Simultaneous Cloud-Point Extraction of Nine Cations from Water Samples and Their Determination by Flame Atomic Absorption Spectrometry

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The cloud-point methodology was successfully employed for the preconcentration of heavy metal cations at trace levels from aqueous samples prior to flame atomic absorption spectrometry (FAAS). Cations were taken into a complex with 8-quinolinol in an aqueous non-ionic surfactant, Triton X-114, medium and concentrated in the surfactant rich phase by bringing the solution to the cloudpoint temperature. The preconcentration of only 100 mL of the solution with 1% Triton X-114 and 10^{-3} M 8-quinolinol at pH 7.0 gave a preconcentration factor higher than 100 for most cations. Under these conditions, the detection limits of the cloud-point extraction-FAAS system were 0.8 - 15 µg/L.

(Received March 18, 2005; Accepted November 7, 2005)

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 applications. However, the determination of trace metal ions in natural water samples is difficult due to various factors, particularly their low concentration and matrix effects. Preconcentration and separation can solve these problems and lead to a higher confidence level and an easy determination of trace elements by less sensitive, but more accessible instrumentation, such as flame atomic absorption spectrometry (FAAAS). There are many methods of preconcentration and separation, such as liquid-liquid extraction (LLE), ion-exchange techniques, coprecipitation, sorption on the various adsorbents, such as activated carbon, Amberlite XAD resins, and other sorbent.

Cloud-point extraction (CPE) is related to the conventional LLE, and is used in micellar liquid chromatography (MLC). The first applications of phase separation based on the cloud-point phenomenon refer to the extraction of metal ions forming complexes that are sparingly soluble in water. The efficiency of the process depends on the hydrophobicity of the ligand and of the complex formed, on the apparent equilibrium constants in the micellar medium, and on the formation kinetics of the complex and on the transference between the phases. This type of extraction by the cloud-point method was initially described by Watanabe and coworkers for the preconcentration of Zn(II) using 1-(2-pyridylazo)naphthol (PAN) as a ligand and PONPE 7.5 as an extractant. Later, this methodology was also applied to the determination of different metal ions in different types of samples. Like for all other established LLE methods, the metal ion is required to be in the uncharged chelated form prior to its extraction to the organic phase. The phase separation phenomenon has also been used for the extraction and preconcentration of metal ions after the formation of sparingly water-soluble complexes. U, Er, and Gd were determined by spectrophotometry by room temperature phosphorescence; Cu, Cd, Ni and Zn, Ag and Au, by FAAS after CPE using complexing agents. Gold and lead were extracted efficiently without a complexing agent, using a non-ionic surfactant, such as poly oxyethylene nonyl phenyl ether (PONPE 7.5). Gold in the aqueous phase was determined by ICP-MS and in the surfactant phase by a calculation based on mass balances. Lead in the surfactant-rich phase was determined by FAAS after diluting with ethanol. Recently, the determination of trace elements by X-ray fluorescence spectrometry and ultrasonic nebulization ICP-MS using phase separation with a surfactant have been reported. Sanz-Medel et al. reviewed the use of surfactant-based assemblies in analytical atomic spectrometry. Also, concentration by CPE has been established for a number of trace organic pollutants from an aqueous phase.

Based on the present work we report on the results obtained in a study of the simultaneous cloud-point preconcentration of Cu, Mn, Ni, Cd, Fe, Co, Zn, Cr and Pb after the formation of a complex with 8-quinolinol, and later analysis by flame atomic absorption spectrometry using octyl phenoxyl poly ethoxy ethanol (Triton X-114) as a surfactant. The proposed method was also applied to the determination of the studied cations in water samples.

Experimental

Apparatus

A Shimadzu atomic absorption spectrophotometer (Model AA-670G) was used for the determination of metal ions in solutions. The operating condition of the AAS instrument (previously standardized) for the determination of metals was used. A WTW pH-meter (Multilab 504, Germany) was used for pH adjustment.

