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Cloud point extraction-preconcentration and flame atomic absorption spectrometric determination of low levels of zinc in water and blood serum samples

Research Article

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Abstract: A simple, sensitive and selective flotation method is described for the preconcentration and atomic absorption spectrometric determination of zinc ion in water and blood samples. At a solution pH of 5.2, 4-(2-pyridylazo-resorcinol) and Triton X-114 were used as hydrophobic ligand and non-ionic surfactant, respectively. The chemical variables affecting the preconcentration process were optimized. Under the optimized experimental conditions, the selective preconcentration and determination of as low zinc concentration as 6.5 μg L^{-1} can be made. The proposed method was successfully applied to the preconcentration and low-level determination of zinc in different water and blood serum samples.

Keywords: *Cloud point extraction • Preconcentration • AAS • PAR • Serum*

1. Introduction

Zinc is one of the less common elements; it has been estimated to make up 0.0005-0.02% of the earth's crust. It is an essential element in the growth of many kinds of organisms including both plants and animals. Zinc is present in all body tissues and fluids [1], and is an essential component of a large number (>300) of enzymes participating in the synthesis and degradation of carbohydrates, lipids, proteins, and nucleic acids as well as in the metabolism of other micronutrients. Zinc is a cofactor of several enzyme systems, constitutes the active centre of carbonic anhydrase, .and is contained in the insulin. Zinc stabilizes the molecular structure of cellular components and membranes and therefore contributes to the maintenance of cell and organ integrity. Furthermore, zinc has an essential role in polynucleotide transcription and thus in the process of genetic expression. Its involvement in such fundamental activities probably accounts for the essentiality of zinc for all life forms. Zinc is present in most foods, especially, those high in protein [2]. Zinc plays a central role in the immune system, affecting a number of aspects of cellular and humoral immunity [3]. Zinc deficiency in the human diet has been found to retard growth and maturity and to produce anemia.

On the other hand, zinc is a human-made environmental pollutant. The concentration of zinc

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in unpolluted natural water is low, and the sensitivity of analytical techniques is often insufficient for its determination. Several methods have been developed for the separation and determination of zinc. Traditionally, organic solvents, such as benzene [4] or chloroform [5-8] have been used for extraction of zinc, but these solvents are often classified as having carcinogenic toxicity and as environmental pollutants which are not desirable traits.

In general, colorimetry has been used as the conventional method in many fields. Almost none of the color reagents are specific for the determination of serum zinc, although various systems have been developed to remove interfering metals (especially iron and copper) [9-11]. In addition, although some of these methods [9,11] are very accurate there are risks associated with them for both the analyst and the environment.

Determination of the serum or plasma zinc concentration by AAS is an effective method for assessing the nutritional status of zinc [12]. However, in this method, a relatively large sample amount is needed in comparison with use of techniques coupled with AAS.

Aqueous solutions of many non-ionic surfactant micellar systems become turbid over a narrow temperature range when the experimental conditions (*i.e.,* temperature or pressure, addition of salt or other additive, *etc.*) have been changed. This temperature range is termed cloud point temperature. Above the cloud point, the aqueous surfactant micellar solution separates into a concentrated phase containing most of the surfactant (termed surfactant-rich phase) and a dilute aqueous phase containing low concentration of surfactant corresponding to critical micellar concentration (cmc). Any component(s) originally present that binds to the micellar aggregate in solution can thus be extracted from the original solution and concentrated in the small volume element of the surfactant-rich phase (usually less than 0.5 mL). In contrast to traditional liquid-liquid extraction (LLE), cloud-point extraction (CPE) has little or no pollution effect at all. Another advantage in the CPE method is that a concentration effect is expected as a function of the small volume of the separated surfactant phase [13].

Thus, there is a growing tendency to use micelles in trace analysis of organic [14-17] and inorganic materials [18-31]. However, despite the critical importance of Zn^{2+} monitoring in many industrial, environmental, clinical and pharmaceutical samples, only a few cases of use of CPE for the separation and preconcentration of zinc has been reported in the literature [32-35].

