ELECTROTHERMAL ATOMIC ABSORPTION SPECTROMETRY OF COBALT AND NICKEL PRECONCENTRATED BY PRECIPITATE FLOTATION

T. Stafilov, K. Čundeva and S. Atanasov*

Institute of Chemistry, Faculty of Science, St. St. Cyril and Methodius University, PO Box 162, 91001 Skopje, Macedonia
*University of Mining and Geology, 1756 Sofia, Bulgaria

Abstract

An experimental investigation of the simultaneous determination of trace levels of cobalt and nickel in fresh water based on precipitate flotation with hydrated iron(III) oxide is presented. All important parameters necessary for the successful precipitate flotation (optimal mass of collector, pH of the medium, induction time) were investigated. In the optimal pH range of 9.5 – 10 established by recommended procedure, cobalt was separated quantitatively (99.7%) with Fe(III) as the constitutive element of the collector used. Nickel was separated quantitatively (96.2%) with Fe(III) in the pH interval 9 – 10. The possibility to use electrothermal atomic absorption spectrometry after separation and preconcentration was studied. The electrothermal atomic absorption spectrometry detection limit for cobalt is 0.15 µg/l, and for nickel it is 0.24 µg/l. The proposed method is simple, rapid and applicable to the cobalt and nickel separation at µg/l levels from a large volume of water.

Keywords: Cobalt, Nickel, Preconcentration flotation, Electrothermal atomic absorption spectrometry

Introduction

In these days of concern over environmental pollution, there is an increasing need for a simple, rapid and precise method for determination µg/l levels of cobalt and nickel in fresh water. Atomic absorption spectrometry (AAS) provides high sensitivity and rapid measurement for a number of heavy metals. However, for low µg/l levels of these metals in fresh water, a precise direct determination is impracticable even by this method. Among the various techniques for separation of trace cobalt and nickel from large volumes of dilute aqueous solutions, the flotation procedures turned out to be very simple compared with classical separation methods such as liquid-liquid extraction, ion-exchange, coprecipitation, etc. [1-3].

There are published methods of precipitate flotation of cobalt and nickel using hydrated metal oxides as collectors in combination with flame atomic absorption spectrometry (FAAS) [4, 5], inductively coupled plasma – atomic emission spectrometry (ICP–AES) [6]. The applying of the precipitate flotation for cobalt and nickel in combination with electrothermal atomic absorption spectrometry (ETAAS) using hydrated metal oxides as collectors is scanty [7]. This paper is the first attempt to use ETAAS for cobalt and nickel determination after their concentration with $Fe_2O_3.xH_2O$ as precipitating collector. The results obtained by this instrumental method were compared with the results obtained by ICP–AES as comparative independent instrumental method. The proposed method is simple, rapid and applica-

ble to cobalt and nickel separation at µg/l levels from a large volume of water, similar to solid phase extraction method for metal concentration [8-10].

Experimental

Apparatus

The apparatus employed in this work has been previously described [11]. The Perkin Elmer hallow cathode lamps were used as light sources. Instrumental parameters (temperature and time) for ETAAS were established by extensive testing and these are given in Table 1. Inductively coupled plasma – atomic emission spectrometry was performed by Varian ICP–AES spectrometer model Liberty 110. The flotation cell used to carry out the preconcentration was a glass cylinder (4 × 105 cm) with a sintered glass disk (porosity № 4) at the bottom to generate air bubbling.

