Eurasian Journal of Analytical Chemistry
Volume 2, Number 3, 2007

Micell-Mediated Extraction for Preconcentration and Determination of Copper and Zinc in Real Samples

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Abstract

Cloud point extraction has been used for the pre-concentration of copper and zinc, after the formation of a complex with N,N'-diacetyl-4-bromo-2,6-di(aminomethyl) phenol(DBDP), and later analysis by flame atomic absorption spectrometry using Triton X-114 as surfactant. The adopted concentrations for DBDP, Triton X-114 and HNO_3, bath temperature, centrifuge rate and time were optimized. Detection limits ($3S_b/m$) of 1.6 and 1.9 ng mL^{-1} for Cu^{2+} and Zn^{2+} along with enrichment factors of 33 for these ions were achieved. The high efficiency of cloud point extraction to carry out the determination of these ions in complex matrices was demonstrated. The proposed procedure was applied to the analysis of natural and waste water, soil and blood samples. The determination of these metal ions content in various real samples showed quantitative recoveries for the spiked samples. The proposed method is characterized by simplicity, efficiency and low cost.

***Key words*: N,N'-diacetyl-4-bromo-2,6-di(aminomethyl)phenol(DBDP), Cloud Point Extraction, Copper and Zinc Ions, Triton X-114, Flame Atomic Absorption Spectrometry.**

1. Introduction

Several analytical techniques such as atomic absorption spectrometry (AAS), inductively coupled plasma atomic emission spectrometry (ICP-AES) and inductively coupled plasma mass spectrometry (ICP-MS) are available for the determination of trace metals with sufficient sensitivity for most of applications. However, the determination of trace metal ions in natural waters is difficult due to various factors, particularly their low concentrations and matrix effects. Pre-concentration and separation can solve these problems and lead to a higher confidence level and easy determination of the trace elements by less sensitive, but more accessible instrumentation such as flame atomic absorption spectrometry (FAAS). There are many methods of pre-concentration and separation such as liquid–liquid extraction (LLE) [1, 2], ion-

ISSN: 1306-3057

exchange techniques [3, 4], co-precipitation [5, 6], sorption on the various adsorbents such as activated carbon [7, 8], Amberlite XAD resins [9, 10] and other sorbents [11, 12].

Separations and pre-concentration based on cloud point extractions are becoming an important and practical application of the use of surfactants in analytical chemistry [13]. The use of pre-concentration steps based on phase separation by cloud point extraction (CPE) [14–16] offers a convenient alternative to more conventional extraction systems. The small volume of the surfactant-rich phase obtained with this methodology permits the design of extraction schemes that are simple, cheap, of high efficiency and of lower toxicity than extractions that use organic solvents. CPE also provides results comparable to those obtained with other separation techniques. Accordingly, any species that interacts with the micellar system, either directly (generally hydrophobic organic compounds) or after a prerequisite derivatization reaction (e.g. metal ions after reaction with a suitable hydrophobic ligand) may be extracted from the initial solution and may also be pre-concentrated.

Cloud point methodology has been used to separate and pre-concentrate organic compounds as a step prior to their determination in hydrodynamic analytical systems such as liquid chromatography [17–21] and capillary electrophoresis [22]. The phase separation phenomenon has also been used for the extraction and pre-concentration of metal ions after the formation of sparingly water-soluble complexes [23–26]. Uranium [27], Er [28] and Gd [29] were determined by spectrophotometry, Pd [30] by room temperature phosphorescence, Cu [31], Cd [32], Ni and Zn [33], Ag and Au [34], Cr(III) and Cr(VI) [35] by flame atomic absorption spectrometry after cloud point extraction using complexing agents. Au and Pb were extracted efficiently without a complexing agent, using polyoxyethylene-nonylphenyl ether (PONPE 7.5) as a non-ionic surfactant. Gold [36] in the aqueous phase was determined by inductively coupled plasma mass spectrometry (ICP-MS) and in the surfactant-rich phase by a calculation based on mass balances. Lead [37] in the surfactant-rich phase was determined by flame atomic absorption spectrometry (FAAS) after diluting with ethanol. Recently determination of trace elements by X-ray fluorescence (XRF) spectrometry [38] and ultrasonic nebulization ICP-MS [39] using phase separation phenomenon with surfactant has been reported.

