Electrothermal Atomic Absorption Spectrometric Determination of Nickel after its Flotation Enrichment by Iron(III) Hexamethylenedithiocarbamate

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Abstract. Nanogram quantities of nickel were removed from 1 L samples of dilute aqueous solutions by coflotation. A mixture of hydrated iron(III) oxide ($Fe_2O_3 \cdot xH_2O$) and iron(III) hexamethylenedithiocarbamate ($Fe(HMDTC)_3$) served as collectors. After flotation separation from the mother liquor, the solid sublate containing nickel traces was dissolved and the analyte was determined by electrothermal atomic absorption spectrometry (ETAAS). All important parameters necessary for the successful collection of nickel were checked. The results of nickel ETAAS analysis in tap and spring waters were compared with inductively coupled plasma-atomic emis-sion spectrometric measurements (ICP-AES). The limit detection of nickel by the ETAAS method is 0.0078 μg/L.

Key Words: Nickel, preconcentration, colloid precipitate flotation, iron(III) hexamethylenedithiocarbamate, collector, water, atomic absorption spectrometric determination

Introduction

Heavy metals have received a great deal of attention in the study of water pollution. Their low concentrations in some fresh waters mean that a preconcentration is unavoidable during their determination. In the last two decades, considerable attention has been paid to flotation techniques as enrichment methods[1-4]. They have been classified into two submethods, colloid precipitate flotation (called coflotation), and ion flotation. On account of much higher enrichment factors being obtained by coflotation than by ion flotation, coflotation is more frequently used. Coflotation has the advantages of the other conventional carrier precipitation techniques also. So the precipitation, as the preconcentration method, needs much more time for troublesome filtration and centrifugation for the separation of the collector precipitate from mother liquor. This inconvenience is avoided by the use of coflotation. The separation of the solid sublate from the processed water phase by the air bubbles is much easier and far more rapid.

There are data in the literature about nickel determination by atomic absorption spectrometry (AAS) or ICP-AES after its coflotation. Many types of collectors, such as hydrated aluminum(III) oxide[1-5],

hydrated indium(III) oxide[1−4,6], hydrated zirconium(VI) oxide[1−4,7] one word $Fe_2O_3 \cdot xH_2O$ [1−4,8], were investigated for this purpose. Our experience has shown that tetramethylenedithiocarbamate (TMDTC⁻) or hexamethylenedithiocarbamate (HMDTC⁻) anions added to the water system containing amorphous bulky precipitate of $Fe_2O_3 \cdot xH_2O$, ameliorates and facilitates the flotation procedure for different heavy metals[9−17]. Dithiocarbamate has a positive effect on the incorporation of metal traces in the structure of sublate, makes easier the separation of the solid phase from the water and shortens the time consumed for the step of aeration. In the previous paper about nickel coflotation and determination by ETAAS, $Fe_2O_3 \cdot xH_2O$ and iron(III) tetramethylenedithiocarbamate, $Fe(TMDTC)_3$, were used as a collector mixture[11]. This is the first attempt to apply HMDTC⁻ for nickel flotation from water samples. The scope of this report is to present the results of nickel flotation by a mixture of $Fe_2O_3 \cdot xH_2O$ and $Fe(HMDTC)_3$, and to identify and show the advantages of using HMDTC⁻ instead of TMDTC⁻.

Experimental

Apparatus

All atomic absorption spectrometric measurements were made with a Perkin-Elmer 1100 B atomic absorption spectrometer with a Perkin-Elmer graphite fur-nace, HGA-700. A nickel Perkin-Elmer hollow cathode lamp was applied as a radiation source. Instrumental parameters (temperature and time) for the ETAAS determination were established by extensive testing and were 90°C and 20 s (for drying), 1200°C and 30 s (for pyrolysis), 2400°C and 5 s (for atomizing) and 2650°C and 3 s (for cleaning). Inductively coupled plasma-atomic emission spectrometric measurements (ICP-AES) were performed by Varian spectrometer Model Liberty 110 with operating frequency of 40.68 MHz, R.F. power of 1.0 kW (for Ni 231.604 nm), spectral resolution of 18 pm, plasma argon flow rate of 12 L/min, auxiliary argon flow rate 0.75 L/min, nebulizer flow rate of 2 L/min and sample flow rate of 2 mL/min. The electrokinetic (ζ) potential of the particle surface was determined electrophoretically by means of a device analogous to Chaikovskiis equipment[18,19]. The flotation separations were carried out in a cylindrical glass cell (4×105 cm) with a sintered glass disk (porosity No. 4) at its bottom to produce air bubbling. A combined glass electrode (Iskra, M 0101) and the pH meter (Iskra, M 5705) were used to monitor the pH of the solutions during the step of incorporation of nickel traces in the collector mixture.

