Cloud Point Extraction, Simultaneous and Preconcentration Spectrophotometric Determination of Nickel and Cobalt in Water Samples

ALI MOGHIMI[1,*] and MOHAMMAD JAVAD POURSHARIFI[2]

[1]Department of Chemistry, Islamic Azad University, East Tehran (Ghiam Dasht) Branch, Tehran, Iran
[2]Department of Chemistry, Islamic Azad University, Saveh Branch, Saveh, Iran

*Corresponding author: E-mail: alimoghimi@iauvaramin.ac.ir

Cloud point extraction has been used for the preconcentration and simultaneous spectrophotometric determination of nickel and cobalt after the formation of a complex with sodium diethyldithiocarbamate (Na-DDTC) and latter analysis by spectrophotometer using Triton X-114 as surfactant. The parameters affecting the separation phase and detection process were optimized. Under the optimum experimental conditions (*i.e.*, pH = 5, 0.07 mM Na-DDTC, Triton X-114 = 0.25 % (w/v)), calibration graphs were linear in the range of 20-440 and 20-210 µg L^{-1} with detection limits of 9.2 and 8.0 µg L^{-1} for Ni and Co, respectively. The method was applied to the determination of Ni and Co in natural and waste water samples with satisfactory results.

Key Words: Nickel, Cobalt, Cloud point extraction, Diethyldithiocarbamate.

INTRODUCTION

Nickel is the metal component of the enzyme urease and as such is considered to be essential to plants and some domestic animals. Cobalt is known to be essential at trace levels to man, animals and plants for metabolic processes[1]. The high consumption of nickel and cobalt-containing products in industry inevitably leads to environmental pollution at all stages of production, recycling and disposal.

Thus, the determination of trace amounts of nickel and cobalt in biological and environmental samples is important in the fields of environmental analysis, process control and medicine. The determination of trace amounts of cobalt in natural waters is of great interest because cobalt is important for living species as complex Vitamin B$_{12}$. Toxicological effects of large amounts of cobalt include vasodilation, flushing and cardiomyopathy in human and animals[2]. The determination of nickel and cobalt in natural water samples of environmental interest in which it is found at very low concentrations requires the use of pre-concentration methods coupled to spectroscopic methods.

Aqueous solutions of non-ionic surfactants become turbid when they are heated above the temperature known as the cloud point[3,4]. The solution is then separated into two isotropic phases, *i.e.*, a surfactant-rich phase and a bulk aqueous phase. The hydrophobic solutes and metal ions, after the formation of sparingly water soluble complex, can be enriched into the surfactant-rich phase. The small volume of the surfactant-rich phase obtained with this methodology permits the design of extraction schemes that are simple, cheap and have lower toxicity than extraction with organic solvents[5].

The micellar-mediated extraction/pre-concentration, practically expressed in the form of CPE (cloud point extraction), has been applied under batch conditions, to the spectrophotometric analysis of trace metal ions in various samples after the complexation with some chelating agents[5]. The cloud point extraction of metals, with spectrophotometric detection, was first reported by Watanabe and co-workers, who studied the extraction for the pre-concentration of Ni with 1-(2-thiazolylazo)-2-naphtol in Triton X-100 micellar solution[6], but this surfactant has a relatively high cloud point, around 70 ºC. Later, cloud point extraction and pre-concentration was applied to determination of Zn, Cd, Cu, Ni[7-9], U[10], Er[11], Gd[12] and Al[13] by spectrophotometric detection. Although inductively coupled plasma atomic emission (ICP-AES) and ICP-mass spectrometry (ICP-MS) are the most commonly used techniques in determination of trace levels of Ni and Co, but, spectrophotometry continues to enjoy wide popularity. The common availability of the instrumentation, the simplicity of procedures, speed, precision and accuracy of the technique still make spectrophotometric methods attractive.

In the present work we report the results obtained in a study of the cloud point extraction and pre-concentration of Ni and Co, after the formation of a complex with sodium diethyldithiocarbamate (Na-DDTC) and later analysis by spectrophotometry at the wavelength of maximum absorption of each

complex, using Triton X-114 as surfactant. The advantage of the method is to simultaneously determine traces of nickel and cobalt without the need for any chemometric method. The proposed method was applied to the determination of Ni and Co in water samples.

