Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Cloud Point Extraction and Preconcentration for the Determination of Cu and Ni in Natural Water by Flame Atomic Absorption Spectrometry

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To cite this Article Shemirani, Farzaneh , Jamali, Mohammad Reza , Kozani, Reyhaneh Rahnama and Salavati-Niasari, Masood(2006) 'Cloud Point Extraction and Preconcentration for the Determination of Cu and Ni in Natural Water by Flame Atomic Absorption Spectrometry', Separation Science and Technology, 41: 13, 3065 — 3077

To link to this Article: DOI: 10.1080/01496390600785970

URL: http://dx.doi.org/10.1080/01496390600785970

Separation Science and Technology, 41: 3065–3077, 2006

ISSN 0149-6395 print/1520-5754 online
DOI: 10.1080/01496390600785970

Cloud Point Extraction and Preconcentration for the Determination of Cu and Ni in Natural Water by Flame Atomic Absorption Spectrometry

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Abstract: In this work, a new cloud point extraction (CPE) method was developed for the separation and preconcentration of copper and nickel. The analyte was complexed with 3-[(8-{[(E)-2-hydroxyimino-1-methylpropylidene] amino}-1-naphthyl) imino]-2-butanone oxime (H_2mdo) in the initial aqueous solution and octylphenoxy polyethoxy ethanol (Triton X-114) was added as a surfactant. After phase separation, based on the cloud point in the mixture, and dilution of the surfactant-rich phase with methanol containing 0.1 mol l^{-1} HNO_3, the enriched analytes were determined by flame atomic absorption spectrometry. After optimization of the complexation and extraction conditions (i.e. pH = 8.5, H_2mdo = 3×10^{-4} mol l^{-1}, Triton X-114 = 0.1% (w/v)) the enhancement factors of 65 and 59 and detection limits of 0.14 and 0.2 ng ml^{-1} were obtained for copper and nickel respectively. The proposed method was applied to the determination of copper and nickel in several natural water samples with satisfactory results.

Keywords: Cloud point extraction, separation, copper, nickel, preconcentration

Received 10 November 2005, Accepted 17 April 2006

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INTRODUCTION

Copper is an essential element not only to life in mammals but also to plants and lower forms of organisms. It has various and many biologic effects as an essential element and also as a toxic one. It is usually used as an algicide and herbicide (1, 2).

Nickel is the metal component of the enzyme urease and as such is considered to be essential to plants and some domestic animals. More attention has been paid on the toxicity of nickel in low concentration, such as the fact that nickel can cause an allergic reaction and that certain nickel compounds may be carcinogenic (3).

Thus, the determination of trace amounts of copper and nickel from different matrices is of great importance. In many cases, the determination of heavy metals in environmental samples is notably difficult due to both the low levels of these metals in the samples and the high complexity of the sample matrices. This is especially true in sea water analysis, and it is usually necessary to carry out a separation step prior to the analysis, to preconcentrate the metal to be analyzed and to separate it from the matrix (4).

A number of preconcentration methods have been used for trace metal determinations, including precipitation and Co-precipitation (5, 6), the use of chelating resins (7, 8) liquid–liquid extraction (9, 10) and solid phase extraction (11, 12).

Cloud point extraction (CPE) is probably the most versatile and simple method for the preconcentration and extraction of hydrophobic species from water. The technique is base on the property of most non-ionic surfactants in aqueous solutions to form micelles and become turbid when heated to a temperature known as the cloud point temperature (CPT). Above this temperature, the micellar solution separates in a surfactant rich phase of a small volume and in a diluted aqueous phase in which the surfactant concentration is close to the critical micellar concentration. The ability of micellar systems to concentrate and extract hydrophobic species from water was demonstrated some years ago (13–15).

In recent years cloud point methodology has been used for the extraction and preconcentration of metal ions after the formation of sparingly water-soluble complexes (16). This method was applied for the determination of uranium (17), Er (18), and Gd (19) by spectrophotometry, Pd (20) by room temperature phosphorescence, Ni and Zn (21), Ag and Au (22), Cd and Pb (23), Cu (24, 25), Fe (26), Cr(III), Cr(VI) (27), Cd, Cu, Pb and Zn (28), and Co and Ni (29) by flame atomic absorption spectrometry using complexing agents.