In this work, we describe the results obtained in a study of the cloud-point preconcentration of zinc after the formation of a complex with 4-(2-pyridylazo)-resorcinol (PAR) followed by analysis by flame atomic absorption spectrometry, using Triton X-114 as a suitable surfactant. Although PAR is not a very lipophilic reagent, it extracts zinc completely from aqueous solution into the concentrated micellar medium, most possibly due to the lipophilicity of the complex formed.

2. Experimental

2.1. Apparatus

A Shimadzu AA-670 atomic absorption spectrometer equipped with deuterium background correction and zinc hollow-cathode lamp as the radiation source was used for absorbance measurements at the wavelength of 213.9 nm. A 10 cm long slot-burner head and an air-acetylene flame were used in the analyses. The instrumental parameters were adjusted according to the manufacturer's recommendations. A Hettich centrifuge was used to accelerate the phase separation process.

Voltammetric measurements were made with a Metrohm 694VA Stand coupled with a Metrohm 693 VA processor. Voltammetric experiments were carried out in a three-electrode arrangement with an Ag/AgCl, 3 M KCl reference electrode, a platinum wire counter electrode, and a multi-mode mercury drop working electrode. Solutions were deoxygenated with high-purity nitrogen for 5 min prior to each experiment and the experiment was performed under a nitrogen atmosphere.

A Metrohm 692 pH meter equipped with a combined glass-saturated calomel electrode was used for pH measurements.

2.2. Reagents and solutions

The non-ionic surfactants, Triton X-114 and Triton X-100, were obtained from Fluka and used without further purification. Standard stock solutions of Zn^{2+} ion at a concentration of 1000 mg L^{-1} were prepared by dissolving proper amounts of extra pure $ZnSO_4$ (Fluka) in a 250-mL volumetric flask and diluting to the mark with deionized distilled water. Working standard solutions were prepared by appropriate dilution of the stock standard solution. A 2.35×10^{-3} M solution of PAR (Merck) was prepared by dissolving appropriate amounts of the reagent in deionized distilled water. A stock buffer solution of pH 5.2, (0.5 M), was prepared using of sodium hydroxide and acetic acid. All solutions were prepared in doubly distilled deionized water. The vessels used for trace analysis were kept in 10% nitric acid for at least 24 hours and subsequently washed several times with doubly distilled deionized water before use.

2.3. Pretreatment of real samples

Analysis of water samples for determination of analyte contents was performed as following: about 500 mL of sample was passed through a sintered glass funnel and 1 mL concentrated HNO_3 was added for elimination and decomposition of organic matter. The water samples were stored in polyethylene bottles. Before the analysis, the pH's of the samples were adjusted to 5.2. Then procedure outlined in general procedure section was applied.

A 5-mL portion of the clear supernatant serum obtained from mixture of 10 samples of males or females within the ages of 20-40 years was pipetted off and treated with 5.0 mL of 1.2 M trichloroacetic acid. The mixture was centrifuged at 3000 rpm, and the deproteinized supernatant was placed in a 50-mL beaker, and the resulting solution was neutralized with 2.0 M NaOH until a pH value of ca. 5.2 was reached. Aliquots (8-mL) of the samples were then analyzed by the proposed method.

2.4. General procedure

Cloud point extraction of 15 mL of the experimental solution containing 0.055 mg L^{-1} of Zn^{2+}, Triton X-114 (0.1% w/v) and PAR (4.0×10^{-4} M), buffered at pH 5.2 were kept for 20 min in a thermostated water bath at 60°C. Separation of the two phases was accomplished by centrifugation for 10 min at 3500 rpm. Upon cooling to 0°C (15 min), the surfactant-rich phase became viscous. The aqueous phase could then be separated completely by a Pasteur pipette. In order to decrease the viscosity and facilitate sample handling, 0.5 mL of a solution of methanol containing 1 M HNO_3 was then added to the surfactant-rich phase. The surfactant-rich phase was finally introduced into the flame of AAS and the absorbance measurements were performed at the previously designated wavelength.