EXPERIMENTAL

A model UV-1601PC spectrophotometer (Shimadzu) with 1.0 cm glass cell was used. The temperature of the cell compartment was kept constant by circulating water from a thermostatic water bath. A centrifuge was used to accelerate the phase separation process. A thermostated bath model LO-Temptrol 154 maintained at the desired temperature was used for the cloud point temperature experiments.

All reagents and sodium diethyldithiocarbamate (Na-DDTC) were of analytical reagent grade. The water utilized in all studies was double-distilled and deionized from a Milli-Q reagent water system from Millipore Corp. Stock solutions of Ni(II) and Co(II) (100 μg mL^{-1}) and those used for the interference study (1000 μg mL^{-1}) were prepared by dissolving appropriate amounts of their corresponding salts in deionized water.

Triton X-114 (Fluka chemie AG) was used without further purification. Fresh 1×10^{-3} M solution of Na-DDTC was prepared daily by dissolving the reagent in least amount of sodium hydroxide and diluting with deionized water. A buffer of pH = 5 was prepared by using sodium acetate and hydrochloric acid at appropriate concentrations.

Procedure: For the cloud point extraction, an aliquot of 10 mL of a solution containing nickel and cobalt, Triton X-114 0.25 % (w/v), 0.07 mM Na-DDTC and 2 mL of buffer acetate (pH = 5), were kept for 15 min in the thermostatic bath at 40 °C. Subsequently, separation of the phases was achieved by centrifugation for 15 min at 5000 rpm. The phases were cooled down in an ice bath in order to increase the viscosity of the surfactant-rich phase. The bulk aqueous phase was easily decanted by simply inverting the tube. The surfactant-rich phase in the tube was made up to 1.0 mL by adding DMF. The absorbance was measured at the wavelength of maximum absorbance of the complex, 534 and 452 nm for Ni and Co, respectively.

RESULTS AND DISCUSSION

Absorption spectra: Fig. 1 shows the absorption spectra for the individual metal complexes in surfactant-rich phase against reagent blank. The nickel and cobalt complexes of Na-DDTC are insoluble in water but are easily dissolved in micelles such as Triton X-114.

Effect of pH: The separation of metal ions by cloud point method involves prior formation of a complex with sufficient hydrophobicity to be extracted into the small volume of surfactant-rich phase; thus obtaining the desired preconcentration[14]. pH plays a unique role on metal-chelate formation and subsequent extraction. Fig. 2 shows the in- fluence of pH on the absorbance of the nickel and cobalt complexes at 534 and 452 nm, respectively. As can be seen, at pH 5 maximum extraction efficiency was obtained. Hence, pH 5 was chosen as the working pH.
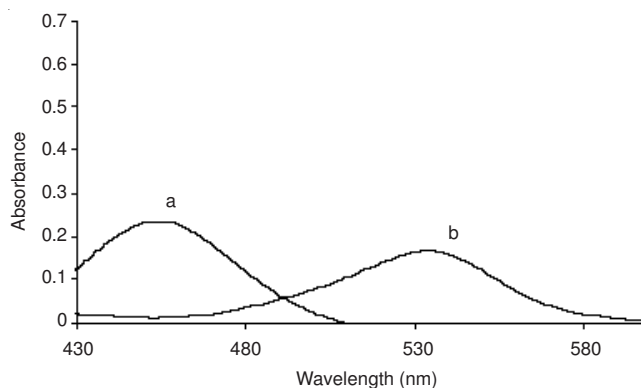