Reagents and standards

All chemicals used for preparation of solutions were of an analytical-reagent grade except for the surfactants sodium dodecylsulfate (NaDDS), sodium oleate (NaOL), sodium palmitate (NaPL), sodium stearate (NaST), benzethonium chloride (BTC), cetyltrimethylammonium bromide (CTAB) and triton X-100 (TX-100). The aqueous solutions were prepared by deionized redistilled water. By dissolving an appropriate amount of $NiCl_2 \cdot 8H_2O$ (Merck) in water, a stock solution of nickel(II) was prepared as 1 mg/mL. Before each investigation, nickel standard solutions were freshly prepared by diluting this stock solution. High-purity iron metal (Merck) served to prepare stock solution of iron(III) in conc. HNO_3, as 30 mg/mL. To convert all iron in iron(III), the dissolution was performed by heating. By diluting this iron(III) stock solution, a series of standards with the concentration of iron ranging from 2.5 to 100 mg/L were obtained. The solution

of HMA-HMDTC was made as 0.1 mol/L in 96% ethanol. The 0.5% solutions of tensides were obtained by dissolving an appropriate amount of surfactant in water (TX-100), in 95% ethanol (NaDDS, NaOL) and in 99.7% propan-2-ol (NaPL, NaST). The pH of the test solutions was regulated by 0.1 mol/L solution of HNO_3 and 2.5% and 10% solutions of KOH. A saturated solution at 20°C of KNO_3 ($c = 2.78$ mol/L) served as the regulator of ionic strength (I_c). To transfer the content from the beaker into the flotation cell a solution of NH_4NO_3 (0.1 mol/L) was used.

Flotation procedure

1 L of acidified water sample was placed in an acid-cleaned beaker. After adding saturated solution of KNO_3 (6 mL), 10 mg of iron(III) as a solution of $Fe(NO_3)_3$ was put into the beaker. The pH was carefully adjusted to 6.0 by means of the solution of KOH (10% and 2.5%). After 5 min of stirring (first induction time - t_1), 2 mL of 0.1 mol/L solution of HMA-HMDTC were added to the solution. The yellow-brown bulky precipitate of $Fe_2O_3 \cdot xH_2O$ was gradually transformed in the black precipitate of $Fe(HMDTC)_3$. After 15 min of stirring (second induction time - t_2), 1 mL of sodium dodecylsulfate (NaDDS) was added to the solution with $Fe(HMDTC)_3$. To avoid dissolution of the sublate, the content of the beaker was quantitatively transferred into the flotation cell with 3-4 mL of 0.1 mol/L NH_4NO_3. Air (50 ml/min) was passed from the perforated bottom of the cell for 1-2 min. Then, the glass pipette-tube was immersed into the cell through the foam layer formed at the surface of liquid in the cell and the water phase was sucked off. Hot 65% HNO_3 solution (2.5 mL) was added to the cell to dissolve the scum. The solution was collected in a 25 mL volumetric flask. The flask was filled up to the mark with 4 mol/L HNO_3 and the sample was ready for ETAAS measurements.