In the present work a simple, selective and sensitive CPE method for pre-concentration and determination of copper and zinc ions in various real samples using N,N'-diacetyl-4-bromo-2,6-di(aminomethyl)phenol (DBDP) as selective and sensitized complexing agent in basic media was established.

2. Experimental

2.1. Apparatus

A Shimadzu UV-VIS 160 spectrophotometer was used to measure the absorbance of complex in Triton X-114 media. A Metrohm 691 pH /Ion meter with a combined glass and calomel electrode has been used for measurement and adjustment of test solutions pH. The evaluation of ions content were carried out on a Shimadzu 680 A atomic absorption spectrometer with a hallow cathode lamp and a deuterium background corrector, at respective resonance line using an air – acetylene flame. A MP4 centrifuge (International Equipment Company) was used to accelerate the phase separation.

2.2. Reagents and Materials

Nitrate salts of copper, zinc and other salts (all from Merck) were of the highest purity available and used without any further purification. A 1.0 % (w/v) Triton X-114 from Merck Company was prepared by dissolving 1.0 g of Triton X-114 in 100 mL volumetric flask with stirring. A stock standard buffer solution, 0.1 mol L^{-1}, was prepared by dissolving appropriate amounts of $NaH_2PO_4·12H_2O$ and $Na_2HPO_4·12H_2O$ in water. The ligand N, N'-diacetyl-4-bromo-2,6-di(aminomethyl) phenol(DBDP) was synthesized according to literature [40].

2.3. Procedures

A typical cloud point experiment required the following steps: an aliquot of 15 mL of a solution containing Cu^{2+} and Zn^{2+}, 0.17 % Triton X-114 and 2.5 mM of DBDP was adjusted to pH 7.0 with 1.0 mL of 0.1 mol L^{-1} NaH_2PO_4–Na_2HPO_4 buffer. The mixture was shaken for 1 min and left to stand in a thermo-stated bath at 45 ^{0}C, for 20 min. Separation of the phases was achieved by centrifugation at 4000 rpm, for 15 min. The whole system was cooled in an ice-bath so for 15 min that the surfactant rich phase would regain its viscosity. In this way, the bulk aqueous phase was easily decanted. The remaining micellar phase was dissolved in 0.5 mL of 0.5 mol L^{-1} HNO_3 in methanol and then the ions content was readily evaluated by FAAS.

2.4. Pretreatment of Real Samples

Analysis of waste water sample for determination of copper and zinc ions content were performed as following: 400 mL of sample was poured in a beaker and 8 mL concentrated HNO_3 and 3 mL of H_2O_2 of (30%) for elimination and decomposition of organic compound were added. The samples, while stirring was heated to one tenth volume. After adjustment of samples pH to desired value the CPE were performed according to general described procedure.

2.5. Blood and Soil

Homogenized soil sample 20 g or blood sample 20 mL was weighed accurately and in a 200 mL beaker was digested in the presence of an oxidizing agent with addition of 10 mL concentrated HNO_3 and 2 mL $HClO_4$ 70 %, and was heated for 1 h. The content of beaker was filtered through a Whatman No. 40 filter paper into a 250 mL calibrated flask and its pH was adjusted to desired value and diluted to mark with de-ionized water. In all of real and synthetic samples amount of copper and zinc ions were found by standard addition method [41].

3. Results and discussion

3.1. Effect of pH on recovery

Cloud point extraction of copper and zinc 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. Cloud point extraction of copper and zinc was performed in different pH buffer solutions.

Fig. 1 shows the effect of pH on the extraction of copper and zinc complexes. It was found that extraction was quantitative for copper and zinc in the pH range 6.5–7.0. Hence, pH at 6.5 was chosen for these analytes.