Several ligands such as 1-(2-pyridylazo)-2-naphthol (PAN), 2-(2-thiazoylazo)-4-methylphenol (TAC), 1-(2-thiazolylazo)-2-naphthol (TAN), dialkyldithiophosphates (DDTP), have been used in cloud point extraction of metal ions.

Schiff base and oxime compounds have been extensively studied because of their biological and structural importance (30, 31) which lies mainly in their specific and selective reactions with metal ions. Therefore, these compounds have been proposed as spectrophotometric reagents for several metal ions (32, 33).

The aim of this work was to apply cloud point extraction as a preconcentration step for flame atomic absorption spectrometric determination of Cu and Ni by the use of a new schiff base as a complexing agent.

EXPERIMENTAL

Reagents and Solutions

All the chemicals used were of analytical reagent grade and free from copper and nickel traces. Stock solutions of Cu(II) and Ni(II) were prepared by dissolving appropriate amounts of Cu $(NO_3)_2$, $3H_2O$ and Ni $(NO_3)_2$, $6H_2O$ in doubly distilled water. Working standard solutions were obtained by appropriate dilution of the stock standard solutions.

The non- ionic surfactant Triton X-114 (Fluka chemie AG, Switzerland) was used without further purification. Nitric acid (Merck) and methanol (Merck) were also used. A stock standard 0.1 mol l^{-1} buffer solution was prepared by dissolving appropriate amounts of $Na_2B_4O_7$, 10 H_2O. Schiff base 3-[(8-{[(E)-2-hydronayimino-1-methylpropylidene] amino}-1-naphthyl) imino]-2-butanone oxime was synthesized and purified as described in "Synthesis of ligand section." The chelating agent solution was prepared by dissolving 0.324 g of H_2mdo in 100.0 ml of ethanol 96%. The pipettes and vessels used for trace analysis were kept in sulfuchromic acid mixture for at least 1 h and subsequently were washed four times with distilled water.

Apparatus

A Varian (Madrid, Spain) model AA-1475 atomic absorption spectrometer equipped with deuterium background correction and copper and nickel hollow cathode lamps as the radiation source was prepared according to the manufacturer's recommendations.

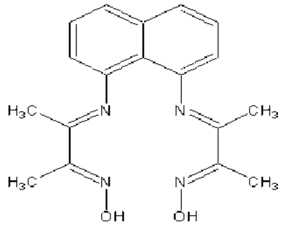
A thermostatic bath (Tokyo Rikakikai Ltd, Japan) model UA-1, maintained at the desired temperatures was used for cloud point temperature experiments and the phase separation was assisted using a centrifuge (Hettich, Universal). The pH of the solutions was controlled with a Metrohm pH-meter (model 713).

Synthesis of Ligand

The ligand, 3-[(8-{[(E)-2-hydroxyimino-1-methylpropylidene] amino}-1-naphthyl) imino]-2-butanone oxime (structure given below) was prepared according to the literature through a well-known method, as follows.

Diacetylmonoxime (2.0 g, 20 mmol) was dissolved in 60.0 ml ethanol and then was transferred into a 250 ml three-necked flask. Under room temperature, 10.0 mmol of 1,8-naphthalenediamine in 60.0 ml ethanol was added drop-wise to the flask.

The stirred mixture was kept reacting for 8 h under reflux, and then was cooled to room temperature. The solid product was filtered and the product was recrystallized from $CHCl_3$, and vacuum dried for 12 h.



H_2mdo

Anal. Calcd. For $C_{18}H_{20}N_4O_2$: C, 66.65; H, 6.22; N, 17.26(%).

Found: C, 66.43; H, 6.10; N, 17.31(%). (Yield 78%)

^{1}H-NMR (400 MHz, $CDCl_3$): δ (2.18, s, $2CH_3$), δ (1.98, s, $2CH_3$), δ (6.43, m, 2H, naphthyl), δ (7.35, m, 4H, naphthyl), δ (9.76, s, 2OH).

The Cloud Point Extraction Procedure

For cloud point extraction, an aliquots of 20.0 ml of the cold solution containing the analyte, 0.1% Triton X-114 and, 3.0×10^{-4} mol l^{-1} H_2mdo was adjusted to the appropriated pH value (pH = 8.5) with a $Na_2B_4O_7$, 10 H_2O buffer. The mixture was kept at 50°C for 10 min in the thermostatic bath. Subsequently, the phase separation was accelerated by centrifugating at 3500 rpm for 10 min. On cooling in an ice–bath the surfactant–rich phase became viscous. Then, the aqueous phase was separated by inverting the tubes.

