

Determination of cadmium(II), copper(II) and zinc(II) in water samples by flame atomic absorption spectrometry after cloud point extraction

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A preconcentration method for determination of low concentrations of Cd(II), Cu(II), and Zn(II) in water, using cloud point extraction is proposed. The analytes in the initial aqueous solution have been complexed with 8-hydroxyquinoline, with 0.06% (w/v) Triton X-114 added as surfactant. The complexation allows the separation of the analytes from other elements, which are not complexed. After phase separation, based on the cloud point of the mixture and dilution of the surfactant-rich phase with acidified methanolic solution, the enriched analytes have been determined by flame atomic absorption spectrometry. After optimization of complexation and extraction conditions, good enrichment factors have been obtained. The detection limits are 0.15 ng ml⁻¹ for Cd(II), 0.72 ng ml⁻¹ for Cu(II) and 0.03 ng ml⁻¹ for Zn(II) in the initial solution. The relative standard deviations are lower than 3.1%. The method has been applied for analysis of the studied ions in tap water and river water samples. The method has been validated by the analysis of standard reference material.

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 applications. However, the determination of trace metal ions in natural waters is difficult due to various factors, in particular their low concentrations and matrix effects. Preconcentration and separation can solve these problems, leading 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 preconcentration and separation such as liquid-liquid extraction¹, ion-

exchange techniques^{2,3}, co-precipitation⁴, sorption on the various adsorbents such as activated carbon⁵, Amberlite XAD resins⁶ and other sorbents⁷⁻⁹. Cloud point extraction is a versatile and simple method for preconcentration, removal of organic pollutants, such as pesticides, polychlorides and phenols¹⁰⁻¹² and for the determination of vitamins¹³. It is also used for the treatment of contaminated environmental compartments, particularly water and soils¹⁴. The technique is based on the property of most non-ionic surfactant 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 into a surfactant-rich phase of a small volume and a dilute aqueous phase, in which the surfactant concentration is close to the critical micellar concentration. This phenomenon is observed in particular with polyoxyethylene surfactants. This can be attributed to the two ethylene oxide segments in the micelle that repel each other at low temperature when they are hydrated, and attract each other as the temperature increases, due to dehydration. This effect causes a decrease in the effective area occupied by the polar group on the micelle surface, increasing the size of the micelle that can be considered to become infinite at the cloud point, resulting in phase separation^{15,16}. This phase separation at the cloud point can be utilized to extract metals from the aqueous detergent solution¹⁷⁻²⁰.

8-hydroxyquinoline (8-HQ) has sufficient hydrophobicity to be used as a complexing agent in cloud point extraction technique²¹. This agent has been used in the preconcentration of heavy metals for the determination by AAS^{22,23} or by ICP-AES²⁴. It was also used for the determination of trace metals of natural waters by ICP-MS with on-line preconcentration²⁵.

In the present study, cloud point extraction using 8-HQ as the complexing agent and Triton X-114 as non-ionic surfactant, is applied to the preconcentration of Cd(II), Cu(II) and Zn(II) in water samples. Flame atomic absorption spectrometry has been used for determination of analytes.

Experimental

All reagents used were of analytical-reagent grade. Stock solutions (1000 mg l⁻¹) of Cd(II), Cu(II) and

Zn(II) and those used for the interference study were prepared by dissolving appropriate amounts of their respective salts in doubly distilled water. The non-ionic surfactant, Triton X-114, (Fluka Chemie AG, Switzerland) was used without further purification. 8-hydroxyquinoline (8-HQ, 99%, Sigma-Aldrich Ltd.) was dissolved in 99.8% methanol. NaOH and HCl were obtained from Sigma-Aldrich Ltd.

A Varian atomic absorption spectrometer (model AA-1475) equipped with deuterium background correction and cadmium, copper and zinc hollow cathode lamp as the radiation source was used. The instrumental parameters were adjusted according to the manufacturer's recommendations. A thermostated bath maintained at the desired temperatures was used for cloud point temperature experiments and phase separation was assisted using a centrifuge (Hettich, Universal).

Procedure

The final volume of the surfactant-rich phase was determined by measuring the phase after cloud point extraction together with the added methanolic solution. The values reported are the average of duplicate measurements and three runs. The CPT of Triton was taken from diagrams of earlier reported work²⁶.