3.2. Effect of DPBP concentration on recovery

The concentration of DPBP was evaluated over the range 0.7-7.0 mM. For this study, 15 mL of a solution containing 0.01 $\mu g\ mL^{-1}$ Cu^{2+} and 0.04 $\mu g\ mL^{-1}$ Zn^{2+} in 0.17% (w/v) Triton- X-114 with various amounts of DPBP was subjected to the cloud point preconcentration process. The extraction recovery as a function of the DPBP concentration is shown in Fig. 2. As it is seen for both Cu and Zn complexes, the recovery increases up to a known concentration of DPBP, reaching a plateau, which is considered as complete extraction. Therefore concentration of 2.5 mM was chosen as the optimum.

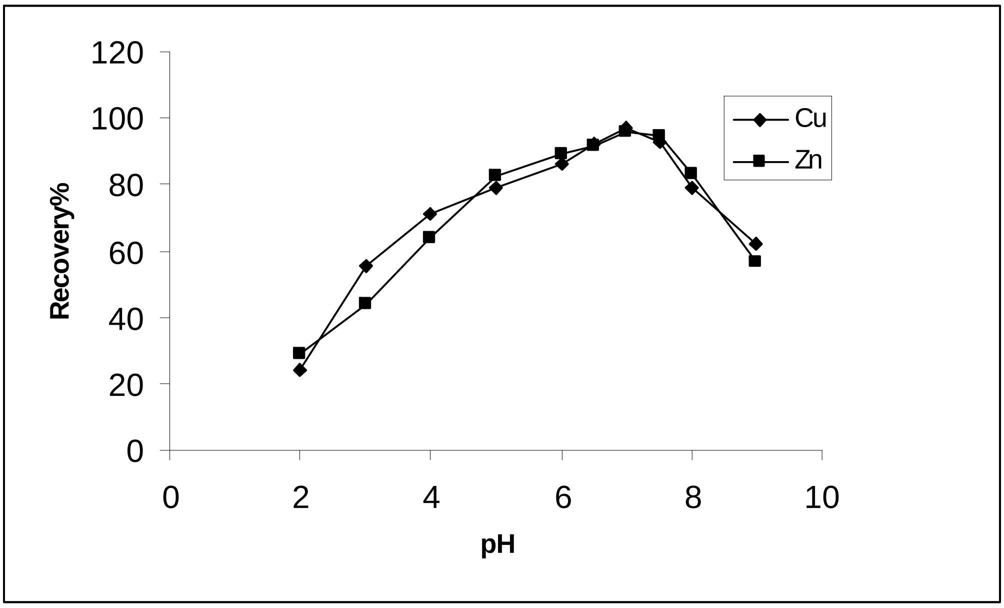

Fig 1. Effect of pH on the extraction recovery of copper and zinc ions. Conditions: 0.01 μg mL^{-1} Cu^{2+}, 0.04 μg mL^{-1} Zn^{2+}, 2.5 mM DPBP, 0.17% (w/v) Triton X-114. Other experimental conditions are described in Procedures.

