Enrichment of Some Heavy Metals With Cloud Point Extraction via 5,7-Diiodo-8-Hydroxyquinoline Ligand and Detection by Ultrasonic Nebulizer-ICP-OES Using Internal Standard Method

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INTRODUCTION

The determination of heavy metals in food and water samples at trace levels is crucial because of their effects on human health and the environment (1). Several techniques commonly used for heavy metal analysis in water include flame atomic absorption spectrometry (FAAS) (2-5), electrothermal atomization atomic absorption spectrometry (ETAAS) (8-13), and inductively coupled plasma-optical emission spectrometry (ICP-OES) (6-7, 14-17). ICP-OES is an efficient technique to determine inorganic elements in environmental and biological samples, and has the ability of multi-element analysis and a high rate analytical efficiency. However, this technique presents reasonable measurability but requires a pre-concentration process for metals determination (18).

Metal ion levels are very low in the samples and detection is quite difficult because of the complex ingredients of the matrix. For that reason, pre-concentration and separation technologies (19-21) are used to extract these metals at proper concentrations. These techniques are liquid-liquid extraction (22, 23), solid phase extraction (24-26), co-precipitation (27-29), electrochemical accumulation (30, 31), ion exchange (32, 33), and cloud point extraction (CPE) (34-38). Cloud point extraction is preferred because it is simple, fast, high yield-

ABSTRACT

In this study, a method was developed in which the heavy metal ions of Cu^{+2} , Cd^{+2} , Co^{+2} , Ni^{+2} , Pb^{+2} , Zn^{+2} in water samples are enriched by using cloud point extraction and detection using ultrasonic nebulization with inductively coupled plasma optical emission spectrometry (USN-ICP-OES). The metal ions, complexed with the Triton X-114 surfactant, were imprisoned in the mycelium after phase separation via the centrifuge. The surfactant phase was diluted with 2 M HNO_3 and measured by USN-ICP-OES. In order to reduce noise and errors, indium was used as the internal standard. The pH, surfactant concentration, ligand concentration, equilibration time, temperature, and foreign ion effects were investigated. The limit of detection of Cu^{+2} , Zn^{+2} , Ni^{+2} , Cd^{+2} , Co^{+2} , Pb^{+2} using $\text{pH}=7$, 0.1 mmol L^{-1} 5,7-diiodo-8-hydroxyquinoline, and 0.06 (w/v) Triton X-114 were found to be 0.076, 0.30, 0.081, 0.022, 0.033, and $0.049 \mu\text{g L}^{-1}$, respectively. The RSD% was between 2.08% and 6.28% ($n=10$). The developed method is in accordance within green chemistry and was successfully applied to certified reference materials and real water samples.

ing, requires less toxic organic solvents and is, therefore, in compliance with the green chemistry principle (39).

Cloud point extraction is based on phase separation in aqueous solution of non-ionic surface activated agents. Phase separation

occurs when the cloud point temperature has been reached, and phase separation may be observed not only with a temperature change but also with any material added or a pressure change. Most non-ionic surface-activated agents may form mycelium and separate into two phases: (a) the phase which is below the critical mycelium concentration or at equal concentration and (b) the surface-activated rich phase which pre-concentrates the analyte ions (40, 41). Metal ion complexes are created with the hydrophobic ligand of the surface-active rich phase environment and are separated by the other phase by staying in the mycelium created by the surface-activated material (42).

The internal standard method was used in order to balance non-spectral interferences, decrease the noise and to eliminate the multiple errors in the ICP devices. This method is based on measurement and calculation of the reference element comparative to its signal instead of measuring the emission of the analyte (43, 44).

In this study, pre-concentration and determination of the Cu^{2+} , Cd^{2+} , Pb^{2+} , Co^{2+} , Ni^{2+} , and Zn^{2+} ions are performed by using the indium internal standard and ICP-OES with the cloud point extraction method and an ultrasonic nebulizer. The ultrasonic nebulizer increases the analytical capacity due to the higher vapor efficiency. The aerosol formation is more efficient at making small droplets and removes the solvent, thus giving a 10 times better detection limit (45, 46). The complexing agent 5,7-diiodo-8-hydroxyquinoline was

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used with Triton® X-114 as the surface-activated agent. The method was applied to the analysis of certified reference material and real water samples.