Results and Discussion

pH of the working solutions

The influence of pH on the nickel flotation recovery (R) was studied within the range 3.0 to 6.5. Standard solutions (1 L) containing 25 and 50 μg of nickel were floated with constant iron mass (20 mg) and amount of $HMDTC^-$ ($2 \cdot 10^{-4}$ mol) at constant ionic strength (0.02 mol/L) by addition of 1 mL 0.5% alcoholic solution NaDDS. The R/pH curves (Fig. 1) illustrate the nickel recovery dependence on medium pH. Within the pH interval of 3.0 to 5.0 there is partial protonation of dodecylsulfate anions (DDS^-) and their transformation in dodecylsulfate molecules (HDDS), which are not able to perform the proper flotation separation. Therefore, within the pHs of 3.0 to 5.0 the nickel recoveries are poor and not quantitative (R<95%). At pHs below 3.0 the protonation of DDS^- is complete and at pH<3.0 could not occur, which may be confirmed by the value of $pK_a = 1.33$ of HDDS (the protonated form of DDS^-). Because the nickel flotation recoveries are quantitative within the pH range 5.0 to 6.5 (95.0-100.0%), for further investigation pH=6.0 was chosen to be the working pH.
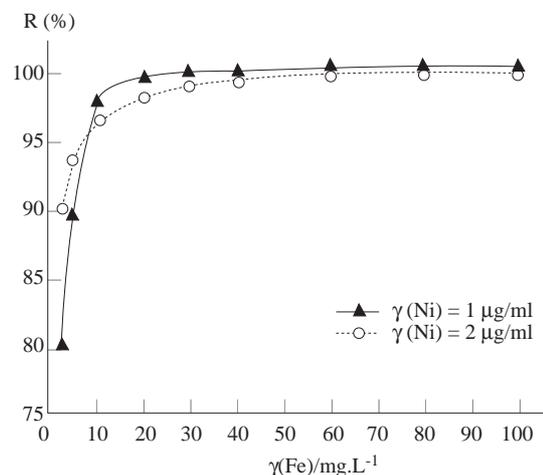
Iron mass

Nickel flotation recoveries depend on iron mass. This effect was investigated by changing the mass of iron added to the test solutions (1 L) containing 25 and 50 μg of nickel from 2.5 to 100 mg. During the

preconcentration all other experimental parameters, i.e., pH $= 6.0$, $I_c = 0.02$ mol/L, $n(\text{HMADTC}^-) = 2 \cdot 10^{-4}$ mol, were kept constant. The data presented in Fig. 2 show that nickel flotation can be performed correctly with 10 mg iron (96.3-97.5%). Therefore, 10 mg of iron per liter of solution was selected as the most appropriate for the procedure.
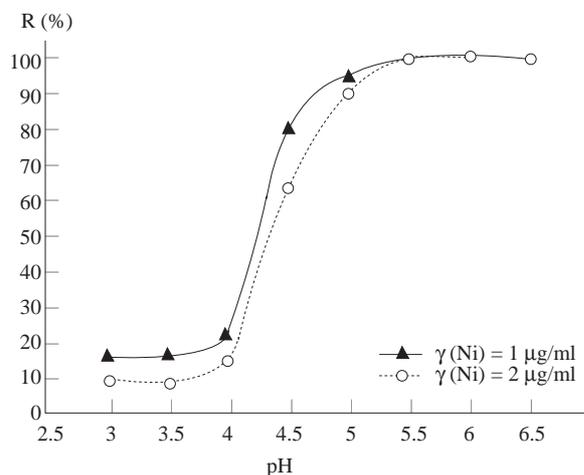
Figure 1. Influence of pH on nickel flotation recoveries (10 mg Fe, $2 \cdot 10^{-4}$ mol of HMDTC$^-$, 0.02 mol/L KNO$_3$, NaDDS as surfactant)

Figure 2. Influence of iron mass on nickel recovery (R) at constant pH $= 6.0$, $I_c = 0.02$ mol/L, and c(HMDTC$^-$) $= 2 \cdot 10^{-4}$ mol/L

Amount of HMDTC$^-$

The effect of HMDTC$^-$ amount was studied by performing four series of flotations at constant pH (6.0) and I_c (0.02 mol/L) using different volumes (1.3, 2, 3 and 6 mL) of a 0.1 mol/L HMA-HMDTC solution. The first series of solutions contained 5, the second 10, the third 20 and the fourth 30 mg of iron(III). Each solution contained 25 μg nickel per L.