Reagents and solutions

The non-ionic surfactant Triton X-114 (cloud point 25°C at 5% concentration) was obtained from Sigma and was used without
further purification. Individual stock solutions of Cu²⁺, Mn²⁺, Ni²⁺, Cd²⁺, Fe³⁺, Co²⁺, Zn²⁺, Cr³⁺ and Pb²⁺ at a concentration of 1000 mg/L were prepared by dissolving pure metals or suitable salts in nitric acid solution. Working standard solutions were obtained by appropriate dilution of the stock solutions. For adsorption studies, solutions having Cu²⁺ 5, Cr³⁺ 10, Mn²⁺ 3, Cd²⁺ 0.5, Ni²⁺ 10, Pb²⁺ 10, Zn²⁺ 0.5, Fe³⁺ 5 and Co²⁺ 5 mg/L were prepared directly from their standard solutions (1000 mg/L). Other compounds, such as HNO₃, methanol and 8-quinolinol, were supplied from E. Merck (Darmstadt, Germany).

**Procedure**

For the CPE, an aliquot of the solution containing the analyte, Triton X-114 and 8-quinolinol at a suitable pH was kept for 15 min in a thermostatic bath maintained at 65°C. Since the surfactant density was 1.37 g/mL, therefore, the surfactant-rich phase could settle through the aqueous phase. Centrifuging at 3000 rpm for 10 min accelerated the phase separation. Upon cooling in an ice-bath, the surfactant-rich phase became viscous, and was retained at the bottom of the tube. The aqueous phases could be readily discarded simply by inverting the tube. Later, in order to decrease the viscosity and to facilitate sample handling prior to the FAAS assay, an acidified methanol solution containing 1 M HNO₃ was added to the surfactant-rich phase. A 5 ml volume of the final solution was introduced into the nebulizer of the spectrometer via a manual sample injector that was connected to the nebulizer by the sample aspiration tubing.

**Results and Discussion**

When a micellar solution of a non-ionic surfactant was heated above the cloud-point temperature, two phases were formed. Above that temperature, the system, initially in an isotropic phase, separated into two isotropic phases, one of them surfactant-rich and the other aqueous, containing a surfactant concentration close to the CMC at that temperature. The phenomenon was reversible and, upon cooling, a single phase was obtained again. The mechanism by which separation occurred is poorly understood. Some authors have proposed that it would be due to an increase in the micellar aggregation number (an increase in micelle size) when temperature is increased. Others have suggested that the phase-separation mechanism would be caused by a change in micellar interactions, which are repulsive at low temperatures, but predominantly attractive at high temperatures. The fact that the presence of salts favors phase separation, when ionic surfactants are used, has been interpreted as being due to the shielding of the repulsive electrostatic effects. Other authors have explained the cloud-point phenomenon based on the dehydration process that occurs in the external layer of the micelles of non-ionic surfactants when the temperature is increased. The dielectric constant of water decreases upon increasing the temperature, rendering it a poorer solvent for the hydrophilic portion of the surfactant molecule. The investigation presented here attempted to elucidate some of the factors affecting extractions by the cloud-point methodology. For this purpose, the extraction of several heavy metal cations from aqueous solutions using the non-ionic surfactant Triton X-114 was studied.

**Selection of surfactant and ligand**

In this study a non-ionic surfactant, octyl phenoxy poly ethoxy ethanol (Triton X-114), was chosen for the formation of the surfactant-rich phase due to its excellent physicochemical characteristics: low CP temperature, high density of a surfactant-rich phase, which facilitates phase separation by centrifugation, commercial availability, relatively low price, and low toxicity. The cloud point of the selected surfactant in the concentrations range 0.1, 5 and 10% is 23.6, 25 and 30°C, respectively. On the other hand, nine cations were selected as analytes, and therefore those ligands must be selected that react with the studied cations and form hydrophobic chelates to be extracted in a surfactant-rich phase. 8-Quinolinol is a relatively hydrophobic ligand which reacts with all selected cations. It is also a very stable, and fairly selective complexing reagent.

**Effect of pH**

The pH was proved to be a critical parameter for the cloud-point extraction of all studied cations. For optimizing the pH, the CPE of Cu²⁺, Mn²⁺, Ni²⁺, Cd²⁺, Fe³⁺, Co³⁺, Zn²⁺, Cr³⁺ and Pb²⁺ was performed in different buffered solutions (V = 100 mL). The separation of metal ions by the CPE method involves the prior formation of a complex with sufficient hydrophobicity to be extracted into the small volume of the surfactant-rich phase, thus obtaining the desired preconcentration. 8-Quinolinol was selected as a complexing agent; produced complexes of the studied cations were extracted. The extraction yield depends on the pH at which complex formation occurs. Figure 1 shows the effect of the pH on the extraction of cations. The extraction yield reaches the highest amounts at pH 7 for most cations. At lower pH values, the formation of complexes is not quantitative, and at higher pH values, the hydrolysis of cations occurs.