3. Results and discussion

PAR is well known as a metallochromic indicator and a spectrophotometric reagent for the determination of a variety of metal ions. The reagent usually behaves as a tridentate ligand to form a colored chelate with cations, especially with Zn^{2+} ion [36]. Although PAR is not a very lipophilic reagent, our preliminary CPE tests revealed that it forms a stable complex of sufficient hydrophobicity to be quantitatively extracted into a small volume of Triton X-114 surfactant-rich phase, thus reaching the desired preconcentration level. Thus, we decided to optimize the experimental conditions for the selective CPE-AAS determination of Zn^{2+} ion using the PAR-Triton X-114 system.

3.1. Effect of pH

Cloud-point extraction of zinc in the PAR-Triton X-114 system was performed in different pH values adjusted by adding appropriate amounts of HCl or NaOH to the test solutions. As is shown in Fig. 1, the efficiency of extraction of zinc complex to the concentrated micellar phase is strongly pH-dependent. A maximum preconcentration of zinc was achieved at pH 5.2 which was selected as the optimum pH in further studies.

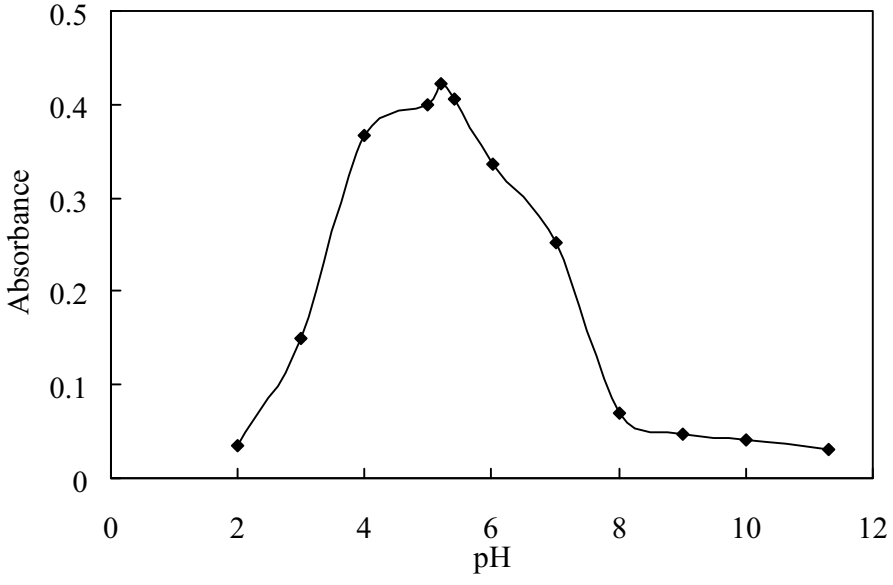

Figure 1. Effect of pH of test solution on the CPE of Zinc (conditions: Zn^{2+}, 0.055 mg L^{-1}; PAR, 3.9×10^{-4} M; Triton X-114, 0.16%)

As is obvious from Fig. 1, within the pH range of 2.0-5.0, the CPE efficiency of Zn^{2+} is sharply decreased, most probably due to the protonation of PAR in acidic media. On the other hand, the possible hydrolysis of the cation at pH > 6.5 will also result in diminished extraction of Zn^{2+} in the surfactant-rich phase.

The pH of the solutions was buffered at pH 5.2 by using acetic acid and sodium hydroxide solutions. The influence of concentration of acetate buffer of pH 5.2 on CPE efficiency was examined. The results showed that above 0.05 M concentration of buffer solution, no variation took place in the extraction efficiency. Thus, a 0.05 M concentration of buffer solution was used in all subsequent experiments.