EXPERIMENTAL

Instrumentation

A model Spectro Arcos ICP-OES (Spectro Arcos, Germany) was used to determine the metal concentrations and was equipped with a CETAC U-5000AT+ ultrasonic nebulizer. The optimum instrumental conditions are listed in Table I. The pH measurements were performed using the Orion 2-Star Plus pH meter (Thermo Scientific, USA) and a NF 400 centrifugation system (Nüve Co., Turkey). A Milli-Q® (18.2 MΩ·cm⁻¹) Integral Water Purification System was used to produce distilled de-ionized ultrapurified water (Millipore Corporation, USA).

Reagents and Standard Solutions

All chemicals used were of analytical grade. The metal solutions were prepared with 1000 mg/L of Cu²⁺, Cd²⁺, Pb²⁺, Co²⁺, Ni²⁺, and Zn²⁺ standard solutions (Merck, Germany). Adjustment of the solutions to the proper pH was performed with 0.1 M NaOH and 0.1 M HCl (Merck) solutions, then the proper buffers were added. The hydrophobic complexing agent of 5,7-diiodo-8-hydroxyquinoline was used and 1,1,3,3-tetramethylbutyl (Triton X-114) as the surface-activated agent with the metal ions. A 5 g amount of Triton X-114 in analytical purity was dissolved in boiling ultrapure water and the volume of the solution completed to 100 mL, resulting in a 5% (w/v) surfactant solution. In order to dilute the surface-active rich phase, ultra-purified 2 mol L⁻¹ HNO₃ solution (Merck) was used. For the prepara-

tion of the solutions, distilled deionized water (Milli-Q Millipore 18.2 MΩ·cm⁻¹ resistance) was used. An internal standard solution was prepared from 1000 mg/L In (Sigma-Aldrich) stock solution.

Sampling

The drinking water and river water samples were obtained in 2015 from the Sakarya river in Adapazari city, Turkey. Polyethylene bottles were used to store the samples which were adjusted to the appropriate pH with HNO₃. Then the samples were filtered with a Millipore nitrocellulose membrane (pore size 0.45 μm) and stored at +4 °C in a refrigerator to prevent microbial activity.

Cloud Point Extraction Procedure

In order to perform cloud point extraction, 10⁻² mol L⁻¹ 5,7-diiodo-8-hydroxyquinoline, buffer, and 5% (w/v) Triton X-114 solutions were added to the various analyte solutions in the range of 10-500 μg L⁻¹ concentration and diluted to 50 mL. This solution was placed into a water bath at 55 °C for 20 minutes and centrifuged for 10 minutes at 4000 rpm. It was then soaked in the ice bath for 20 minutes to increase the viscosity of the surface-active rich phase, and the liquid phase of the solution was removed with a micropipette. Following the cooling procedure and because the surface-active rich phase obtained at the bottom of the test tube is viscous, the separation operation can be easily performed. The indium added into the separated surface-active rich phase was diluted with 2 mol L⁻¹ HNO₃ solution to 2 mL, and the solution analyzed by USN-ICP-OES.

RESULTS AND DISCUSSION

Effect of pH

Because the pH is one of the basic parameters in complexation

TABLE I
ICP-OES and Ultrasonic Nebulizer Operating Conditions

ICP-OES Spectrometer	
Viewing Height	12 mm
Element Wavelength	Cd: 214.438 nm
	Co: 228616 nm
	Cu: 324.754 nm
	Ni: 231.604 nm
	Pb: 220.353 nm
	Zn: 213.856 nm
Replicates	3
RF Power	1450 W
Spray Chamber	Cyclonic
Nebulizer	Modified Cetac ultrasonic nebulizer
Nebulizer flow	0.8 L/min
Plasma Gas Flow	13 L/min
Auxiliary Gas Flow	0.7 L/min
Sample Aspiration Rate	2.0 mL/min
Sample Pump Rate	25 rpm
Ultrasonic Nebulizer Conditions	
Desolvation Temperature	140 °C
Condenser Temperature	5 °C

reactions, it is the first variable that has to be examined. Scanning was performed between the pH levels of 2 to 12, and the proper pH value was found between 7–8. It was observed that using this pH, the 5,7-diiodo-8-hydroxyquinoline complexing agent creates the highest and efficient complexes with the Cu^{2+} , Cd^{2+} , Pb^{2+} , Co^{2+} , Ni^{2+} , and Zn^{2+} metal ions. The reason of inefficient recovery on the lowest pH values may be due to the decrease in stability of the metal complexes of 5,7-diiodo-8-hydroxyquinoline. Precipitation of the metals with hydroxides may affect recovery at high pH values. The effect of the pH on the recovery percentages of the metal ions is shown in Figure 1.

