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Determination of copper and nickel in real samples by rubeanic acid in micelle-mediated

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ABSTRACT

Cloud point extraction (CPE) has been used for the simultaneous pre-concentration of copper and nickel after the formation of a complex dithioxamide (rubeanic acid) (DTO), and later analysis by flame atomic absorption spectrometry (FAAS) 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 = 6.0, 0.09mM DTO, Triton X-114 = 0.07% (w/v)), calibration graphs were linear in the range of 20-650 and 15-850 ng ml^{-1} with detection limits of 0.9 and 1.5 ng ml^{-1} for Cu and Ni, respectively. The method was applied to the determination of Cu and Ni in natural and waste water samples with satisfactory results. © 2008 Trade Science Inc. - INDIA

KEYWORDS

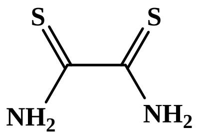
Dithioxamide (rubeanic acid) (DTO);
Copper and Nickel Ion;
Triton X-114;
Flame atomic absorption spectrometry.

INTRODUCTION

The determination of heavy metals at trace levels in environmental is one of the targets of analytical chemists, due to their important roles in our life[1-3]. There are many difficulties in determining trace amounts of heavy metals in environmental samples by flame atomic absorption spectrometry due to insufficient sensitivity of instrument and/or matrix interferences. In order to achieve detection limits within the range of flame atomic absorption spectrometry. An initial pre-concentration step allows lower limits of detection for analytes, as well as the separation of the analytes from its matrix, which may interfere in atomic absorption spectrometric determinations[4].

There are many methods of pre-concentration and separation such as liquid–liquid extraction (LLE)[5,6], ion-exchange techniques[7,8], co-precipitation[9,10], sorption on the various adsorbents such as activated carbon[11,12], amberlite XAD resins[13,114] and other sorbents[15,16].

Separation procedures based on the peculiar properties of aqueous non-ionic and zwitterionic surfactant solution has also been proposed as an alternative to the use of traditional organic solvents. Aqueous solutions of almost all non-ionic surfactants become turbid when heated to a temperature known as the cloud point. Above this temperature, the isotropic micellar solution separates into two transparent liquid phases: a surfactant-rich phase of very small volume composed mostly of the surfactant plus a small amount of water, and an aqueous phase, in equilibrium with the former, which contains a surfactant concentration close to its critical micellar concentration, is the base of cloud point extraction (CPE). The small volume of the surfactant-rich phase obtained with this methodology permits the design of extraction schemes that are simple, cheap, highly



SCHEME 1

efficient, and of lower toxicity to the environment than those extractions that use organic solvents. The CPE phenomenon has been used for the extraction and preconcentration of metal cations after the formation of sparingly water-soluble complexes. CPE has been shown to be an effective sample pre-concentration technique for improving sensitivity and selectivity prior to atomic spectrometry[17].

In the present work we report on the results obtained in a study of the cloud point extraction and preconcentration of Cu and Ni, after the formation of a complex with dithioxamide (rubeanic acid) (DTO) (SCHEME 1), and later analysis by spectrophotometry at the wavelength of maximum absorption of each complex, using Triton X-114 as surfactant.. The proposed method was applied to the determination of Cu and Ni in water samples.

EXPERIMENTAL

Apparatus

A Shimadzu AA-680 atomic absorption/flame emission spectrometer equipped with deuterium background correction was used with copper and nickel hollow-cathode lamps as radiation sources. The operating conditions were those recommended by the manufacturer, unless specified otherwise. The acetylene flow rate and the burner height were adjusted in order to obtain the maximum absorbance signal, while aspirating the analyte solution in methanol containing 0.5mol l^{-1} nitric acid. For discrete volume sampling, a volume of 200µl of the final solution was introduced into the nebulizer of the spectrometer by a manual sample injector that was connected to the nebulizer by the sample aspiration tubing. Absorbance signals as peak height were measured. A MP4 centrifuge (International Equipment Company, USA) was used to accelerate the phase separation.

Reagents and materials

All chemicals used in this work, were of analytical reagent grade and were used without further purification. Deionised water was used for all dilutions. Metal standards were prepared by dissolving appropriate amount of nitrate salt of ions including copper, nickel and other cathions were of the analytical grade purchased from Merck Company, solution (Merck, Darmstadt, Germany). A 0.5 % (W/v) Triton X-114 from Merck Company was prepared by dissolving 0.5 g of Triton X- 114 in 100 mL volumetric flask with stirring. dithioxamide (rubeanic acid) (DTO), methanol solvents were purchased from Merck Company. A buffer of pH = 6.0 was prepared by using sodium acetate and hydrochloric acid at appropriate concentrations.

