

Determination of Trace Amounts of Lead and Copper in Water Samples by Flame Atomic Absorption Spectrometry after Cloud Point Extraction

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Received February 9, 2004

The need for highly reliable methods for the determination of trace metals is recognized in analytical chemistry and environmental science. A method based on the cloud-point extraction (CPE) technique for the trace analysis of Pb and Cu in water samples is described in this study. The analytes in the initial aqueous solution are complexed with pyrogallol, and 0.1% (w/v) Triton X-114 is added as surfactant. Following phase separation at 50 °C, based on the cloud point of the mixture and dilution of the surfactant-rich phase with acidified methanolic solution, the enriched analytes are determined by flame atomic absorption spectrometry. After optimization of the complexation and extraction conditions, the enrichment factors of Pb and Cu were found to be 72 and 85, respectively. Under optimum conditions, the preconcentration of 60 mL of samples in the presence of 0.1% (w/v) Triton X-114 permitted the detection of 0.4 μgL^{-1} of Pb and 0.05 μgL^{-1} of Cu. The proposed method was applied successfully to the determination of Pb and Cu in water samples.

Key Words : Cloud point extraction, Pyrogallol, Micelle

Theoretical

In recent years, the pollution of the environment by heavy metals including Pb and Cu has received considerable attention. These elements accumulate in living organisms and have high toxic potentials. Moreover, the levels of these elements in biological samples may indicate malfunction or contamination. Hence, rapid and sensitive methods for their determination in environmental and biochemical research are in great demand.^{1,2}

Pb, even at low concentration, is toxic to animals and humans.³ This metal inhibits biosynthesis and affects the kidneys, brain cells and liver-membrane permeability, reducing some of these organs' functions.⁴ It can accumulate in the body and can promote disturbances such as nausea, vomiting, diarrhea, sweating, and in some cases, convulsions, coma and death.⁵

Cu is an essential element for enzymes, but above a healthy limit it accumulates in the liver, causing dizziness, vomiting, diarrhea, transpiration and, depending on its concentration, death from bleeding.⁶

The quantification of low concentrations of metals requires either very sensitive instrumental techniques or preconcentration to achieve detection limits within the range of the available equipment.⁷ This procedure is attractive when flame atomic absorption spectrometry (FAAS), a relatively simple and available technique in many laboratories, is used. The classical Liquid-Liquid extraction and separation methods are usually time consuming and labor extensive and require relatively large volumes of high-purity solvents. Of additional concern is disposal of the solvent following use, which creates a severe environmental problem.⁸

Cloud-point extraction (CPE) is an attractive technique that reduces the consumption of and exposures to a solvent, and it also reduces disposal costs and extraction time.⁹⁻¹⁷

Cloud-point extraction is probably the most versatile and simple method for the preconcentration and extraction of hydrophobic species from water. The technique is based on a 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 in which the surfactant concentration is closed to the critical micellar concentration.¹⁸ This phenomenon, which is especially observable with polyoxyethylene surfactants, can be attributed to the ethyl oxide segments in the micelle, which repel each other at low temperature and attract each other at high temperatures.¹⁹ The cloud point phenomenon is reversible and when the temperature falls below the CPT a single phase appears again.

Compared to the recent developments in preconcentration and determination of Pb and Cu, the proposed method is simple and sensitive.^{3,4,9,16,20-22}

In the present work, we report the results obtained in a study of the CPE for the determination of Pb and Cu, in water samples *i.e.* tap water and river water by using pyrogallol as complexing agent and Triton X-114 as surfactant. FAAS was used for the detection. Triton X-114 was chosen as the non-ionic surfactant because of its low cloud-point temperature and high density of the surfactant rich phase as well as its low cost, commercial availability and lower toxicity.

Experimental Section

Apparatus. A Varian Model AA-1475 atomic absorption

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spectrometer equipped with deuterium background correction was used to determine Pb and Cu. Pb and Cu hollow cathode lamps operating at 217.0 and 324.7 nm, respectively, were used as the radiation sources. A thermostated bath maintained at the desired temperatures was used for cloud-point temperature experiments and phase separation was assisted using a centrifuge.

Materials. All reagent used were of analytical-reagent grade. Stock solutions of Pb and Cu (1000 mgL^{-1}) and those used for the interference study (100 mgL^{-1}) 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. Pyrogallol (Merk, Darmstadt, Germany) was dissolved in 99.8% methanol.

A stock buffer solution (1 M) was prepared by dissolving appropriate amounts of acetic acid and sodium acetate in water. The pipettes and vessels used for trace analysis were kept in sulfochromic acid mixture for at least 1h and subsequently washed four times in succession with water.