The results in Table 1 show that nickel could be floated quantitatively (99.5-100.0%), if 5 mg of iron together with $3 \cdot 10^{-4}$ or $6 \cdot 10^{-4}$ mol of HMDTC$^-$ were applied. When 10, 20 or 30 mg of iron were used, $2 \cdot 10^{-4}$ mol of HMDTC$^-$ was enough for quantitative separation of nickel from the mother liquor. All further increases of $n(\text{HMDTC}^-)$ did not change the results of the flotation collection of nickel.

By comparing the ratio $n(\text{Fe}) : n(\text{HMDTC}^-)$ with the flotation efficiency, it can be concluded that nickel could be floated quantitatively with 5 mg Fe, when iron-to-HMDTC$^-$ reached a stoichiometric mole ratio of 1 : 3 (Table 1). The preconcentration performed by 10, 20 and 30 mg iron did not need to reach a stoichiometric ratio of 1 : 3 for effective flotation to occur, because the further addition of iron significantly influence nickel flotation recovery. It is obvious that the collection of nickel depends on Fe(HMDTC)$_3$, but nickel traces are coprecipitated by Fe$_2$O$_3 \cdot$xH$_2$O too. The experimental data of nickel recoveries at pH=6 and $I_c = 0.02$ mol/L are 45.6%, performed only by Fe$_2$O$_3 \cdot$xH$_2$O, show that the precipitation of this reagent in the whole collection of nickel traces is significant. For the proposed procedure 10 mg iron and $2 \cdot 10^{-4}$ mol/L of HMDTC$^-$ per liter were selected as the most appropriate.

Table 1. Influence of amount of HMDTC$^-$ and the stoichiometric ratio n(Fe) : n(HMDTC$^-$) on nickel recoveries R (%) at pH = 6.0 and I_c = 0.02 mol/L

n(Fe)/mol	n(HMDTC$^-$)/mol	n(Fe) : n(HMDTC$^-$)	R (%)
5 mg Fe			
8.95·10^{-5}	1.3 · 10^{-4}	1 : 1.4525	85.5
8.95·10^{-5}	2.0 · 10^{-4}	1 : 2.2346	92.1
8.95·10^{-5}	3.0 · 10^{-4}	1 : 3.3519	99.5
8.95·10^{-5}	6.0 · 10^{-4}	1 : 6.7039	100.0
10 mg Fe			
1.79·10^{-4}	1.3 · 10^{-4}	1 : 0.7263	87.5
1.79·10^{-4}	2.0 · 10^{-4}	1 : 1.1173	96.4
1.79·10^{-4}	3.0 · 10^{-4}	1 : 1.6760	99.0
1.79·10^{-4}	6.0 · 10^{-4}	1 : 3.3520	99.8
20 mg Fe			
3.58·10^{-4}	1.3 · 10^{-4}	1 : 0.3630	88.3
3.58·10^{-4}	2.0 · 10^{-4}	1 : 0.5585	95.1
3.58·10^{-4}	3.0 · 10^{-4}	1 : 0.8378	97.1
3.58·10^{-4}	6.0 · 10^{-4}	1 : 1.6755	98.9
30 mg Fe			
5.37·10^{-4}	1.3 · 10^{-4}	1 : 0.2420	92.0
5.37·10^{-4}	2.0 · 10^{-4}	1 : 0.3724	95.6
5.37·10^{-4}	3.0 · 10^{-4}	1 : 0.5586	100.0
5.37·10^{-4}	6.0 · 10^{-4}	1 : 1.1171	100.0