Fig. 1.   Absorption spectra of (a) Co(II) -DDTC complex, (b) Ni(II)-DDTC complex. Conditions: 0.2 % (w/v) Triton X-114, 0.05 mM Na-DDTC and 90 μg L^{-1} Ni and 50 μg L^{-1} of cobalt
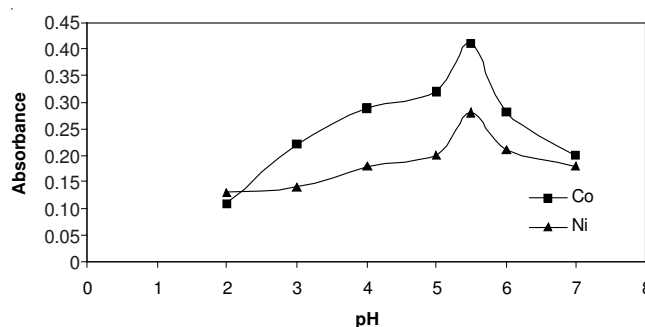

Fig. 2.   Effect of pH on the absorbances of the complexes. Conditions: 0.2 % (w/v) Triton X-114, 0.05 mM Na-DDTC and 100 μg L^{-1} of both analytes (■) Co, (▲) Ni

Effect of Na-DDTC concentration: The effect of concentration of Na-DDTC on analytical response is shown in Fig. 3. As it is seen for both Ni and Co complexes, the signal increases up to a known concentration of Na-DDTC, reaching a plateau, which is considered as complete extraction. A concentration of 0.07 mM was chosen as the optimum.
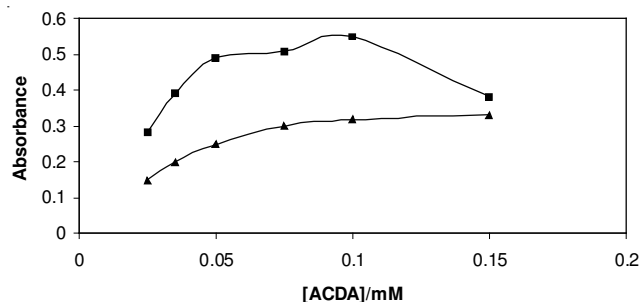

Fig. 3.   Effect of Na-DDTC concentration on the absorbances of the complexes. Conditions: 0.2 % (w/v) Triton X-114, pH = 5 and 100 μg L^{-1} of both analyte. (■) Co, (▲) Ni

Effect of Triton X-114 concentration: The non-ionic surfactant Triton X-114 was chosen because of its commercial availability in a high purified homogeneous form, low toxicological properties and cost. Also, the high density of the surfactant-rich phase, facilitates phase separation by centrifugation. Additionally the cloud point (23-26 °C) of Triton X-114 permits its use in the extraction and/or pre-concentration of a large number of molecules and chelate[10,15]. The variation of absorbance at λ_{max} of each complex as a function of the

concentration of Triton X-114 is shown in Fig. 4. A concentration of 0.25 % (w/v) was chosen as optimum concentration for the determination of both analytes. At lower concentrations, the extraction efficiency of complexes is low probably because of the inadequacy of the assemblies to entrap the hydrophobic complex quantitatively.
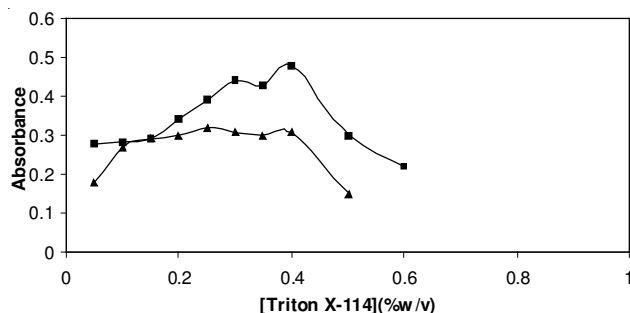

Fig. 4.   Effect of Triton X-114 concentration on the absorbances of the complexes, Conditions: 0.07 mM Na-DDTC, pH = 5 and 100 µg L^{-1} of both analyte. (■) Co, (▲) Ni

Effects of the equilibration temperature and time: Optimal incubation time and equilibration temperature are necessary to complete reactions and to achieve easy phase separation and pre-concentration as efficient as possible. Providing that the complexation reaction has been completed under certain conditions, relevant data show that, for equilibration times of some minutes up to a few days, extraction efficiency increases very slightly and the phase-volume ratio decreases a little[15]. On the other hand, it appears that the phase volume ratio of all non-ionic surfactants decrease as the equilibration temperature increase. The greatest analyte pre-concentration factors are thus expected under conditions where the CPE is conducted using equilibration temperatures that are well above the cloud point temperature of the surfactant. It was found that a temperature of 40 ºC is adequate for both analytes.