Typically, a cloud point extraction experiment was performed as follows: An aliquot of 50 ml of a solution containing of Cd(II), Cu(II) and Zn(II), 0.06% (w/v) Triton X-114 and 0.9×10^{-3} M 8-HQ was adjusted to pH 5.0 with either HCl or NaOH. It was left to stand in a thermostated bath for 10 min at 60°C. Separation of the phases was achieved by centrifugation for 15 min at 3500 rpm. The phases were cooled in an ice bath in order to increase the viscosity of the surfactant-rich phase. The bulk aqueous phase was easily decanted and the micellar phase was treated with a methanolic solution of 1.0 M HNO₃ in order to reduce its viscosity. The final solution was aspirated directly into the flame of the AAS.

Results and discussion

The pH was the first critical parameter evaluated for its effect on the determination of the three species. It was found that extraction was quantitative for cadmium(II) and copper(II) in the pH range 4.8-6.4 and for zinc(II) in the range 4.0-6.0. Hence, a middle range of pH at 5.0 was chosen for these analytes.

The effect of concentration of the chelating agent on the analytical response was studied. The concentrations of the analytes were 40 ng ml⁻¹ for Cd(II), 50 ng ml⁻¹ for Cu(II) and 40 ng ml⁻¹ for Zn(II). The chelating concentration increased up to certain values, which were sufficient for total complexation, and levelled off thereafter.

The signal increased up to a 8-HQ concentration of 0.9×10^{-3} M for Cd(II), Zn(II) and up to 0.7×10^{-3} M 8-HQ for Cu(II) and reached near quantitative extraction efficiency. A concentration of 0.9×10^{-3} M was chosen as the optimum concentration for the subsequent experiments.

A successful cloud point extraction should maximize the extraction efficiency by minimizing the phase:volume ratio, thus improving its concentrating ability. 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. The results show that Triton X-114 effectively extracts the metal species from liquid samples at concentration of 0.06% (w/v). With increase of Triton X-114 concentration above 0.06%, the signals decrease because of the increment in the overall analyte volumes and the viscosity of the surfactant phase. The optimum surfactant concentration used for the three metals was the same, 0.06% (w/v) Triton X-114, in order to achieve the optimal analytical signal in conjunction with the highest possible extraction efficiency.

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 60°C 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 10 min was chosen as optimum to achieve quantitative extraction.

In order to increase the accuracy and reproducibility of the measurements, a simplified method was adopted, where the surfactant phase (ca. 200 µl) was analyzed after its uptake with 1800 µl of methanolic solution of 1.0 M nitric acid.

The presence of methanol and surfactant in the aspirated sample solutions can change the physical properties of the liquid sample by altering the solution environment²⁷. As reported, organic solvent in the flame increases atomization temperature, whilst both organic solvent and surfactant can promote generation

of small droplets during nebulization causing positive surface effects. The signal enhancement in the presence of organic solvents has been widely applied to increase the sensitivity during the analysis of a variety of metallic ions²⁸.

Calibration curves were obtained by preconcentrating 50 ml of standard solution with Triton X-114. Under the specified experimental conditions, the calibration curves were rectilinear up to 128 ng ml⁻¹ for Cd(II), 628 ng ml⁻¹ for Cu(II) and 28 ng ml⁻¹ for Zn(II). At the 40 ng ml⁻¹ level of Cd(II), Cu(II) and Zn(II), the relative standard deviations (10 replicate analyses) were 2.4% for Cd(II), 3.1% for Cu(II) and 2.7% for Zn(II).