Ionic strength

The proper coagulation of the system is the criterion for successful flotation, which depends of the ionic strength (I_c). Therefore, to optimize this very important parameter, which regulates the coagulation of the system I_c, three standards of nickel were floated at pH 6.0 with 10 mg iron and $2 \cdot 10^{-4}$ mol of HMDTC$^-$ without adding any ionic strength adjuster. Tested solutions were of varying volumes (250, 500 and 1000 mL). Each standard contained 25 μg nickel, so that the final solutions concentrated by flotation (25 mL) had a concentration of 1 μg/mL. To each standard solution 10 mg Fe was added by 1 mL of 0.179 mol/L solution of Fe(NO$_3$)$_3$. The ionic strength of the first, second and third solution were 0.0043 mol/L, 0.0022 mol/L and 0.0011 mol/L respectively (Table 2). After flotations, nickel was determined by AAS. The recovery value of the first solution was 100%, of the second was 86.9%, while of the third was 78.5%. These data showed that it is necessary to adjust the ionic strength of the system to higher than 0.0011 mol/L to obtain the proper coagulation. Therefore, an ionic strength of 0.02 mol/L was chosen for further investigations.

ζ potential and selection of surfactant

The foaming agents investigated within the pH interval 3.5 to 6.5 (Table 3) were cationic surfactants (BTC and CTAB), anionic surfactants (NaDDS, NaOL, NaPL and NaST) and non-ionic surfactant triton X-100 (TX100). BTC and CTAB over the whole pH range of investigation, produced foam but there was no flotation. TX100 was ineffective also. Unlike cationic surfactants, anionic surfactants were shown to be much more capable of performing the flotation.

Table 2. Dependence of the nickel flotation recoveries on the ionic strength (I_c) of the solutions (1 μg/mL Ni in the final solution)

m(Fe) / V		R (%)
10 mg / 250 mL		
$c(\text{Fe}_3^+) = 0.0007162$ mol/L $c(\text{NO}_3^-) = 0.0021487$ mol/L	$I_c = 0.0043$ mol·L^{-1}	100
10 mg / 500 mL		
$c(\text{Fe}_3^+) = 0.0003581$ mol/L $c(\text{NO}_3^-) = 0.0010743$ mol/L	$I_c = 0.0022$ mol·L^{-1}	86.9
10 mg / 1000 mL		
$c(\text{Fe}_3^+) = 0.0001791$ mol/L $c(\text{NO}_3^-) = 0.0005372$ mol/L	$I_c = 0.0011$ mol·L^{-1}	78.5

The value of ζ potential of the Fe(HMDTC)$_3$ flocs (68.0-69.0 mV) explained why BTC and CTAB could not be effective during the flotation. The positive sign of the collector floc surfaces repulsed the cationic surfactants. The situation with anionic surfactants is different. Having an opposite sign to the collector particle surfaces, anionic surfactants and collector flocs were attracted and made the micelles, which carried out the flotation.

Among the anionic surfactants, NaDDS was shown to be the most effective within the pH range 5.0 to 6.5 (94.9-97.7%). The recoveries of nickel obtained by the combination NaDDS/NaOL within a narrow pH interval of 5.5 to 6.5 were satisfactory (95.3-97.7%) as well, but this combination of surfactants gave an unnecessarily copious scum, which was very difficult to destroy with conc. HNO$_3$. So NaDDS was selected as the most appropriate reagent.

Table 3. Applicability of divers surfactants for colloid precipitate flotation of nickel using Fe(HMDTC)$_3$ as collectors ($I_c = 0.02$ mol/L, 10 mg iron, $2 \cdot 10^{-4}$ mol HMDTC$^-$)

Ni	R (%)				
pH	4.5	5.0	5.5	6.0	6.5
BTC	foam, no flotation				
CTAB	foam, no flotation				
NaDDS	39.7	94.9	97.7	97.7	97.7
NaOL	76.5	88.2	88.2	95.2	97.7
NaPL	no foam	62.5	90.5	95.2	95.2
NaST	no foam	83.5	85.7	88.3	88.3
TX-100	foam, no flotation				
NaDDS/NaOL	33.7	80.5	95.3	95.3	97.7
NaST/NaOL	33.0	64.7	64.7	85.7	93.7
NaPL/NaOL	65.5	87.0	89.3	91.3	91.3

Detection limit

The detection limit of the method was estimated as three values of the standard deviation of the blank signal because the ordinate value of the linear calibration curve is near to zero ($s = 0.0026$ μg/L). For this purpose, ten successive blank measurements were made. The ETAAS detection limit of nickel is 0.0078 μg/L. The relative standard deviation of the method was 3.5%.