It was desirable to employ the shortest equilibration time and the lowest possible equilibration temperature, which compromise completion of reaction and efficient separation of phases. The dependence of absorbance upon equilibration and centrifugation times was studied within the range of 5-25 min. Times of 10 and 15 min were chosen as optimal times for equilibration and centrifugation, respectively.

Effects of added electrolyte: The cloud point of micellar solutions can be controlled by addition of salts, alcohols, nonionic surfactants and some organic compounds (salting-out effects). To date, most of the studies conducted have shown that ionic strength has no appreciable effect on the extraction efficiency. An increase in the ionic strength in the CPE does not seriously alter the efficiency of extraction of the chemical forms. Moreover, the addition of a salt can markedly facilitate the phase-separation process, as demonstrated with some non-ionic surfactant systems, since it alters the density of the bulk aqueous phase[5,16]. It was observed that the addition of NaNO$_3$ within the interval of 0.1-0.8 mol L^{-1} had no significant effect on the cloud point extraction efficiency.

Figures of merit: Calibration graphs were obtained by pre-concentrating 10 mL of a sample containing known amounts of both analytes under the experimental conditions.

Table-1 features the analytical characteristics of the method. Under the specified experimental conditions the calibration curves for Ni and Co were linear from 20-440 and 20-210 µg L^{-1}, respectively.

TABLE-1 ANALYTICAL CHARACTERISTICS OF THE METHOD		
Parameters	Ni	Co
Linear range (µg L^{-1})	20-440	20-210
LOD (µg L^{-1})	9.2	8.0
RSD % (50, 100 µg L^{-1})	2.9, 3.2	2.6, 2.9
Phase volume ratio*	0.1	0.1

*Phase volume ratio is the ratio of the final volume of surfactant-rich phase to that of aqueous phase.

Interferences: There can be two types of interference depending on whether pre-concentration or detection is affected[10]. For detection of interferences, the influence of several ions was tested, including those that most frequently accompany Co and Ni in real samples. The effect of interfering ions at different concentrations on the absorbance of a solution containing 50 µg L^{-1} of each analyte was studied. An ion was considered to interfere when its presence produced a variation in the absorbance of the sample of more than 5 %. This increment of absorbance was evaluated at two wavelengths 534 and 452 nm (corresponding to maximum absorption of Ni and Co complexes), to establish the different effects of the interfering ions on each analyte. Among the interfering ions tested; CO$_3$$^{2-}$, CN$^-$, F$^-$, I$^-$, Br$^-$, CH$_3COO^-$, NO$_3$$^-$, PO$_4$$^{3-}$, Ba^{2+}, Mg^{2+}, Ca^{2+}, Li$^+$, Na$^+$, Zn^{2+}, Mo^{6+}, Fe^{3+} and Al^{3+} did not interfere at concentrations 1000 times higher than those of the analytes. However Cu^{2+}, V^{4+}, V^{5+}, CrO$_4$$^{2-}$ and Cd^{2+} (at concentration of 50 µg L^{-1} each) showed interferences only in the determination of cobalt. Most of these interferences can be easily overcome, for example by masking with appropriate reagents. Two types of pre-concentration interferences may be identified; firstly cations that react with Na-DDTC and secondly ligands that form complexes with Ni and Co, including some anions and ligands. Interference by foreign cations only affects the Na-DDTC concentration because the detection step is approximately selective; therefore, any reagent loss could be avoided by increasing the Na-DDTC concentration.