**Salting-out study**

In the case of most non-ionic surfactants, the presence of salts may facilitate phase separation, since it increases the density of the aqueous phase. Nevertheless, it has been observed that the volume of the surfactant-rich phase does not depend on the ionic strength. In order to evaluate the effect of the salt concentration on the extraction recovery of cations, sodium chloride was used as a salting-out agent. The obtained data indicate that the extraction process was improved at a concentration of 0.1 M relative to sodium chloride compared with other concentrations in the cases of Fe³⁺, Ni²⁺, Cr³⁺ and Zn²⁺. At concentrations of 1 and 2 M the extraction was decreased (except for Mn²⁺) owing to complexation or precipitation (especially Pb²⁺) of some cations with chloride ions; hence, a salting-in effect was observed in these cases.

![Fig. 1 Influence of the pH on the extraction yield of cations by cloud-point extraction. Sample volume, 100 mL; surfactant, Triton X-100 1%; ligand, 8-quinolinol 10⁻³ M; dilution solvent, 1 M HNO₃; equilibration temperature, 65°C; equilibration time, 15 min.](image)
HNO₃, the concentration of the analytes decreased. On the other hand, by this dilution the viscosity of the solution also decreased, and thereby the yield of the transport of the analytes to the atomizer unit (flame) increased. It is mentioned that due to using a flame atomic absorption spectrophotometer as a detection system and the simultaneous extraction of nine cations, we needed at least a 3 mL solution; therefore, it was selected as a dilution solution volume in other studies.

**Sample sizes**

The phase ratio (Vₛ/Vₚ) is the ratio between the volume of an aqueous solution to be preconcentrated and the volume of the surfactant-rich phase. This ratio increases with a decrease in the concentration of the surfactant. However, since the volume of the surfactant-rich phase must be manageable, a compromise must be reached so that the surfactant concentration will allow a high phase ratio and a manageable surfactant-rich phase. The phases ratio is an important factor, which has an effect on the extraction recovery of cations. A low phases ratio improves the recovery of extraction, but decreases the preconcentration factor. However, to determine the optimum amount of the phase ratio, different volumes of the sample and a constant volume of the surfactant solution were chosen, and experiments performed. In this study the volume of the surfactant-rich phase obtained after separation was about 0.2 mL, and the initial solution was 100 mL. The obtained results show that with increasing sample volume the extracted cations decreased. By increasing the sample size from 25 mL to 100 mL (phase ratio from 125 to 500), less than a 50% decrease in the recovery (relative to 25 mL) was observed in the case of most cations.

**Preconcentration factor**

The preconcentration factor Fₛ is defined by the expression Fₛ = Cₛ/Cᵢₚ, where Cₛ is the concentration of the analyte in the surfactant-rich phase, after phase separation, and Cᵢₚ is the concentration of the analyte in the initial solution, before the preconcentration step. Among the other factors, this depends on the phase relationship, on the distribution constant of the analyte between the phases, and on the surfactant concentration used. The data in Table 1 represent a high preconcentration factor for most cations.

**Selection of a dilution solution for the surfactant-rich phase**

Metal-ions complexes extracted into a surfactant-rich phase can be released by using various kinds of diluents. In this work, pure methanol and an aqueous solution of 1 M HNO₃ were used for dilution of the surfactant phase. The obtained results showed that the nitric acid had a relative preference over methanol. The results indicate that increasing the volume of the dilution solution from 3 mL to 5 mL had no significant effect on the absorbance recorded by FAAS. However, at a higher volume (10 mL) a reasonable decrease in the absorbance was observed. By diluting the surfactant-rich phase with 1 M HNO₃, the concentration of the analytes decreased. On the other hand, by this dilution the viscosity of the solution also decreased, and thereby the yield of the transport of the analytes to the atomizer unit (flame) increased. It is mentioned that due to using a flame atomic absorption spectrophotometer as a detection system and the simultaneous extraction of nine cations, we needed at least a 3 mL solution; therefore, it was selected as a dilution solution volume in other studies.