Effect of Ligand Concentration

Formation of a hydrophobic and high stability complex with metals of the ligands is significant for the performance of the extraction. 5,7-diiodo-8-hydroxyquinoline forms hydrophobic complexes with the metal ions and pre-concentration is performed by imprisoning these complexes in the mycelium. Because reaction of the metals in the environment of the complexation agent is intended, enough complexation agent is required. Measurements were performed in

the concentrations between 0.02 mmol L^{-1} and 0.4 mmol L^{-1} . Recovery values were found to be appropriate at concentrations of 0.08 mmol L^{-1} and above. The possible reason is the increase in complexation efficiency of the excessive ligand molecules and simplification of entrance to the mycelium. The effect of ligand concentration on recovery percentages of the metal ions is shown in Figure 2.

Effect of Triton X-114

Triton X-114 was selected as the surface-activated agent because of high density during phase separation

tion and use of lower mycelium temperature (23–26 °C). The Triton X-114 surface-activated agent was tested between the concentration range of 0.005–0.2% (w/v) which gives the highest recovery rates at 0.04–0.125% (w/v) concentration. Thus, 0.06% (w/v) was chosen as the optimum rate. The effect of the recycling percentage of the metal ions on the surface-activated agent concentration is shown in Figure 3.

Effect of Equilibration Time and Temperature

In order to form stable hydrophobic complexes in cloud point

Fig. 1. Effect of pH on the recoveries of the metal ions. Conditions: 50 mL solution, 0.2 mmol L^{-1} 5,7-diiodo-8-hydroxyquinoline, 100 $\mu\text{g L}^{-1}$ metal ions, 0.1% (w/v) Triton X-114.

Fig. 2. Effect of complexing agent concentration on the recoveries of the metal ions. Conditions: 50 mL solution, pH 7.0, 100 $\mu\text{g L}^{-1}$ metal ions, 0.05% (w/v) Triton X-114.

Fig. 3. Effect of Triton X-114 concentration on the recoveries of metal ions. Conditions: 50 mL solution, 0.1 mmol L^{-1} 5,7-diiodo-8-hydroxyquinoline, pH 7.0, 100 $\mu\text{g L}^{-1}$ metal ions.

extraction and to imprison the hydrophobic structure complexes with the surface-activated agent, the cloud point temperature has to be reached. Complexation efficiency may decrease at low temperatures or remain below the critical concentration of the surface-activated agent. Formations may become unstable at higher temperatures. In this study, it was observed that the recovery value is good for 15 minutes or above and between 45–60 °C. Thus, 20 minutes with 50 °C was the accepted optimum value.

Effect of Interfering Ions

Because of the reasons stated in the previous section, a common ion effect study was performed in order to obtain at least 95% recovery during the enrichment of the metal ions in the presence of various anions and cations. While conducting the experiment, common ion solutions at various concentrations were added to 100 ng mL⁻¹ concentration of the metal ions and cloud point extraction was tested. No undesired interferences were observed up to the specified values as are listed in Table II.

Analytical Performance

After the optimum conditions of the proposed method were

TABLE II
Effect of Matrix Ions

Ions	Tolerance Limit
Na ⁺	5000 : 1
K ⁺	5000 : 1
Mg ²⁺	2000 : 1
Ca ²⁺	1000 : 1
Al ³⁺	100 : 1
Ba ²⁺	10 : 1
Fe ³⁺	5 : 1
Cl ⁻	5000 : 1
NO ₃ ⁻	5000 : 1
F ⁻	5000 : 1
SO ₄ ²⁻	500 : 1

obtained, enrichment factor, limit of quantification, limit of detection and precision were calculated as the analytical performance values. The enrichment factor is calculated as the proportion of the slope of the calibration curve obtained by pre-concentration to the slope of the calibration line without pre-concentration. The LOD values are calculated using 3 times the 10 independent blank standard deviation divided by the calibration line slope (3σ/m). The LOQ values are calculated using 10 times the standard deviation of the blanks divided by the calibration line slope of (10σ/m). Other measurements and the results are listed in Table III.