Procedures. For CPE, aliquots of 60 mL of the cold solution containing the analytes, 0.1% (w/v) Triton X-114 and 1×10^{-4} M pyrogallol buffered at a suitable pH were placed for 10 min in a thermostatic bath maintained at 50°C . Separation of the phases was achieved by centrifugation at 3500 rpm, for 10 min. The phases were cooled in an ice bath to increase the viscosity of the surfactant-rich phase. The bulk aqueous phase was easily decanted. To reduce its viscosity, the remaining micellar phase ($200 \mu\text{L}$) was dissolved in $800 \mu\text{L}$ of methanolic solution of 0.1 M HNO_3 . The final solution (approximately 1.0 mL) was introduced into air acetylene flame by conventional aspiration.

Results and Discussion

Effect of the pH. The pH was the first critical parameter evaluated for its effect on the determination of the two species. As can be seen in Figure 1, for Pb and Cu in the pH range of 5.4-6.2, extraction was quantitative. Hence, a middle range of 5.8 was chosen for these analytes.

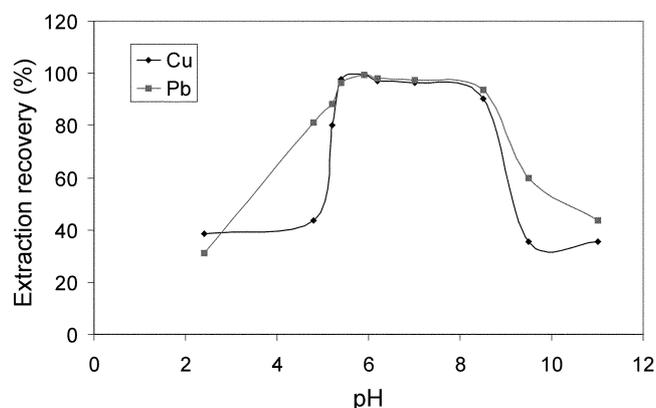


Figure 1. Effect of the pH on the CPE-preconcentration performance: Pb ($50 \mu\text{gL}^{-1}$) and Cu ($20 \mu\text{gL}^{-1}$); Triton X-114 0.1% (w/v); Pyrogallol 1×10^{-4} M.

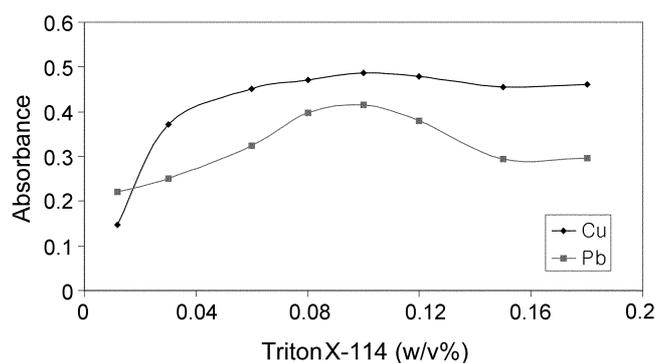


Figure 2. Effect of the Triton X-114 concentration on the CPE-preconcentration performance: Pb ($50 \mu\text{gL}^{-1}$) and Cu ($20 \mu\text{gL}^{-1}$); pH 5.8; Pyrogallol 1×10^{-4} M.

Effect of Pyrogallol Concentration. Under the optimum pH, the effect of the pyrogallol concentration as a chelating agent on the analytical signal was studied and the results are shown in Figure 2. In both cases, the signal increases up to a concentration of $0.8 \times 10^{-4} \text{ mol dm}^{-3}$, reaching a plateau, considered as complete extraction. A concentration of $1 \times 10^{-4} \text{ mol dm}^{-3}$ was chosen as the optimum concentration for the subsequent experiments.

Effect of Triton X-114 Concentration. The variation of the analytical signal as a function of the concentration of Triton X-114 is shown in Figure 3, when 60 mL solution containing all reagents in the presence of Triton X-114 with a concentrations from 0.01 to 0.18% (w/v) was used for CPE. The optimum concentration of Triton X-114 falls in the range of 0.08-0.12% (w/v) in both cases (Pb and Cu). A concentration of 0.1% (w/v) was chosen as the optimum concentration for the determination of both ions. At lower concentrations, the extraction efficiency of the complexes is low, probably because of an inadequacy in the assemblies to entrap the hydrophobic complex quantitatively. At higher concentrations of Triton X-114 the signals decrease because of the increment in the volumes and the viscosity of the surfactant phase.