Procedure

For the cloud point extraction, aliquots of the cold solution containing the analytes, Triton X-114 and DTO, buffered at a suitable pH, were placed into water bath. The temperature of the solutions was controlled by the thermometers dived both in the tubes and in the bath. The heating was performed with 0.5°C min^{-1} rate and were kept for 15 min at 40°C. Separation of the two phases was accomplished by centrifugation for 15 min at 4000 rpm. The phase was cooled down in an ice bath in order to increase the viscosity of the surfactant-rich phase. After the cloud point extraction, the aqueous phase was decanted by inverting the tube. To decrease the viscosity of the surfactant-rich phase and facilitate introduction in flame atomic absorption nebulizer, 200µl of methanol solution containing 0.5 mol l^{-1} HNO_3 was added. The resultant solution was directly introduced into the FAAS by conventional aspiration.

RESULTS AND DISCUSSION

Effect of pH

Cloud point extraction of copper and nickel was performed in different pH buffer solutions. The separation of metal ions by the 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 pre-concentration. Extraction yield depends on the pH at which complex formation is carried out.

The effects of pH on the extraction of copper and nickel complex are given in figure 1. In the pH range 5.5-6.0, extraction was quantitative. The decrease in recoveries at pH > 6.0 is probably due to the precipitation of copper ions in the form of hydroxide, and at pH<5.5 may be due to competition from hydronium ion toward ions for complexation with DTO or decomposition of complex at pH values smaller than 5.5, which led to the decrease in recoveries. In subsequent experiments a pH of 6.0 was.

Effect of NDTT concentration

The yield of the extraction as a function of the concentration of the complexing agent is shown in figure 2. For both cations 10 ml of a solution containing 50.0 ng ml^{-1} copper and nickel in 0.07% Triton X-114 and medium buffered at pH 6.0 containing various amounts of DTO were subjected to the cloud point pre-concentration process. At this stated concentration of ions, ~100% extraction was achieved for a DTO concentration of 0.09 mM, which this concentration was chosen for subsequent experiments.

Effect of triton X-114 concentration

A successful cloud point extraction should maximize the extraction efficiency by minimizing the phase volume ratio (Vorg/Vaqueous), thus improving its enrichment factor. Reports showed that Triton X-114 and PONPE-7.5(CPT near room temperature) were proper surfactants to perform CPE for trace elements[18-19]. Triton X-114 was chosen as a non-ionic surfactant because of its commercial availability in a high purified homogeneous form, low toxicological properties and cost. Also, low cloud point temperature (23-26°C) and high density of the surfactant- rich phase facilitates phase separation by centrifugation. The effect of surfactant concentration was studied within the Triton X-114 concentration range from 0.01 to 0.15% (w/v). Figure 3 shows the effect of the surfactant concentration on the intensity. Quantitative extraction obtained at its maximum when triton X-114 concentration was 0.07% (v/v). With increase of Triton X-114 concentration above 0.07%, the analytical sensitivity decreased, probably, due to dilution of the sample by additional surfactant solution. Accordingly, a concentration of 0.07% (v/v) Triton X-114 was chosen.

Effects of equilibration temperature and time

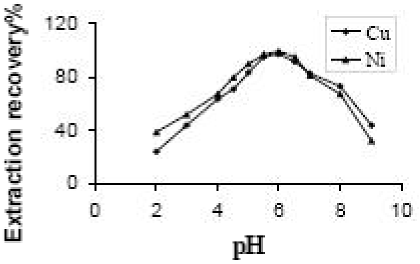


Figure 1: Effect of pH on the extraction recovery of copper and nickel. Conditions: Triton X-114: 0.07%(w/v) mM, DTO: 0.09 mM

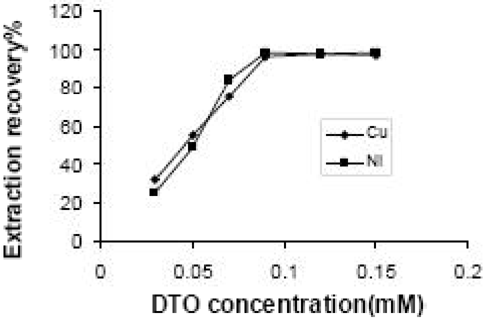


Figure 2: Effect of DTO concentration on the extraction recovery of copper and nickel. Conditions: pH: 6.0, Triton X-114: 0.07%(w/v) mM

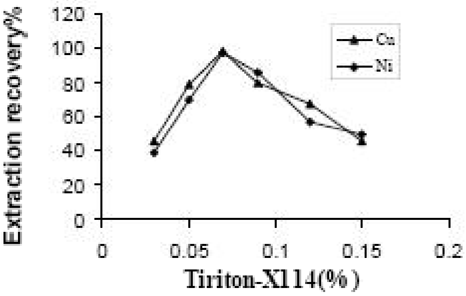


Figure 3: Effect of Triton X-114 concentration on the cloud point extraction of copper and nickel. Conditions: pH: 6.0, DTO: 0.09 mM

It was desirable to employ the shortest equilibration time and the lowest possible equilibration temperature, as a compromise between completion of extraction and efficient separation of phases. It was found that 40^0C is adequate for these analyses. The dependence of extraction efficiency upon equilibration time was studied for a time span of 5-30 min. An equilibration time of 15 min was chosen the optimal to achieve quantitative extraction.