Later, in order to decrease the viscosity and facilitate sample banding, 500.0 μl of a solution of methanol containing 0.1 mol l^{-1} HNO_3 was added to the surfactant–rich phase. The samples were introduced into the flame by conventional aspiration.

RESULTS AND DISCUSSION

Effect of pH

CPE of nickel and copper was performed in different buffer solutions. The separation of the metal ions by CP method involves prior formation of a complex of sufficient hydrophobicity to be extracted into the small volume of the surfactant–rich phase, and thus obtaining the desired preconcentration. The extraction yield depends on the pH at which complex formation occurs.

Figure 1 shows the effect of pH on the extraction of nickel and copper complexes. It can be seen that for both nickel and copper the yield increases with increasing in pH up to 7.5, and thereafter the yield is almost constant and close to 100%. At lower pH values (<7), the nitrogen atoms of the H_2mdo are to be protonated and reduce the stability of the complex formation between the ligand and Cu and Ni ions and therefore the extraction yield decreases. Hence, a pH of 8.5 was chosen for both analytes.

Effect of H_2mdo Concentration

The yield of the extraction as a function of concentration of the complexing agent is shown in Fig. 2. The copper and nickel complexes formed with this multidentate complexing agent (H_2mdo) are 1 : 1. For both cations 20.0 ml of a solution containing 50.0 ng ml^{-1} copper and nickel in 0.1% Triton X-114 and medium buffered at pH 8.5 containing various amounts of H_2mdo were subjected to the cloud point preconcentration process. The yield increased up to a H_2mdo concentration of 2.0×10^{-4} mol l^{-1} and reached 100% extraction efficiency. A concentration of 3.0×10^{-4} mol l^{-1} was chosen to account for other extractable species.

Effects of Buffer Concentration and Ionic Strength

The influence amounts of buffer were tested. During these experiments, all of the other experimental variables remained constant.

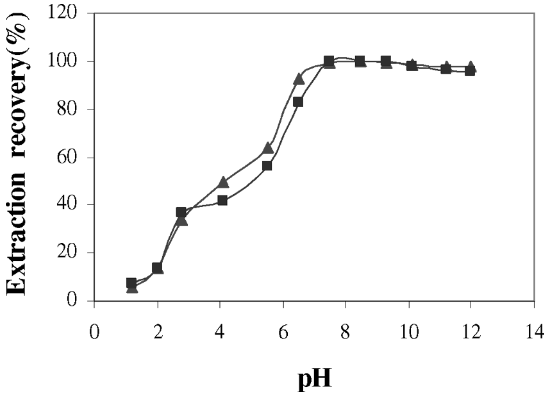


Figure 1. Effect of pH on the extraction recovery of (▲) copper and (■) nickel. Conditions: Cu(II), Ni(II) 50.0 μg l^{-1}; Triton X-114 0.1% (w/v); H_2mdo 3.0×10^{-4} mol l^{-1}.

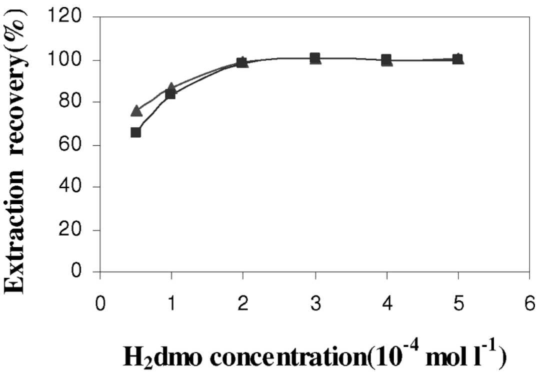


Figure 2. Effect of H_2mdo concentration on the extraction recovery of (▲) copper and (■) nickel. Conditions: Cu(II), Ni(II) 50.0 μg l^{-1}; pH 8.5; Triton X-114 0.1% (w/v).

The results showed that above 2.0×10^{-3} mol l^{-1} buffer solution no obvious variation took place in the extraction yield. Thus a 4.0×10^{-3} mol l^{-1} buffer solution was chosen as the optimum concentration.