3.2. Effect of PAR concentration

Fig. 2 shows the effect of varying concentrations of PAR as a suitable complexing agent on the CPE efficiency of zinc. As is obvious, complete CPE of the cation was achieved at PAR concentrations greater than 2.0×10^{-4} M. Thus, for subsequent work, a PAR concentration of 4.0×10^{-4} M was selected. It is interesting to note that the presence of excess amounts of the ligand revealed no adverse effect on the CPE process. This is an advantageous point as the procedure could be applied to the analysis of Zn^{2+} in real samples.

3.3. Effect of Triton X-114 concentration

In this work we examined both Triton X-100 and Triton X-114 as extracting surfactants. Triton X-100 had a higher cloud-point temperature and, consequently, separating the concentrated phase was more difficult. On the other hand, Triton X-114 with a lower cloud point temperature and easier separation of the preconcentrated phase was found to be more convenient for the extraction of zinc-PAR complex. The selection of Triton X-114 is also beneficial because of its commercial availability in a highly purified homogenous form, low toxilogical properties and cost.

In the next step, we examined the effect of the concentration of Triton X-114 on the CPE efficiency. In the CPE processes, it is desirable to maximize the extraction efficiency *via* diminishing the phase volume ratio to increase the process concentration factor. As it is seen in Fig. 3, the variation in extraction efficiency within the Triton X-114 range of 0.02-0.45% (w/v) was examined. Quantitative extraction was observed when the surfactant concentration was >0.1% (w/v). A surfactant concentration of 0.16% (w/v) was selected for further studies.

3.4. Effects of equilibrium temperature and time

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. The dependence of extraction efficiency upon equilibration temperature and time above the cloud point in the range of 30–70°C and 5–30 min were thoroughly optimized, respectively. It was found that holding the sample solutions for 15 min at 60°C was quite satisfactory to achieve small volumes of the surfactant-rich phase, quantitative extraction and experimental convenience.

3.5. Effects of ionic strength

It is known that ionic strength of the solution has a strong effect on cloud point temperature and efficiency

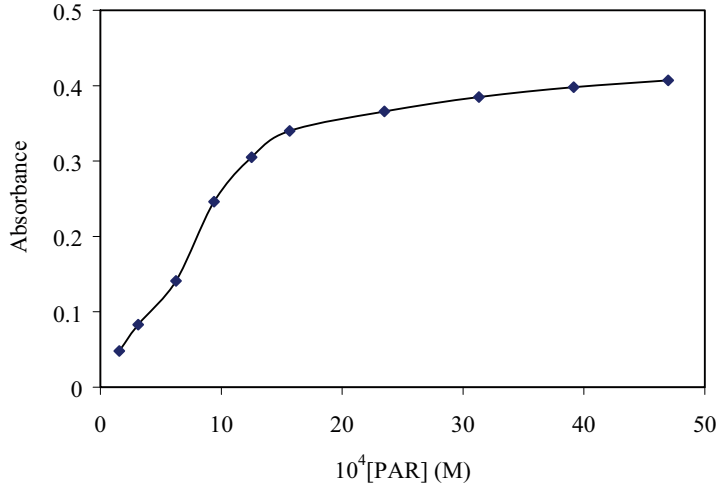

Figure 2. Effect of PAR on the CPE of Zinc (conditions: Zn^{2+}, 0.055 mg L^{-1}; Triton X-114, 0.16%, pH, 5.2)