Effect of Buffer Concentration and Ionic Strength. The acetic acid - acetate system was used as buffer solution. The

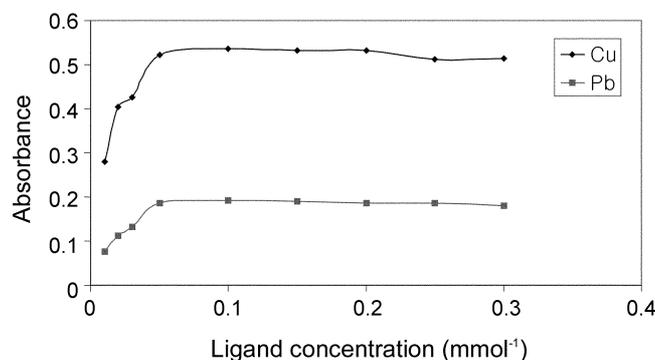


Figure 3. Effect of the Pyrogallol concentration on the CPE-preconcentration performance: Pb ($50 \mu\text{gL}^{-1}$) and Cu ($20 \mu\text{gL}^{-1}$); pH 5.8; Triton X-114 0.1% (w/v).

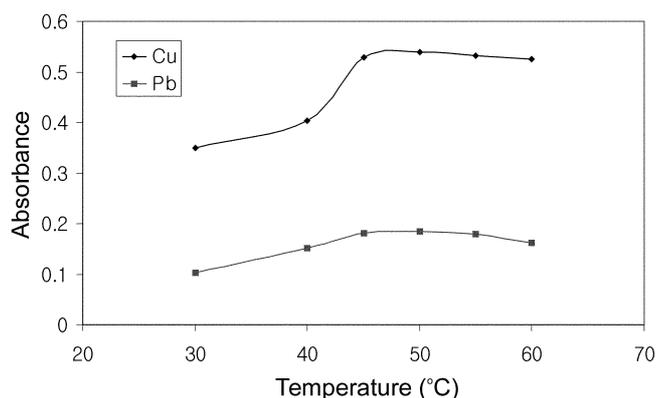


Figure 4. Effect of the temperature on the CPE-preconcentration performance: Pb ($50 \mu\text{g L}^{-1}$) and Cu ($20 \mu\text{g L}^{-1}$); pH 5.8; Triton X-114 0.1% (w/v); Pyrogallol $1 \times 10^{-4} \text{ mol dm}^{-3}$.

effect of changes in the amount of buffer was studied, while the other experimental variables remained constant. The results show that above 4.0 mL of buffer solution added to 60 mL of solution, no variation took place in the extraction yield. Thus, 5.0 mL of buffer solution was added in all subsequent experiments.

The influence of ionic strength was examined by studying the effect of KCl concentration in the range of 0–1.0 M. Ionic strength had no significant effects upon the extraction efficiency and sensitivity up to 0.5 M. This is in agreement with the results reported in the literature, which demonstrate that an increase in the ionic strength in micelle-mediated systems does not seriously alter the extraction efficiency of the analyte.^{23,24}

Effect of Equilibration Temperature and Time. The equilibration temperature above the cloud point and equilibration time were thoroughly optimized. It was desirable to employ the shortest equilibration time and the lowest possible equilibration temperature, a compromise between completion of extraction and efficient separation of the phases. Figure 4 clearly shows that a temperature of 50 °C is adequate for these analyses. At lower temperature the separation of the two phases is not complete. The dependence of extraction efficiency on equilibration time was studied for a time span of 5–25 min. An equilibration time of 10 min was chosen to be the optimal to achieve quantitative extraction.

Effect of Viscosity on Analytical Signal. Since the surfactant-rich phase obtained after cloud point extraction is rather viscous, methanol containing 0.1 M nitric acid was added to the surfactant-rich phase after the separation of the phases facilitating its introduction into the spectrometer nebulizer. For smaller added volumes of acidified methanol, reproducibility of the signals was very poor, whereas for higher volumes, there was a decrease in the signal due to dilution, a phenomenon also observed by other workers.^{17,25}

A volume of 800 μL of methanolic solution of 0.1 M HNO_3 was added to the surfactant-rich phase. This added volume of methanol was chosen to ensure a sufficient volume of sample for the analysis of two metals.