The ionic strength had no appreciable effect upon extraction efficiency and sensitivity up to 0.5 mol l^{-1}. This is in agreement with the results reported in the literature, which demonstrate that an increase in the ionic strength in a micelle-mediated system does not seriously alter the extraction efficiency of the analyte (34, 35).

Effect of Triton X-114 Concentration

A successful cloud point extraction should maximize the extraction efficiency by minimizing the phase: volume ratio ($V_{org}/V_{aqueous}$), thus improving its concentration factor.

Triton X-114 was chosen for the formation of the surfactant–rich phase due to its low cloud point temperature and high density of the surfactant rich phase, which facilitates phase separation by centrifugation (13).

The variations in extraction efficiency within the Triton X-114 range of 0.02–0.2% (w/v) were examined. Quantitative extraction was observed when the Triton X-114 concentration was 0.08%. Fig. 3 highlights the differences observed in the signals at different surfactant concentrations.

At lower concentrations of the surfactant, the extraction efficiency is low probably due to the inadequacy of assemblies to entrap the hydrophobic complex quantitatively. Increasing of Triton X-114 concentration above 0.11%, the signals decreased because of the increments in the volumes and the viscosity of surfactant phase. The optimum surfactant concentrations are the same for both analytes. An amount of 0.1% Triton X-114 was chosen in order to achieve the greatest analytical signal and thereby the highest extraction efficiency.

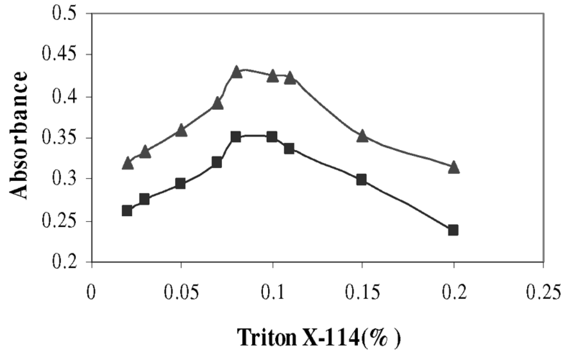


Figure 3. Effect of Triton X-114 concentration on the absorbance of (▲) copper and (■) nickel. Conditions: Cu(II), Ni(II) 50.0 μg l^{-1}; pH 8.5; H_2mdo 3.0 × 10^{-4} mol l^{-1}.

Effect of Equilibration Temperature and Time

The temperature above the cloud point was thoroughly optimized. It is desirable to employ the shortest equilibration time and the lowest possible equilibration temperature, as a compromise between the completion of extraction and an efficient separation of phase.

Previous workers have reported that by increasing the temperature, a reduction in the phase volume ratio of the surfactant is seen (36). More sufficiently, the Triton X-114 surfactant rich phase decrease by a 1.5–3.5 factor and thereby the preconcentration factor increased depending on the surfactant concentration (37).

Therefore, these parameters were studied within the ranges: 25–70°C and 2–30 min, respectively. A temperature of 50°C was selected in order to achieve the minimum equilibration time (10 min), to avoid complex decomposition and to reach the optimal enrichment factor.

Effect of Centrifugation Time

An insignificant increase in the preconcentration factor was observed, when the centrifugation time at 3500 rpm was increased from 2 up to 20 min. A centrifugation time of 10 min was selected as the optimum, since complete separation occurred during this time and no appreciable improvements were observed for a longer interval.

Characteristics of the Method

A calibration curve was constructed by preconcentrating 20.0 ml of sample standard solutions with Triton X-114 under the optimum experimental conditions.

Table 1. Analytical characteristics of the method

Parameter	Analytical feature	
	Cu	Ni
Enhancement factor[a]	65	59
LOD[b] (ng ml^{-1})	0.14	0.2
R.S.D %(n = 5)[c]	2.2	2.4
Correlation coefficient (r)	0.997	0.995
Linear range (ng ml^{-1})	0.4–150	0.5–170

[a] Calculated as the ratio of absorbance of preconcentrated samples to that obtained without preconcentration.

[b] Limit of detection defined as three times the signal–to–noise ratio.

[c] Copper and nickel concentration were 20.0 ng ml^{-1} for which the RSDs were obtained.

Table 1 shows the analytical characteristics of the method. Under the optimum experimental conditions, the calibration curve for copper and nickel were linear from 0.4 to 150 and 0.5 to 170 ng ml^{-1} respectively.