Reagents

All reagents used were of analytical-reagent grade except for tensides sodium dodecyl sulfate (NaDDS) and sodium oleate (NaOL). Aqueous solutions were prepared in deionized redistilled water. Stock solutions of cobalt and nickel, respectively, were made from $CoCl_2.5H_2O$ and $NiCl_2.8H_2O$ as 1 mg/ml solutions. Before each investigation, standard solutions of these colligends were freshly prepared by diluting the corresponding stock solutions. Iron(III) stock solution (30 mg/ml) was prepared by dissolving high-purity iron metal in conc. HNO_3. Series of standard solutions with mass concentrations of iron (γ_{Fe}) ranging from 2.5 to 100 mg/ml were obtained by dilution of this Fe(III) stock solution. The diluted

Table 1. Optimal instrumental parameters for AAS

Parameter	Co	Ni
Wavelength	240.7 nm	232.0 nm
Spectral slit	0.7 nm	0.7 nm
Lamp current	30 mA	25 mA
Drying	120°C, 30 s	90°C, 30 s
Charring	1300°C, 30 s	1200°C, 30 s
Atomization	2600°C, 5 s	2400°C, 5 s
Cleaning	2650°C, 5 s	2650°C, 5 s
Purge gas	Argon	Argon

standard solutions of cobalt, nickel and iron serve to investigate the optimal conditions for performing the flotation procedure and for the method of standard additions of the natural water analysis. The 0.5% solutions of tensides used were prepared by dissolving appropriate amounts of NaDDS and NaOL in 95% ethanol. The pH was regulated by diluted HNO_3 (0.1 mol/l) and KOH (2.5% and 10%). Saturated solution of KNO_3 (c = 2.78 mol/l) was used to adjust the ionic strength.

Procedure for flotation

The presented method utilises clear and uncontaminated fresh water. The samples investigated were tap water from the city of Skopje (from the source Rašče) and source water from St. Pantelejmon. The water was not filtered. Immediately after the sampling, to prevent the possible hydrolytic precipitation of some mineral salts, a few millilitres of conc. HNO_3 had to be added to 1 l of natural water. The pH had to be *ca.* 2.8 – 3.

The water sample (1 l) was placed in a 1 l beaker. After adding 6 ml of saturated solution of KNO_3 and suitable mass of Fe(III), the pH was carefully adjusted to 9 – 9.5 by KOH solution (2.5% or 10%). The system with the red-brown precipitate was stirred for 15 min (induction time). Afterwards, tenside solutions (1 ml NaDDS and 1 ml NaOL ethanolic solutions) were added and the content of the beaker was transferred into the cell with a small portion of 0.1 mol/l NH_4NO_3 solution. Air (50 ml/min) was passed through the perforated bottom of the cell for 2 – 3 min. Then, a glass pipette-tube was immersed into the cell trough the foam layer and the water phase was sucked off. The foam layer remained in the cell. Hot 4 mol/l HNO_3 solution was added into the cell to destroy the scum. The solution was sucked off and collected in a volumetric flask (25 ml), which was filled up to the mark with 4 mol/l HNO_3 solution and the sample was ready for AAS measurement.

Results and Discussion

Influence of the collector mass on colligend flotation recoveries
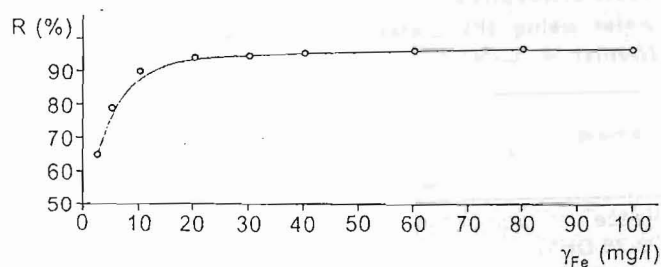
Adding different masses of Fe(III) (from 2.5 to

Fig. 1. Dependence of cobalt flotation recovery (R) on iron(III) mass concentration (γ_{Fe}) at a constant pH (9.5) and ionic strength (I_c = 0.02 mol/l)
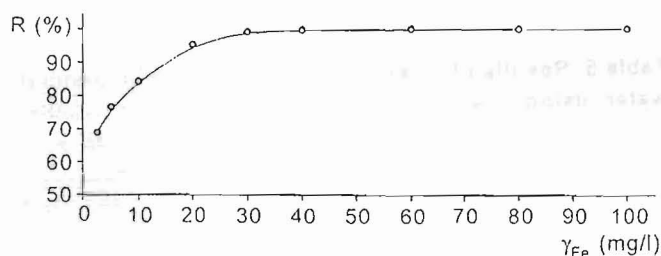