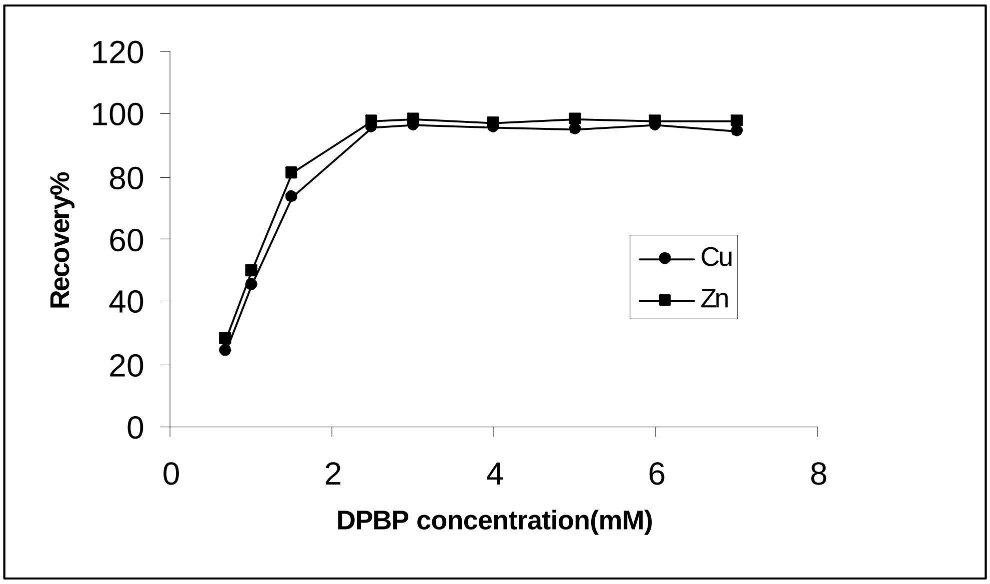

Fig. 2. Effect of DPBP concentration on the extraction recovery of copper and zinc ions. 0.01 μg mL^{-1} Cu^{2+}, 0.04 μg mL^{-1} Zn^{2+}, 0.17% Triton X-114, pH 7.0. Other experimental conditions are described in Procedures.

3.3. 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 [27, 42]. The preconcentration efficiency was evaluated using Triton X-114 concentrations ranging from 0.1 to 0.3% (w/v). The highest copper and zinc ions recovery was obtained with 0.17% (w/v) Triton X-114. By decreasing the surfactant concentration to 0.1% (w/v) the recovery was reduced. The copper and zinc ions recovery also decreased for a higher Triton X-114 concentration (0.2% w/v). This result might be related to the presence of the high amount of surfactant, resulting in an increase in the volume of the surfactant-rich phase. In addition, the viscosity of the surfactant-rich phase increases, leading to poor sensitivity [32, 43]. At lower Triton X-114 concentrations (below 0.1% w/v), the preconcentration efficiency of the complex was very low, probably due to assemblies that were inadequate to quantitatively entrap the hydrophobic complex [44]. Since, 0.17% (w/v) of Triton X-114 showed the highest copper and zinc ions recovery; a surfactant concentration of 0.17% (w/v) was selected as a compromise between the results obtained (in terms of sensitivity) and the surfactant concentration.

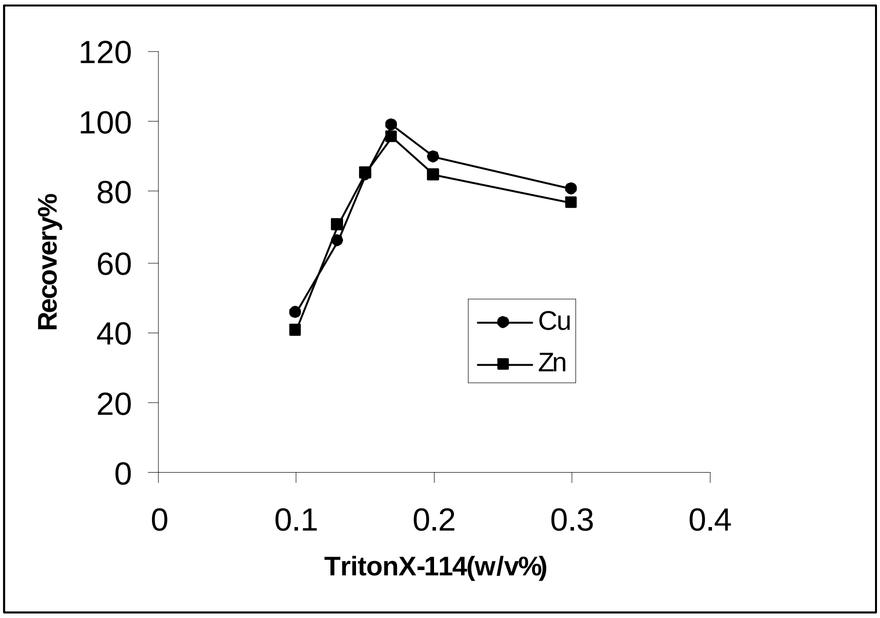

Fig. 3. Effect of Triton X-114 concentration on absorbance of copper and zinc ions Conditions: 0.01 μg mL^{-1} Cu^{2+} and 0.04 μg mL^{-1} Zn^{2+}, 2.5 mM DPBP, pH 7.0. Other experimental conditions are described in Procedures.