Analysis of Reference Material and Real Water Samples

Good agreement of the results of the proposed method was also verified by using the standard reference material (SRM) INCT-TL-1 Tea Leaves (Institute of Nuclear Chemistry and Technology, Poland). For all studies, In was used as the internal standard which was added dur-

ing the optimization phase resulting in sample measurements at the final value of 100 µg L⁻¹. Excellent recovery of the metals for 500-mL water samples with the cloud point extraction method is demonstrated by using the optimum UN-ICP-OES conditions and the results are listed in Tables IV and V.

CONCLUSION

A method which allows detection of the heavy metals (copper, cobalt, nickel, lead, and cadmium) at trace levels was evaluated. Indium (In) was used as the internal standard, and the internal standard technique is applied successfully in order to prevent the entrance of noise and various interferences. The ultrasonic nebulizer was mounted to the ICP-OES device and similar detection limits of the metals were obtained. The method was also applied to a certified reference material with successful recovery results between 97.4% and 102.7%. Heavy metal ions (Cu²⁺, Zn²⁺, Ni²⁺, Cd²⁺, Co²⁺, Pb²⁺) in water samples

TABLE III
Analytical Performance Parameters of the Proposed Method

Parameters	Cu	Zn	Ni	Cd	Co	Pb
Enrichment Factor	21.04	18.79	21.85	21.73	14.06	13.33
Correlation Coefficient ^a	0.9984	0.9885	0.9977	0.9987	0.9985	0.9980
RSD (n=10)	3.63	6.28	2.08	2.11	3.45	3.87
LOQ (ng mL ⁻¹)	0.250	0.99	0.27	0.076	0.1	0.16
LOD (ng mL ⁻¹)	0.076	0.30	0.081	0.022	0.033	0.049

^aCorrelation coefficient after CPE.

TABLE IV
Analysis of Certified Reference Material for the Determination of Analytes After Application (n=3)

Ions	Certified Values (µg g ⁻¹)	Values of Present Study (µg g ⁻¹)	Recovery (%)
Cu	20.400 ± 1.500	20.920 ± 0.460	102.7
Zn	34.700 ± 2.700	33.900 ± 2.960	97.7
Ni	6.120 ± 0.520	5.960 ± 0.960	97.4
Cd	0.030 ± 0.004	0.032 ± 0.003	106.6
Co	0.387 ± 0.042	0.385 ± 0.031	99.5
Pb	1.780 ± 0.240	1.733 ± 0.180	97.4

TABLE V
Recovery of Metals in
Water Samples (n=3)

Sample	Ions Added	Measured	Recovery
	($\mu\text{g L}^{-1}$)	($\mu\text{g L}^{-1}$)	(%)
Tap Water			
Cu	0	0.48	
	5	5.45	99.0
	10	10.72	102.4
Zn	0	1.12	
	5	6.27	103.0
	10	11.74	106.0
Ni	0	BDL	
	5	4.9	98.0
	10	10.22	102.0
Cd	0	BDL	
	5	5.05	101.0
	10	9.94	99.0
Co	0	BDL	
	5	4.82	96.0
	10	10.18	102.0
Pb	0	BDL	
	5	5.23	105.0
	10	10.32	103.0
River Water			
Cu	0	1.62	
	5	6.69	101.0
	10	11.91	103.0
Zn	0	3.22	
	5	8.43	104.0
	10	13.9	107.0
Ni	0	0.57	
	5	5.61	101.0
	10	10.23	97.0
Cd	0	BDL	
	5	4.86	97.0
	10	9.77	98.0
Co	0	BDL	
	5	5.31	106.0
	10	9.78	98.0
Pb	0	BDL	
	5	5.19	104.0
	10	10.07	101.0

BDL : Below detection limit.

are enriched by using cloud point extraction and at optimum conditions the limit of detection of the metals were found at 0.076, 0.30, 0.081, 0.022, 0.033, and 0.049 $\mu\text{g L}^{-1}$, respectively. Also, an enrichment factor between 13.33 and 21.85 was obtained. This study shows a method which can perform metals detection in accordance with the green chemistry concept by eliminating the harmful use of chemicals. In addition, the method is fast, simple, efficient, and low cost for use in the determination of heavy metals at the $\mu\text{g L}^{-1}$ levels.

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