Fig. 2. Dependence of nickel flotation recovery (R) on iron(III) mass concentration (γ_{Ni}) at a constant pH (9.5) and ionic strength (I_c = 0.02 mol/l)

Fig. 3. Dependence of the cobalt flotation recoveries (R) on the medium pH: γ_{Co} = 1 µg/ml (•); γ_{Co} = 2 µg/ml (o)

100 mg) to the working solutions at a constant pH (9.5) and ionic strength (I_c = 0.02 mol/l) adjusted with KNO_3, series of flotation were carried out. The collector precipitate was obtained from water solutions containing 25 and 50 µg cobalt and nickel, respectively. The final volume of solution concentrated by flotation was 25 ml. The effects of the collector mass on the cobalt and nickel recoveries as a function on the amount of iron(III) added as a constitutive element of the collector $Fe_2O_3.xH_2O$ are presented in Figs. 1 and 2. The results show that the optimal value of cobalt flotation recovery (94.6%) was reached by addition of 30 mg Fe(III) at pH about 9.5. The nickel flotation was quantitative (R = 95.1%) by addition of 20 mg Fe(III) at pH about 9.5.

Influence of the medium pH on the colligend flotation recoveries

The effect of the medium pH on cobalt and nickel was studied by floating series of solutions containing 25 and 50 µg Co and Ni. The influence was investigated within the pH range from 3 to 10.
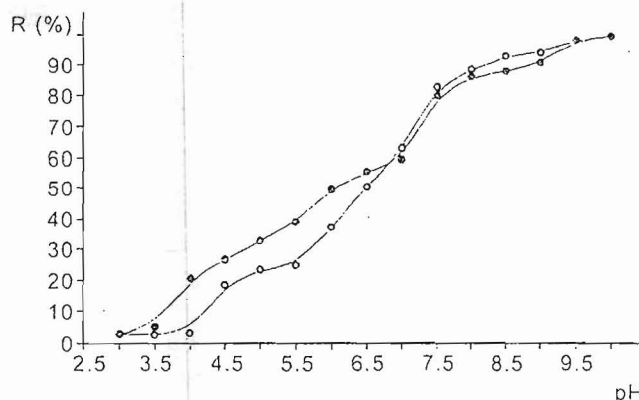
The Fe(III) mass added was constant (30 mg for cobalt, 20 mg for nickel). The ionic strength was always constant (I_c = 0.02 mol/l), too. Fig. 3 illustrates a significant effect of pH on the cobalt recoveries and maximum is achieved within the range of 9.5 to 10. Fig. 4 illustrates a significant effect of pH on the nickel recoveries and maximum is achieved within the pH interval from 9 to 10. For successful simultaneous preconcentration of both colligends, the pH of 9.5 was chosen as the working pH.

Induction time

The time necessary for incorporation of the colligends in the collector precipitates is termed the induction time τ [1]. The investigation of the relation between the cobalt and nickel recoveries and τ, are given in Table 2. From the results, it can
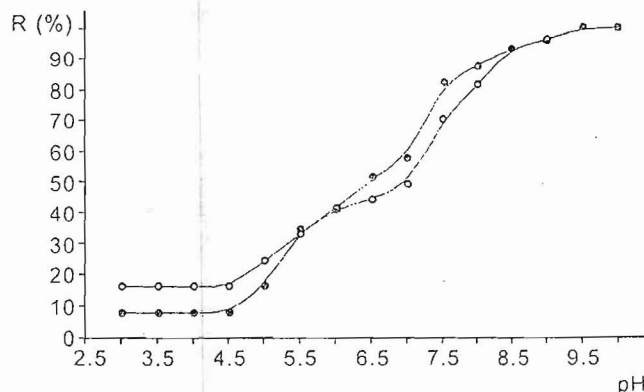