The concentrated samples were introduced into the flame by conventional aspiration following the addition of 2 ml of a methanolic solution containing 1.0 M HNO₃. The preconcentration factors calculated as the ratio of absorbance of

preconcentrated samples to that obtained without preconcentration were 15.0, 20.9 and 66.4 for cadmium(II), copper(II) and zinc(II), respectively. The preconcentration factors reported by these studies were usually obtained by using larger sample volumes. Furthermore, the need-to-handle volume of the final methanolic solution was estimated to be sufficient for the analysis of the three metal ions and therefore had to be increased in order to allow for multiple runs of the same samples. The limits of detection were satisfactory (0.15 ng ml⁻¹ for Cd(II), 0.72 ng ml⁻¹ for Cu(II) and 0.03 ng ml⁻¹ for Zn(II)), although further improvement is feasible, either by preconcentrating larger amounts of sample solution, using the respective higher concentrations of both surfactant and chelating agent, or by diluting the surfactant-rich phase in a smaller volume of methanolic solution. In the latter case, the determination of the metal species may require the preparation of separate samples for each metal, as the final volume may not be adequate for the determination of all three species in a single sample. In this case, preconcentration of only 50 ml of sample in the presence of 0.06% (w/v) Triton X-114 permitted the detection of 0.15, 0.72 and 0.03 ng ml⁻¹ for cadmium(II), copper(II) and zinc(II), respectively.

Interference studies

In view of the high selectivity provided by flame atomic absorption spectrometry, the only interferences studied were those related to the preconcentration step. Other cations that may react with 8-HQ were studied. The results show (Table 1) that Cd(II), Cu(II) and Zn(II) recoveries are almost quantitative in the presence of interfering cations.

Analysis of real samples

In order to test the reliability of the proposed method for assay of the three targeted metal ions, it was applied to determination of their concentration in tap water and river water. For this purpose, 50 ml of

Table 1—Effect of foreign ions on the preconcentration and determination of Cd(II) (40 ng ml⁻¹), Cu(II) (60 ng ml⁻¹) and Zn(II) (40 ng ml⁻¹)

Ions	Conc (mg L ⁻¹)	Recovery (%)		
		Cd(II)	Cu(II)	Zn(II)
Cl ⁻	100	99.2	100.5	100.4
F ⁻	100	98.3	100.2	99.8
SO ₄ ²⁻	100	100.2	99.8	99.9
CO ₃ ²⁻	100	99.7	97.2	100.3
Na ⁺	10000	98.5	100.2	98.3
K ⁺	5000	100.3	98.1	97.8
Ca ²⁺	500	97.2	100.6	101.3
Mg ²⁺	500	103.1	101.1	103.1
Ag ⁺	10	100.8	98.9	100.3
Co ²⁺	5	102.3	98.9	100.3
Ni ²⁺	5	100.2	97.8	96.7
Fe ³⁺	5	99.8	100.4	102.1
Al ³⁺	5	102.5	101.5	99.6
Pb ²⁺	5	103.4	98.9	98.7
Li ⁺	5	99.1	98.5	100.6
Cr ⁶⁺	2	101.5	101.0	99.2
Hg ²⁺	2	102.9	100.5	99.6
Cr ³⁺	1	98.5	99.3	99.2
Mn ²⁺	1	102.3	99.6	101.5

Table 2—Determination of Cd(II), Cu(II) and Zn(II) (ng ml⁻¹) in water samples and standard reference material

Sample	Added (ng ml ⁻¹)			Measured (ng ml ⁻¹)			Recovery (%)		
	Cd(II)	Cu(II)	Zn(II)	Cd(II)	Cu(II)	Zn(II)	Cd(II)	Cu(II)	Zn(II)
Tap water	—	—	—	nd	15.3	12.7	—	—	—
	10	10	10	10.3	25.6	22.3	102.9	101.3	98.9
River water	—	—	—	nd	20.6	17.3	—	—	—
	10	10	10	10.4	30.3	27.1	103.8	99.2	99.2
SRM 1640	Cert. Value (ng ml ⁻¹)			Found (ng ml ⁻¹)					
	22.79 (± 0.96)			53.2 (± 1.1)			22.81 (± 0.82)		
							86.9 (± 1.6)		
							51.7 (± 1.2)		

each of the sample was preconcentrated with 0.06% (w/v) Triton X-114 and 0.9×10^{-3} M 8-HQ following the proposed method. For calibration purposes, working standard solutions were subjected to the same preconcentration procedure as used for the analyte solutions. Study shows good recovery for all the three analytes. In addition, validation of the method was carried out using standard reference material SRM 1640 recovery experiments for Cd(II), Cu(II) and Zn(II). There is good agreement between the certified values and those obtained using the proposed method (Table 2).

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