**Effects of the equilibration temperature and time**

When working with a given surfactant concentration, the volume of the surfactant-rich phase may decrease when the cloud-point temperature and the phase equilibrium time are increased. At 70˚C the surfactant-rich phase volume of some surfactants is about half of what it is at room temperature. For Triton X-114, an increase in the cloud-point temperature also leads to a slight decrease in the volumes of the surfactant-rich phase. This can be interpreted in terms of the fact that as the temperature increases, the hydrogen bonds are disrupted and dehydration occurs. As the temperature increases, the amount of water in a surfactant-rich phase decreases, and hence the volume of that phase decreases. It is desirable to employ the shortest equilibration time and the lowest possible equilibration temperature, as a compromise between completion of extraction and efficient separation of the phases. The studies carried out indicate that in order to obtain a more favorable preconcentration factor, CPE should be performed at a temperature higher than the cloud-point temperature, and the phases at that temperature should be maintained for a given time. It was found that 65˚C is adequate for these analyses. The dependence of the extraction efficiency upon the equilibration temperature and time was studied for a time span of 5 to 40 min. An equilibration time of 15 min was chosen to be optimal to achieve higher extraction recoveries.

**Effect of the Triton X-114 concentration**

A successful CPE would be that which maximizes the extraction efficiency through minimizing the phase volume ratio, and thus maximizing its concentrating factor. The variation in the extraction efficiency within the Triton X-114 range of 0.5 - 5% (w/v) was examined (Fig. 2). The maximum extraction was observed when the Triton X-114 concentration was 0.5, or 1% in the cases of most cations. With an increase of the Triton X-114 concentration to above 1%, the signals decreased because of the increment in the overall analyte volumes and the viscosity of the surfactant phase. The optimum surfactant concentration used for most cations was the same, 1% Triton X-114, in order to achieve the optimal analytical signal in conjunction with the highest possible extraction efficiency.

**Analytical performance**

To determine the repeatability of the method, five repeated
periments were performed with 50 mL of a sample solution under the optimum conditions. As can be seen from Table 2, the recovery of all cations (except Pb\textsuperscript{2+}) was higher than 55\%, and in the cases of Zn\textsuperscript{2+} and Cr\textsuperscript{3+} it was nearly 100\%. It is mentioned that with a high phase ratio of 250, a recovery of 55\% can be considered acceptable. The precision of the method is good, and the relative standard deviation (RSD\%) is less than 7\%, except for Pb\textsuperscript{2+}.

The linear calibration ranges for measurements under the optimum conditions were relatively extensive (2.5 - 4500 \mu g/L). The correlation coefficient of the calibration curve equations was higher than 0.990 for all elements, which indicates that a good linear regression was established between the absorbances and the concentrations. To determine the detection limits, 50 mL of a blank solution was used. The detection limits based on three-times the standard deviation of the blank solution were found to be 0.8 - 15 \mu g/L for different cations. By applying the preconcentration factors (Table 1), detection limits of 25, 75, 105, 33, 167, 16, 4.5, 130, 35 and 3.7 ng/L were obtained for Cu\textsuperscript{2+}, Cr\textsuperscript{3+}, Fe\textsuperscript{3+}, Mn\textsuperscript{2+}, Pb\textsuperscript{2+}, Cd\textsuperscript{2+}, Co\textsuperscript{2+}, Ni\textsuperscript{2+} and Zn\textsuperscript{2+}, respectively.

Application to water samples

The method was applied to distilled water, Urmia tap water, wastewater and Urmia Lake water (brine having total dissolved solids, TDS, about 280 g/L). Samples (100 mL of each) were preconcentrated with 1% Triton X-114 and 10\textsuperscript{3} M 8-quinolinol by following the proposed method. Table 3 gives the slopes of the calibration lines using different matrices. The slope of the calibration line obtained for distilled water approximates those obtained by the standard addition to other samples, indicating a lack of the matrix effect. The concentrations of some cations in the studied sample were higher than the limit of detection of the method.

Conclusion

In this study Triton X-114 was chosen for the formation of the surfactant-rich phase due to its excellent physicochemical characteristics: low CP temperature, high density of the surfactant-rich phase, which facilitates phase separation by centrifugation, commercial availability, relatively low price, and low toxicity. 8-Quinolinol is a very stable, and fairly selective complexing reagent. After CPE, the diluted surfactant-rich phase with a 1 M HNO\textsubscript{3} solution was introduced into the nebulizer of a flame atomic absorption spectrometer by manual injector. The detection limits were obtained in the range of 0.8 - 15 \mu g/L and improved by an order of magnitude of one or two

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with such a simple CP preconcentration procedure.

References