Fig. 4. Dependence of the nickel flotation recoveries (R) on the medium pH: γ_{Ni} = 1 µg/ml (o); γ_{Ni} = 2 µg/ml (•)

Table 2. Influence of the induction time (τ) on cobalt and nickel flotation recoveries; γ_{Co} = 1 μg/ml; γ_{Ni} = 1 μg/ml

τ (min)	Recovery (%)	
	Co	Ni
5	94.0	93.6
10	96.3	95.0
15	97.9	99.9
20	97.1	95.8

be concluded that the separation of colligends (cobalt and nickel) was quantitative within 10 – 20 min. In practice, an induction time of 15 min was used.

Detection limit

To evaluate the detection limit of the method, ten successive blank measurements were made. The detection limit (L_d) was estimated as 3s, where s is the standard deviation. The results are presented in Table 3.

Analysis of natural water

The applicability of the proposed procedure has been verified by the ETAAS analysis of natural water samples with the method of standard additions. Known amounts of cobalt and nickel were added to 1000 ml aliquots of spring and tap water samples. Then they were floated with 30 mg Fe (pH value of 9.5 and ionic strength of 0.02 mol/l) and tested by ETAAS. The recoveries of 100.8 – 103.6% for cobalt (Table 4) and 96.0 – 103.2% for nickel (Table 5) show that the preconcentration and separation of these colligends are satisfactory. The results obtained by ETAAS were compared with the results obtained by ICP–AES as an independent method. The samples for ICP–AES were concentrated by evaporation (from a volume of 1000 ml to 25 ml) of spring and tap water (Tables 4 and 5).

Table 3. Standard deviation (s), relative standard deviation (s_r) and detection limit (L_d) of cobalt and nickel determined by ETAAS

Element	s (μg/l)	s_r (%)	L_d (μg/l)
Co	0.05	4.55	0.15
Ni	0.08	5.45	0.24

Table 4. Results of ETAAS determination of Co in natural water using the method of standard additions; DH° (*Deutsche Härte*) – German degree of water hardness

Sample	ETAAS				ICP-AES
	Added (μg/l)	Estimated (μg/l)	Found (μg/l)	R (%)	Found (μg/l)
Rašče*	0.00	–	< 0.15	–	< 0.1
20.26 DH°	1.25	1.25	1.26	100.8	
pH = 7.08	2.50	2.50	2.55	102.2	
St. Pantelejmon**	0.00	–	< 0.15	–	< 0.1
14.9 DH°	1.25	1.25	1.28	102.4	
pH = 7.6	2.50	2.50	2.59	103.6	

*Tap water from the city of Skopje (a spring of Rašče)
**Water from the source of St. Pantelejmon

Table 5. Results of ETAAS determination of Ni in natural water using the method of standard additions; DH° (*Deutsche Härte*) – German degree of water hardness

Sample	ETAAS				ICP-AES
	Added (μg/l)	Estimated (μg/l)	Found (μg/l)	R (%)	Found (μg/l)
Rašče*	0.00	–	0.76	–	0.65
20.26 DH°	1.25	2.01	1.98	98.5	
pH = 7.08	2.50	3.26	3.13	96.0	
St. Pantelejmon**	0.00	–	0.30	–	0.32
14.9 DH°	1.25	1.55	1.60	103.2	
pH = 7.6	2.50	2.80	2.74	97.9	

*Tap water from the city of Skopje (a spring of Rašče)
**Water from the source of St. Pantelejmon

Conclusions

The results presented in this paper confirm that the recommended precipitate flotation procedure can be applied as a separation and preconcentration method of cobalt and nickel in fresh water before their determination by ETAAS. The use of this preconcentration method in combination with ETAAS as an instrumental method moves the colligend detection limit towards lower concentrations and improves their determinations in the fresh water samples. Cobalt and nickel can be determined separately or simultaneously in mixtures by preliminary selection and correlation of their optimal experimental parameters.

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