Determination of nickel and cobalt in water samples: In order to validate the proposed methodology, the developed procedure was applied to the determination of Ni and Co in tap water, rain water, sea water and some waste water samples. For this purpose, 10 mL of each of the samples were pre-concentrated with 0.25 % (w/v) Triton X-114 and an Na-DDTC concentration of 0.07 mM, following the proposed procedure. The results are shown in Table-2.

TABL-2 DETERMINATION OF Ni AND Co IN NATURAL AND WASTE WATER SAMPLES								
Sample	Conc. (µg L^{-1})		Added (µg L^{-1})		Found (µg L^{-1})		Recovery (%)	
	Ni	Co	Ni	Co	Ni	Co	Ni	Co
Tap water	ND	ND	15	20	15.6	19.2	98.6	97.3
Sea water	12.2	15.1	20	20	32.0	36.2	99.8	101.2
Rain water	10.4	9.2	50	20	59.9	28.1	98.9	97.3

ND: Not detected.

Conclusion

The combined advantages of the cloud point methodology (easy, safe, rapid and inexpensive) and the use of Na-DDTC as a chromogenic reagent (selectivity and sensitivity) for Ni and Co were utilized for their determination in water samples. The main advantage of the method is simultaneouse determination of traces of nickel and cobalt without the need for any chemometric method. The method gives a very low limit of detection and good RSD values. The results of this study clearly show the potential and versatility of this method, which could be applied to monitoring Ni and Co spectrophotometrically in various water samples.

REFERENCES

1. E.J. Underwood, Trace Elements in Human and Nutrition, Academic Press, New York, edn. 4 (1977).
2. A.I. Yuzefovsky, R.F. Lonardo, M. Wang and R.G. Michel, *J. Anal. At. Spectrom.*, **9**, 1195 (1994).
3. H. Watanabe, in eds.: K.L. Mittal and E.F. Fendler, Solution Behavior of Surfactants, Plenum Press, New York, Vol. 2, p. 1305 (1982).
4. W.L. Hinze, in eds.: W.L. Hinze and A.W. Armstrong, Ordered Media in Chemical Separations, ACS Symposium Series, No. 342, Washington DC (1987).
5. C.D. Stalikas, *Trends Anal. Chem.*, **21**, 243 (2002).
6. J. Miura, H. Ishii and H. Watanabe, *Bunseki Kagaku*, **25**, 808 (1976).
7. H. Watanabe, T. Saitoh, T. Kamidate and K. Haraguchi, *Mikrochim. Acta*, **106**, 83 (1992).
8. A. Moghimi, *Orient. J. Chem.*, **22**, 527 (2006).
9. A. Moghimi, *Chin. J. Chem.*, **25**, 640 (2007).
10. M.E.F. Laepsada, J.L.P. Pavon and B.M. Cardero, *Analyst*, **118**, (1993) 209.
11. M.F. Silva, L.P. Fernandez, R.A. Olsina and D. Stacchiola, *Anal. Chim. Acta*, **342**, 229 (1997).
12. M.F. Silva, L.P. Fernandez and R.A. Olsina, *Analyst*, **123**, 1803 (1998).
13. L. Sombra, M. Luconi, M.F. Silva, R.A. Olsina and L.P. Fernandez, *Analyst*, **126**, 1172 (2001).
14. J. Chen and K.C. Teo, *Anal. Chim. Acta*, **434**, 325 (2001).
15. R.P. Frankewich and W.L. Hinze, *Anal. Chem.*, **66**, 944 (1994).
16. T. Gu and P.A. Galera-Gomez, *Colloid. Surf. A*, **104**, 307 (1995).

6TH INTERNATIONAL SYMPOSIUM ON MACROCYCLIC AND SUPRAMOLECULAR CHEMISTRY (ISMSC)

3 — 7 JULY, 2011

BRINGHTON, U.K.

Contact:

RSC Events, Royal Society of Chemistry, Thomas Graham House, Science Park, Milton Road, Cambridge, CB4 0WF, U.K.

Tel:+44-(0)1223-432554, Fax:+44-(0)1223-423623,

http://www.rsc.org/ConferencesAndEvents/RSCConferences/6-ISMSC/

E-mail:info@filtech.de, Web site: http://www.filtech.de/