Table 1. Analytical characteristics of method

Parameter	Analytical feature	
	Pb	Cu
Preconcentration factor ^a	72	85
LOD ^b ($\mu\text{g L}^{-1}$)	0.4	0.05
R.S.D (%)	2.5	1.9
Regression equation,	$5.4 \times 10^{-3} C$	$4.1 \times 10^{-2} C$
C ($\mu\text{g L}^{-1}$)	+0.003	+0.010
Correlation coefficient (r)	0.9969	0.9991
Linear range ^c ($\mu\text{g L}^{-1}$)	0.4 – 185.0	0.05 – 50.0

^aThe ratio of the concentration of analyte without the application of CPE technique to that after the CPE, giving the same analytical response. ^bLimit of detection defined as three times the signal-to-noise ratio. ^cFor surfactant concentration: 0.1% (w/v)

Calibration, Precision and Detection Limits. Calibration graphs were obtained by preconcentration of 60 mL of sample in the presence of 0.1% Triton X-114, under the optimum experimental conditions. Table 1 gives the parameters of the calibration graphs, the relative standard deviations obtained for ten samples subjected to the complete procedure and the detection limits. The preconcentration factors calculated as the ratio of the concentration of the analyte after preconcentration to that before preconcentration which give the same absorbance peak area were 72 and 85 for Pb and Cu, respectively. However, the preconcentration factors reported by other 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 two metals and therefore it had to be increased, to allow multiple runs for the same samples. The limits of detection were satisfactory, although further improvement is feasible, either by preconcentrating larger amounts of sample solution, using

Table 2. Effect of Foreign Ions on the Preconcentration and Determination of Pb (50 ng mL^{-1}) and Cu (50 ng mL^{-1})

Ions	Concentration / mg L^{-1}	Recovery, %	
		Cd	Cu
Na^+	30×10^3	99.3	101.2
K^+	30×10^3	100.3	99.1
Ca^{2+}	100	98.2	100.6
Mg^{2+}	50	102.1	100.1
Al^{3+}	2	101.5	101.5
Ag^+	2	100.8	97.9
Co^{2+}	2	101.3	98.9
Ni^{2+}	10	101.2	97.8
Fe^{3+}	3	99.8	101.4
Hg^{2+}	2	103.9	100.5
Zn^{2+}	3	102.4	99.5
Mn^{2+}	5	102.3	99.6
Cd^{2+}	5	99.6	102.5
Cr^{3+}	1	98.5	99.3
Cr^{6+}	1	102.5	101.0

Table 3. Determination of Pb and Cu in Water Samples

Sample	Added/ $\mu\text{g L}^{-1}$		Found ^a / $\mu\text{g L}^{-1}$		Recovery, %	
	Pb	Cu	Pb	Cu	Pb	Cu
Tap water	–	–	4.4	15.2	–	–
	4	4	8.3	19.1	98.8	99.4
	10	10	14.4	25.6	100.0	101.6
River water	–	–	5.4	20.6	–	–
	4	4	9.5	24.7	100.0	100.4
	10	10	15.8	30.5	102.6	99.7

Sample volume 60 mL. ^aMean of three determinations.

higher concentrations of both surfactant and chelating agent, or by diluting the surfactant-rich phase in a smaller volume of methanolic solution. In the later 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 both species in a single sample. In this case, preconcentration of only 60 mL of samples in the presence of 0.1% Triton X-114 permitted the detection of 0.4 and 0.05 $\mu\text{g L}^{-1}$ for Pb and Cu, respectively. The precision of this method was established by repeatedly ($n = 10$) using 10.0 $\mu\text{g L}^{-1}$ solutions of Pb and Cu. The relative standard deviations were 2.5 and 1.9 for Pb and Cu respectively.

Interferences Effects. In view of the high selectivity provided by flame atomic absorption spectrometry, the only interferences studied were those related to the preconcentration step. The results shown in Table 2, show that the Pb and Cu recoveries are almost quantitative in the presence of interfering cations.

Preconcentration and Determination of Pb and Cu in Water Samples. To test the reliability of the proposed method for the assay of the two metal ions, it was applied to an analysis of tap water and river water. Water samples were filtered using a 0.45- μm pore size membrane filter to remove suspended particulate matter.

As shown in Table 3, the proposed method was applied successfully to the preconcentration of trace amounts of Pb and Cu in tap water, river water, and spiked water samples.

Conclusion

We have proposed the use of cloud-point extraction as an alternative method for the preconcentration of Pb and Cu before determination by FAAS. The surfactant-rich phase can be introduced into the nebulizer of a flame atomic absorption spectrometry after dilution with acidified methanol. The lowest levels of Pb and Cu determination by this method are 0.4 and 0.05 $\mu\text{g L}^{-1}$, and the relative standard deviations

are 2.5 and 1.9 for Pb and Cu respectively. The method allows the determination of Pb and Cu at ppb levels in water samples by FAAS which is available in most laboratories. The proposed method is simple, sensitive, inexpensive 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.

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