Application of the method

The basic procedure relates to uncontaminated water samples (spring and tap water). Samples were collected in polyethylene containers (pretreated by conc. HNO_3, washed by deionized redistilled water, and then with a portion of the water sample) without filtration. To prevent the possible hydrolytic precipitation of some mineral salts, a few milliliters of conc. HNO_3 had to be added to 1 L of natural water. The pH had to be *ca.* 3.

The new flotation method was applied for analyzing five samples of natural water by a calibration curve and by the method of standard addition. For this purpose, to 1000 mL aliquots of water samples known amounts of nickel were added. Then they were floated and 40-fold concentrated. The concentration of total nickel in the final concentrated samples was tested by ETAAS (Table 4). The results obtained by ETAAS were compared with the results obtained by ICP-AES determinations. The samples for ICP-AES were prepared by concentration, by evaporation (from 1 L to 25 mL) of water samples. It was found that high Ca content in the Kapistec water sample (which is evident from the high DH^o value) influenced nickel determination by ICP-AES.

Table 4. ETAAS determination of nickel in natural water samples by the method of standard additions compared with ICP-AES results

Sample of water	ETAAS				ICP-AES[a]
	Added μg/L Ni	Estimated μg/L Ni	Found μg/L Ni	R (%)	Found μg/L Ni
Pantelejmon	-	-	0.06	-	-
15.05 DH^o [b]	1.25	1.31	1.25	95.4	
pH = 7.84	2.50	2.56	2.50	97.7	
Sreden Izvor	-	-	0.29	-	0.31
17.65 DH^o	1.25	1.54	1.47	95.5	
pH = 7.36	2.50	2.79	2.73	97.8	
Raduša	-	-	0.62	-	0.66
25.57 DH^o	1.25	1.87	1.92	102.7	
pH = 8.50	2.50	3.12	3.08	98.7	
Kavadarci	-	-	0.15	-	0.17
5.71 DH^o	1.25	1.40	1.35	96.4	
pH = 7.58	2.50	2.65	2.63	99.2	
Rašče	-	-	0.25	-	0.25
16.49 DH^o	1.25	1.50	1.50	100.0	
pH = 7.18	2.50	2.75	2.80	101.8	
Kapištec	-	-	1.17	-	1.05
23.36 DH^o	1.25	2.42	2.32	95.9	
pH = 7.5	2.50	3.67	3.58	97.5	

[a] Results of ICP-AES as independent method. Water samples were enriched by evaporation.
[b] DH (*Deutsche Härte*) German degree of water hardness.

Conclusion

The optimal conditions for the determination of nickel by ETAAS following colloid precipitate flotation enrichment with two collectors were established. The presence of $HMDTC^-$ improves the separation of nickel from the processed water phase. This dithiocarbamate anion increases the hydrophobicity of

the sublate, which is the most important criterion for the successful flotation. The value of ζ potential of the Fe(HMDTC)$_3$ flocs (68.0 mV) is more positive than the ζ potential of Fe$_2$O$_3$·xH$_2$O (25.0 mV) and Fe(TMDTC)$_3$ (46.5 mV) flocs[11]. This results in more stable micelles obtained from Fe(HMDTC)$_3$ particles and dodecylsulfate anions, and consequently better separation efficiency. The reason this better hydrophobicity is the larger hydrocarbon ring of HMDTC$^-$. The froth layer obtained on the water surface in the flotation cell is better fixed at the gas/liquid interface, and its separation from the processed water phase is easier. The better hydrophobicity of the sublate with HMDTC$^-$ (instead of the sublate with TMDTC$^-$ [11]), needs only one surfactant and consequently an amount of conc. HNO$_3$ four times lower. The recommended method extends the concentration range of the conventional atomic absorption determination of nickel and can be applied for trace analyses of this analyte in dilute aqueous solutions.

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