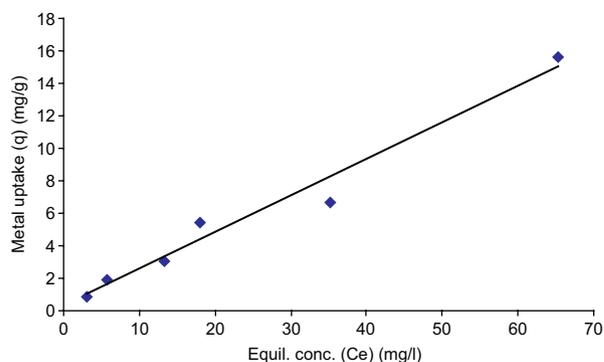


Figure 5 Adsorption isotherm for Zn.

The Langmuir adsorption model was in correlation with the experimental data for Zn, Ni and Cd. The fitness of the Langmuir model for this system indicates that the monolayer coverage of metals on the outer surface occurred uniformly on the active part of the surface. A b value higher than 1.0 implies that adsorption was rather intense. The magnitude of K and b also show easy uptake of metals and high capacity of adsorbent.

Flotation results

The flotation method was applied with $\text{Co}(\text{HMDTC})_3$ for heavy metal separation and analyses included drinking waters, treated waters and filtered raw waters from Turkey. Water samples were floated, 40-fold concentrated, and tested by FAAS. Results are shown in Table 2. The recoveries show the successfulness of the preconcentration and separation of Zn, Cd and Ni by the recommended procedure. The recommended preconcentration procedure is rapid (approx. 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 would not permit some serious contamination risks, which could be manifested by the high blank values.

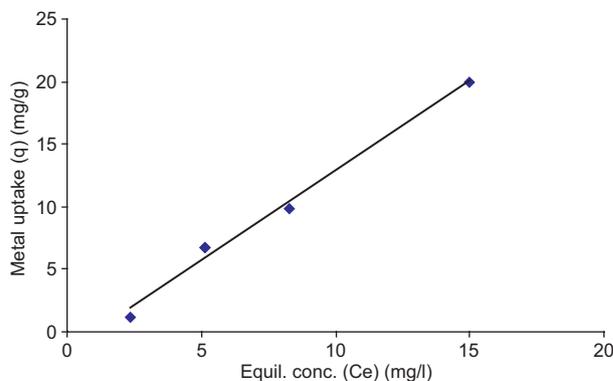


Figure 6 Adsorption isotherm for Cd.

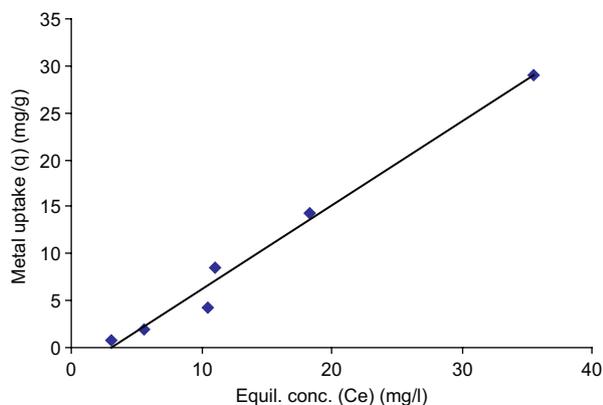


Figure 7 Adsorption isotherm for Ni.

Conclusion

Two methods, ion exchange and flotation techniques, were used for the preconcentration of Ni(II), Zn(II) and Cd(II) ions in natural water. The ion exchanger resin, Lewatit TP 207 iminodiacetate, examined in this paper provides a simple, rapid, accurate and reliable technique for the preconcentration of metal separation from water sample. The recovery yields obtained with standard metal solutions in deionized water were 95% and the lowest detection limit for Ni(II), Zn(II) and Cd(II) based on three times the standard deviations of the blank ($K=3$, $n=21$) was 0.010 mg/l, respectively. The flotation technique with Co(HMDTC)_3 as collector can be used for the successful determination of trace elements. The flotation recoveries achieved were higher than 99%. The benefit of this method is the elimination of matrix interferences on Ni, Zn and Cd ion determination. The flotation procedure is rapid and extends the range of conventional AAS determination of heavy metals. Flotation equipment is simple and inexpensive. Detection limits for flotation are approximately 0.010 mg/l.

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