The enhancement factors calculated as the ratio of absorbance of preconcentrated samples to that obtained without preconcentration, were 65 for copper and 59 for nickel. The limit of detections was sufficiently low as compared to those attained by FAAS without preconcentration and lie around 0.14 and 0.2 ng ml^{-1} for copper and nickel.

Interferences

In view of the high selectivity provided by flame atomic absorption spectrometry, the only interferences studied were those related to the preconcentration step. The effect of interfering ions at different concentrations on the extraction and determination of a solution containing 50.0 ng ml^{-1} of copper and nickel was studied. An ion was considered to interfere when its presence produced a variation in the recovery of the sample of more than 5%.The results are shown in Table 2. It was proved that copper and nickel recoveries were almost quantitative in the presence of foreign cations.

Accuracy of the Method for Copper and Nickel

The accuracy of the system was evaluated with a water reference material SLEW-3. The results are shown in Table 3. Application of *t*-test to the results of the proposed method and the certified values for copper and nickel demonstrated that there were no significant differences at the 5% probability level for the results.

Table 2. Effect of foreign ions on the preconcentration and determination of copper and nickel (50.0 ng ml^{-1})

Ion	Ion/(Cu^{2+} or Ni^{2+}) (w/w)	Recovery (%)	
		Cu^{2+}	Ni^{2+}
Na^+	1000	100	100.3
K^+	1000	101.3	99.8
Mg^{2+}	1000	98.7	102.3
Ca^{2+}	1000	99.6	97.8
Ag^+	100	97.6	98.4
Cd^{2+}	100	99.3	98.2
Fe^{2+}	50	99.5	98.5
Pb^{2+}	50	102.1	101
Zn^{2+}	50	100	97.6
Co^{2+}	50	99.2	98.4
Al^{3+}	10	99.5	98.8
Mn^{2+}	10	98.5	97.8
Fe^{3+}	10	96.5	97.6
Cu^{2+}	10	–	99.2
Ni^{2+}	10	99.4	–

Application to Samples

The proposed method was applied to the preconcentration and determination of Cu(II) and Ni(II) in several water samples. Water samples were filtered using a 0.45-μm pore size membrane filter to remove suspended particulate matter. As shown in Table 4, the proposed method could be applied successfully to the preconcentration and determination of trace amounts of copper and nickel in water samples.

CONCLUSION

The use of the micellar system as an alternative to other techniques of separation and preconcentration offers several advantages including

Table 3. Determination of copper and nickel in a water reference material

	Cu^{2+}	Ni^{2+}
Certified value (ng ml^{-1})	1.55 ± 0.059	1.23 ± 0.07
Found (ng ml^{-1})	1.51 ± 0.04	1.19 ± 0.03

Table 4. Recovery of copper and nickel from 20.0 ml of different water samples

	Added (ng ml^{-1})		Determined (ng ml^{-1})	
Sample	Cu	Ni	Cu	Ni
Tap water	0.0	0.0	1.71 ± 0.03[a]	2.87 ± 0.07
	10.0	10.0	11.68 ± 0.25	12.85 ± 0.31
Snow water	0.0	0.0	3.44 ± 0.07	4.52 ± 0.12
	10.0	10.0	13.40 ± 0.28	14.50 ± 0.36
Rain water	0.0	0.0	3.49 ± 0.06	4.58 ± 0.11
	10.0	10.0	13.48 ± 0.29	14.53 ± 0.35
Sea water	0.0	0.0	12.91 ± 0.29	13.84 ± 0.34
	10.0	10.0	22.88 ± 0.50	23.84 ± 0.57

[a] Mean of three extraction ± SD.

experimental convenience, safety, and being a rapid and inexpensive method. The results demonstrate the usefulness of the cloud point extraction system to quantitatively extract and preconcentrate copper and nickel schiff base complexes. The extent of extraction was remarkably influenced by the presence of additives, pH, time and temperature of the equilibration step. This method gives a very low limit of detection (sub ng ml^{-1}) and good RSD for both of the analytes. The applicability of the method was verified with real samples and it was proven satisfactory for simultaneous extraction and determination of Cu and Ni in variety of water matrixes. In addition, it is possible to obtain a better limit of detection by extraction of Cu and Ni from large volumes of sample solution and diluting the surfactant-rich phase to smaller volume, or using electrothermal atomic absorption spectrometry.

ACKNOWLEDGMENT

The authors thank the research council at the University of Tehran for financial support.

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