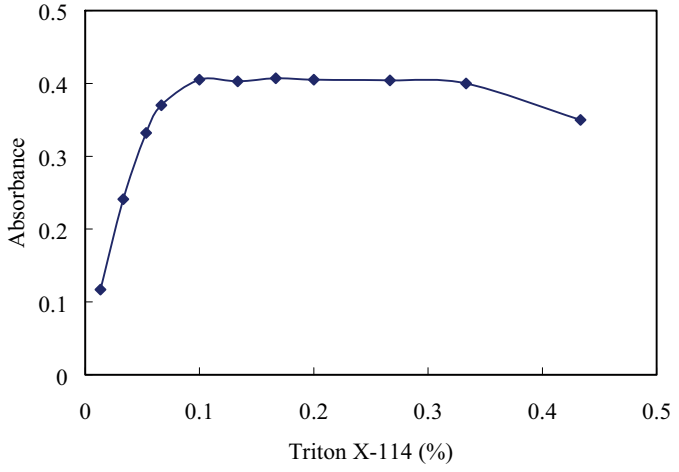

Figure 3. Effect of Triton X-114 concentration on the CPE of Zinc (conditions: Zn^{2+}, 0.055 mg L^{-1}; PAR, 3.9×10^{-4} M; pH, 5.2)

of separation. Sodium acetate in buffer solution was investigated as the electrolyte in the concentration range from 0.01 to 0.2 mol L^{-1} and the highest sensitivity was obtained at 0.05 mol L^{-1}. The signal decreased slowly with increasing buffer concentrations. This effect might be explained by the additional surface charge when the buffer concentration is very high, thus changing the micelle and cloud formation process. In this way, the ionic strength parameter was fixed by buffering the solution with a high concentration of sodium acetate (*i.e.,* 0.05 M).

3.6. Effects of centrifugation rate and time

It is necessary to preconcentrate trace amount of Zn^{2+} ion with high efficiency within a short time. Therefore, CPE on a set of experiments using 15 mL sample to determine optimum conditions was carried out by heating to 60°C and centrifuging at various rates and times with further cooling in 4 min intervals. It was found that centrifugation at 3500 rpm for 10 min separates the two phases completely. The enrichment phase did not separate completely within shorter rates and times centrifuged.

3.7. Calibration, precision and detection limits

A calibration graph was obtained by pre-concentrating 15 mL sample of 0.16% Triton X-114 in a medium buffered at pH 5.2 (0.05 M). A volume of 0.5 mL of the final solution was introduced into the nebulizer of the spectrometer. A linear relationship between the absorbance measured and the concentration of Zn^{2+} prepared for the calibration solution was obtained. Table 1 gives the calibration parameters for the proposed CPE method including the linear ranges, the relative standard deviation obtained for 10 analyte samples subjected to the complete procedure and the limit of detection. A calibration graph was obtained without pre-concentration in order to calculate the enhancement factor. Table 1 also includes the calibration parameters obtained with standard solutions of zinc not subjected to the preconcentration step. The enhancement factor calculated as the ratio of the absorbance of preconcentrated sample to that obtained without preconcentration was 18. As is obvious from Table 1, zinc concentrations as low as 0.0065 mg L^{-1} in solution can be detected by the proposed CPE method.

Table 1. Analytical characteristics of the method.

Conditions	Concentration range (mg L^{-1})	Slope	Intercept	r^2	RSD (%)[a]	LOD (mg L^{-1})[b]	Volume ratio
Without pre-concentration[c]	0.40-1.60	0.238	0.003	0.998	2.7(0.8)	0.2	0.033
With pre-concentration (0.16% Triton X-114)[d]	0.01-0.10	4.20	0.019	0.998	2.5(.05)	0.0065	0.033

[a] Value in parenthesis is the zinc concentration (ppm) for which the RSD was obtained.
[b] Limit of detection, calculated as three times the standard deviation of the blank signal.
[c] Standard solutions of zinc.
[d] Dilution of the surfactant-rich phase with 500 μL of 1 M HNO_3 in methanol.

3.8. Interference study

In the view of high selectivity provided by FAAS, the interferences studied, especially anion and cations, were those related to preconcentration step, *i.e.,* those cations that may react with PAR and anions that may form complexes with zinc and decrease extraction efficiency.