3.4. Effect of ionic strength

The addition of an inert salt can facilitate the phase-separation process for some nonionic surfactant systems, since it increases the density of the bulk aqueous phase [45, 46]. When the salt concentration is increased, the micelle size and the aggregation number are increased and the critical micellar concentration remains constant [47]. In addition, non-polar analytes may become less soluble in the solution at higher salt concentrations and thus contribute to higher recoveries. The results obtained indicate that the addition of salt produces an increase in the extraction of the more polar solutes while the recoveries of the less polar compounds are not affected [48, 49, 50, 51]. Based on this discussion, NaCl was investigated as electrolyte in the concentration range from 0.1 to 1% (w/v) and the highest copper and zinc ions recovery was obtained at 0.2% (w/v) NaCl concentration. The signal decreased considerably for increasing NaCl concentrations (0.3–1% w/v). This effect might be explained by the additional surface charge when the NaCl concentration is very high, thus changing the molecular architecture of the surfactant and consequently the micelle formation process. It is necessary to emphasize that different blank solutions were also evaluated and no significant signal was obtained. In this way, 0.1% (w/v) NaCl concentration was used in all further experiments.

3.5. Effects of equilibration temperature and time

The cloud point temperature of Triton X-100 is 67.3 ^{0}C. However, room temperature is the preferred cloud point temperature for analytical purposes. In order to decrease the cloud point temperature of micellar solution of Triton X-100, NaCl solution was used. The effect of additives organic or inorganic on cloud point temperature of micellar solution of surfactants is reported in the literature [44, 52]. 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. It was found that a temperature of 45 ^{0}C is adequate for both analyses. The dependence of extraction efficiency upon equilibration time was studied within a range of 5–30 min. An equilibration time of 20 min was chosen as the best.

3.6. Effect of methanol

Since the surfactant-rich phase obtained after the cloud point preconcentration contains a high concentration of Triton X-114 and, at the same time, the volume obtained is rather small (500 μL), methanol containing 0.1 mol L^{-1} HNO_3 was added to the surfactant-rich phase after phase separation. Moreover, it was necessary to decrease the viscosity of the rich phase without excessive dilution of the micelle to facilitate the introduction of the sample into the atomizer of the spectrometer. There is an optimum volume (500 μL) with respect to the copper ion recovery. Smaller volumes of methanol were not tested because in this case it was not possible to quantitatively transfer the rich phase from test tubes to the graduated tubes and measuring the absorbance. Larger volumes of acidified methanol dilution are clearly predominated resulting in a gradual absorbance reduction. A 500 μL volume of methanol was therefore used throughout the remaining experiments.

3.7. Effect of Centrifuge time and rates

It is required to preconcentrate trace amount of copper and zinc ions with high efficiency in short time. Therefore, CPE on a set of experiments of 15 mL sample at pH 7.0, 2.5 mM DPBP, 0.01 μg mL^{-1} Cu^{2+} and 0.04 μg mL^{-1} Zn^{2+} ions, 0.17% Triton X-114 and 0.1% NaCl by heating 45 ^{0}C and centrifuging in various rate and time further cooling in various time has been carried out. The results indicate the experiment in the optimized reagent concentration after heating for 20 min in 45 ^{0}C and centrifuging by 15 min in 4000 rpm and cooling in 15 min in ice-bath lead to high recovery of copper and zinc ions in short time.

3.8. Characteristics of the method

Calibration graphs were obtained by preconcentrating 2.0 mL of standard solution in the presence of pH 7.0, 0.17% (w/v) Triton X-114, pH 7.0, 2.5 mM DPBP with 0.1% (w/v) NaCl, under the experimental conditions specified in the optimized procedure section. The solutions were introduced into the flame by conventional aspiration. The characteristics of the proposed method are shown in Table 1.

Table 2 gives the characteristic performance of the proposed method of standard solutions subjected to the entire procedure. Limits of detection and quantification according to IUPAC are also included. The limit of detection and the linear range of the proposed method are comparable to other methods that also employed FAAS.