Effects of buffer concentration and ionic strength

The influence of buffer amount was carried out in which the other experimental variables remained constant. The results have shown that above 0.5 ml of buffer solution added in 10 ml of solution, no obvious variation took place in the extraction yield. A 1.0 ml aliquot of buffer solution was added in all subsequent experiments. Ionic strength had no appreciable effect upon extraction efficiency and sensitivity up to 0.5 mol l^{-1}.

Effect of viscosity

The surfactant- rich phase obtained after cloud point pre-concentration is very viscose (-20 cP) owing to the high concentration of Trion X-114. Accordingly, after phase separation it is necessary to decrease the viscosity of the surfactant-rich phase to facilitate its handling and introduction into the atomizer. Several organic solvent and their acid mixtures were investigated, to increase the analytical signal of the FAAS. Solvents tested include acetone, acetonitrile, ethanol and methanol and the best results were obtained using methanol. A methanol solution containing 0.5 mol l^{-1} nitric acid was added to surfactant-rich phase after the separation of two phases. Results showed that the optimum volume of methanol was 200μl.

Calibration, precision and detection limits

Calibration graphs were obtained by pre-concentrating 10 ml of sample (copper or nickel) in the presence of 0.07% Triton X-114 in a medium buffered at pH 6.0. The samples were introduced into the flame by conventional aspiration following the addition of 200μl of a methanol solution containing 0.5 mol l^{-1} HNO_3. In both the cases, linear relationships between the recovery measured and the concentration of metal in solution were obtained. TABLE 1 gives the calibration parameters, the relative standard deviation obtained for five samples subjected to the complete procedure, at two different concentration levels, and the detection limits. Pre-concentration of only 10 ml of sample in the presence of 0.07% Triton X-114 permitted the detection of 0.9 ng mL^{-1}copper and

1.5 ng mL^{-1}nickel. The enrichment factors, calculated as the ratio of recovery of pre-concentrated samples to that obtained without pre-concentration, were 36 for copper and 39 for nickel.

Interferences

In view of the high selectivity provided by flame atomic absorption spectrometry, the only interferences studied were those related to the pre-concentration step. Cations that may react with DTO and anions that may form complexes with the metal ions were studied. The results were shown in TABLE 2. It was proved that copper and nickel recoveries were almost quantitative in the presence of foreign cations.

TABLE 1: Specification of method at optimum conditions for each element

Parameter	Cu	Ni
Linear Range (ng ml$^{?1}$)	20–650	15–850
Detection Limit (ng mL^{-1})	0.9	1.5
RSD %	1.1	1.9
Recovery %	99.4	98.9
Enrichment factor	36	39

TABLE 2 : Effects of the matrix ions on the recoveries of the examined metal ions (N=3)

Ion	Ion/ (Cu or Ni)	Recovery (%)	
		Cu	Ni
Na^+, K^+	1500	100	99.4
Ca^{2+}	1000	99.1	98.6
Mg^{2+}	1000	98.5	101.2
Al^{3+}	700	98.8	99.3
Cd^{2+}, Mn^{2+}	550	100	103
Pb^{2+}	400	100	97.6
Co^{2+}	200	99.2	98.4
Fe^{3+}	150	95.5	98.8
Zn^{2+}	100	99.5	101.5
Cl^-	1500	100.4	99.3
HCO_3^-	800	98.6	98.0
PO_4^{3-}	500	100.3	98.3

TABLE 3 : Recovery of trace elements from spiked real sample after CPE

Real sample	Ion	Added (μg g^{-1})	Found (μg g^{-1})	RSD %	Recovery %
Cow liver	Cu	0	6.72	0.8	-
	Cu	5	11.78	1.3	101.2
	Ni	0	1.32	1.6	-
	Ni	5	6.23	1.3	98.2
Chocolate	Cu	0	0.41	1.7	-
	Cu	0.5	0.92	1.5	100
	Ni	0	0.45	1.1	-
	Ni	0.5	0.96	1.5	102
River water	Cu	0	43.9	1.7	-
	Cu	50	95.8	1.2	103.8
	Ni	0	10.34	1.9	-
	Ni	50	61.89	1.7	103.1

Accuracy and applications

We have explored the feasibility of the methodology using pre-concentration with DTO in surfactant media for the determination of copper and nickel ions in different matrices treated according to Experimental section. The procedure was applied to the determination of copper and nickel ions in different samples, including river water, cow liver and chocolate samples by standard addition method. Reliability was checked by spiking experiments and independent analysis. The results are presented in TABLE 3. The recovery of spiked samples is satisfactory reasonable and was confirmed using addition method, which indicate the capability of the system in the determination of lead in natural real samples.

CONCLUSION

The micellar extraction of copper and nickel ions with DTO into the phase of non-ionic surfactant Triton X-114 has been investigated. The sensitivity, metrological characteristics, ecological safety, simplicity, and convenience of the suggested procedure are competitive with respect to the methods based on the extraction with organic solvents. The results presented have confirmed its applicability to the separation and preconcentration of copper and nickel ions, which due its high stability constant and high pH dependency with high selectivity loading and elution has been carried out. The low RSD of real sample analysis is an indication of methods versatility for real sample.

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