Table 2. Effects of the interferences ions on the recovery of the analyte

Ion	Interference/ analyte amount
Ba^{2+}, Mg^{2+}, Ca^{2+}, Na^{+}, K^{+}, Li^{+}	1000
Ni^{2+}, Cd^{2+}, Pb^{2+}, Cu^{2+}	100
Co^{2+}, Al^{3+}	50
CH_3COO^{-}, Cl^{-}, Br^{-}, I^{-}, $B_4O_7^{2-}$, PO_4^{3-}, SO_4^{2-}	>100

As it is seen in Table 2, study of the possible interferences caused by cationic species was conducted with Ni^{2+}, Pb^{2+}, Cd^{2+}, Cu^{2+}, Co^{2+}, Al^{3+}, Ba^{2+}, Mg^{2+}, Ca^{2+}, Na^{+}, K^{+} and Li^{+} ions under the experimental conditions used in the presence of a fixed concentration of 0.055 mg L^{-1} of zinc. There was no significant interference at a 1:100 ratio of Zn^{2+} to the cations Ni^{2+}, Pb^{2+}, Cd^{2+} and Cu^{2+} and at a ratio of 1:50 Zn^{2+} to the metal cations Co^{2+} and Al^{3+}, the other cations revealed no significant effect on the sensitivity to the 1:1000, Zn^{2+}/cation. Although the complexes between these cationic species and PAR formed, the relatively low pH value of 5.2 and high concentration of the ligand used avoided their interference. With respect to anions, bromide, iodide, sulfate, borate and phosphate were tested and no interference was observed even at ratios of Zn^{2+} to anion ratios greater than 1:100.

The effect of adding EDTA to the test solution was examined, and because of high complexing affinity of this ligand, extraction efficiency was reduced. The addition of ethanol revealed no significant effect on the CPE efficiency to 7% (v/v). The effect of addition of a cationic surfactant such as acetyltrimethylammonium bromide (CTAB) was also tested. It was observed that the presence of CTAB precludes the cloud formation and separation of phases.

3.9. Determination of zinc in real samples

The proposed method was applied to the determination of Zn^{2+} ion in four different water samples including river, sea, tap and mineral drinking water and the results obtained by the proposed CPE method were compared with those obtained from anodic stripping voltammetry (ASV) as a standard method for zinc determination. In Table 3, the results obtained from the two methods were compared and the applicability of the proposed method to the determination of zinc in water samples was confirmed.

This method was also applied to the determination of zinc content of two blood serum samples as mentioned in experimental section. The results obtained are summarized in Table 4. As it is seen, the proposed method resulted in the accurate determination and quantitative recovery of added Zn^{2+} from the blood serum samples.

4. Conclusion

A method for the preconcentration of trace Zn^{2+} ion based on CPE were developed in this paper. The methods

Table 3. Zinc determination different water samples.

Sample	Mean concentration (mg L^{-1}) ± SD (n=3)	
	Proposed method	ASV
Sea-water	0.110 ± 0.011	0.100 ± 0.008
River water	0.046 ± 0.003	0.044 ± 0.003
Mineral drinking water	0.013 ± 0.002	0.013 ± 0.001
Tap water	0.029 ± 0.003	0.027 ± 0.002

Table 4. Analytical results for zinc determination in serum of two healthy blood samples.

Sample	Sex	Age	Mean concentration (mg L^{-1}) ± SD (n=3)		%Recovery
			Added	Found	
1	Male	20-40	-	1.21 ± 0.07	-
			0.38	1.60 ± 0.10	102.6 ±4.2
2	Female	20-40	-	1.09 ± 0.06	-
			0.38	1.46 ± 0.10	97.4 ±4.4

involved the extraction of Zn-PAR chelate in micellar solutions of Triton X-114 followed by the determination of the Zn^{2+} ion by FAAS. The CPE method developed here can be used to preconcentrate Zn^{2+} ion from aqueous samples in only one step which reduces the possibility of contamination. The detection limit obtained is 6.5 μg L^{-1}, thus the using of CPE-FAAS offers the possibility of attaining lower detection limit by FAAS. The method can be advantageously applied to the analysis of environmental and biological samples containing Zn^{2+} ion at trace levels.

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