Table 1. Optimum Conditions for the Presented CPE Method

Parameter	Optimum Value for ions
pH	7.0
DPBP concentration (mM)	2.5
Triton X-114(w/v)	0.17%
Eluting agent	0.5 mL 0.1 mol L^{-1} HNO$_3$ in methanol
Bath temperature	45^{0}C
Temperature time	20 min
Centrifuge time	15 min
Centrifuge rates	4000 rpm

Table 2. Specification of Method at Optimum Conditions for Each Element

Parameter	Element	
	Zn	Cu
Linear Range (µg mL^{-1})	0.03-1.6	0.04-1.2
Detection Limit (ng mL^{-1})	1.9	1.6
RSD %	1.3	1.2
Recovery %	98.6	98.8
Enrichment factor	33	33

3.9. Interferences

In view of the high selectivity provided by flame atomic absorption spectrometry, the only interferences studied were those related to the preconcentration step. Cations that may react with DPBP, and anions that may form complexes with the metal ions were studied. The results were shown in Table 3. It was proved that copper and zinc recoveries were almost quantitative in the presence of foreign cations.

Table 3. Effects of the matrix ions on the recoveries of the examined metal ions (N=3)

Ions	Added As	Tolerance Limit Ion mg L^{-1}	Recovery%	
			Cu	Zn
Cl^-, K^+,Na^+	KCl, NaCl	1000	100	97.9
Mg^{2+}, Ca^{2+}	$MgCl_2$, $CaCl_2$	700	97.8	97.5
Cr^{3+}, Cd^{2+}, Ba^{2+}, Ni^{2+},Co^{2+}	Nitrate salt	350	97.5	96.8
HCO_3^-	$NaHCO_3$	300	97.3	96.9
PO_4^{3-}	Na_3PO_4	300	97.8	96.5
Cr^{3+}, Ag^+, Al^{3+}, Co^{2+}, Hg^{2+}	Nitrate salt	300	97.4	98.3
Fe^{2+}	Nitrate salt	150	98.9	99.4
Pb^{2+}, Hg^{2+}	Nitrate salt	100	97.4	97.9
Fe^{3+}	Nitrate salt	50	96.3	97.0

3.10. Accuracy and applications

We have explored the feasibility of the methodology using preconcentration with DPBP in surfactant media for the determination of copper and zinc ions in different matrices treated according to experimental section. The procedure was applied to the determination of copper and zinc ions in different samples, including waste water, river water, soil and blood sample by standard addition method. Reliability was checked by spiking experiments and independent analysis. The results are presented in Table 4. 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 water samples.

Table 4. Recovery studies of Copper and Zinc in Real Samples (N=3)

Sample	Element	Added	Found	RSD, **%**	Recovery, %
Soil [a]	Cu	0	0.213	1.4	---
		0.2	0.408	0.9	97.5
	Zn	0	0.340	1.4	---
		0.2	0.545	1.2	102.5
River water [b]	Cu	0	79.3	1.1	---
		100	182.1	1.4	102.8
	Zn	0	56.0	1.6	---
		100	154.3	0.9	98.3
Blood [b]	Cu	0	79.8	1.3	---
		100	182.6	0.8	102.8
	Zn	0	32.6	1.8	---
		100	129.9	1.0	97.3
Waste water [b]	Cu	0	88.9	1.3	----
		100	192.1	0.9	103.2
	Zn	0	42.4	1.3	---
		100	142.5	1.4	100.1

a) All values are mg g^{-1} after suitable dilution
b) All values are µg L^{-1}

5. Conclusion

The proposed method for the separation, pre-concentration and speciation of Zn and Cu are simple, sensitive and accurate. Further, in comparison to solvent extraction methods, it is much safer, since only a small amount of the surfactant, which has a low toxicity, is used. The limits of detection are sufficiently low as compared to those attained by FAAS without pre-concentration. Besides, the method can be applied to the determination of trace amount of both Zn and Cu species in various Real samples.

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Received: November 02, 2007; Accepted: December 22, 2007

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