Determining the Trace Amounts of Zinc by Membrane Filtration-Sensitized Flame Atomic Absorption Spectrometry in Water Samples

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Abstract

The spectrophotometric determination of zinc (Zn^{2+}) in water samples by Flame Atomic Absorption Spectrometry (FAAS) was studied in micellar media of Sodium dodecyl sulfate (SDS), cetyltrimethyl ammonium bromide (CTAB), and polyoxyethylene(10)isooctylphenyl ether (TX100). The effects of the nature and concentration of surfactants on the analytical signal of the Zn^{2+} were investigated and optimized. The limits of detection (LODs) 0.4, 0.2, and 0.3 ppm for Zn^{2+} are SDS, CTAB, and TX100 respectively. The sensitivity and selectivity were largely increased in SDS micellar media. The proposed method was applied to the determination of Zn^{2+} in distilled water samples by using SDS.

Key Words: Zinc (II) ; FAAS; Sodium dodecyl sulfate; Cetyltrimethyl ammonium bromide; Triton-X-100

1. Introduction

Recently, heavy metal toxicity is a growing concern all around the world, because of the adverse affect they pose to the all forms of living organisms in the biosphere. Heavy metal is non-biodegradable in the environment, and can accumulate to toxic concentrations in the bodies of animals and humans. The situation have been further complicated with the rapid population growth and the progress in agriculture and industry (GIGUERE et.al. [1]). Untreated or partly treated industrial effluents containing a large number of heavy metals discharged to the water bodies, nearby lakes and rivers. This can affect in aquatic ecosystem and they bioaccumulated along the food chain. Food chain biomagnification of heavy metals cause adverse health effects in both humans and other living organisms. Furthermore, these metals affect the stability, structure, and biological function of biomolecules (MCCORMICK et.al.[2];). Heavy metals are also known to interfere with hormone biosynthesis, and metabolism (RIDDELL et.al. [3] ; GUPTA et.al.[4]).

Zinc is vital and beneficial for organisms. It is considered to be relatively non-toxic, especially if taken orally. However, *too much* zinc in the body *leads to* dysfunctions that result in impairment of growth and reproduction (INECAR [5]). Common symptoms of zinc's toxicity have been reported as irritability, muscular stiffness, diarrhea, kidney failure, and anemia (FOSMIRE [6]; PLUM et.al [7]).

The World Health Organization (WHO) has recommended 5.0 mg/L as the permissible limit of zinc in drinking-water (WHO [8]). Zinc contamination in water sources can be attributed to wastewater of the industry which utilizes zinc as the processing medium. Water sources may be heavily polluted with zinc due to its increasing amount in the wastewater of industrial plants. Oxides, sulphate, and chloride salts tend to hydrolyze to produce zinc hydroxide and zinc carbonates. Zinc imparts an undesirable taste to water at a concentration of about 4mg/litre (as zinc sulfate) (NEETHU & PUTTAIAH [9]; WHO [10]). Generally, zinc reaches in aquatic

ecosystem by galvanic industries and battery production (Lenntech [11]). Zinc is also used in some fertilizers, therefore leaches into water. Common sources of zinc compounds on roads are car tires containing zinc and motor oil from zinc tanks (TRIVUNAC et.al. [12]). Thus, sensitive, selective and accurate analytical methods are required for the determining the trace amounts of zinc in environmental samples. Several spectral and electrochemical methods have been developed for determination of heavy metal ions (OEHME et.al. [12]; PESAVENTO et.al. [14]; SITKO et.al. [15]; LI et.al. [16]; HUANG et.al. [17]). Flame atomic absorption spectrometry (FAAS) with its relatively low cost and high analytical performance, is the main instrument in the research laboratories for determining a variety of zinc (SHE et.al. [18]; DIMA et.al. [19]; SIRAJ & KITTE [20]; YURCHENKO et.al. [21]. In most cases pretreatment of samples, physical separation and non-universal instrumentation are required. For this reason, membrane separations are being used more and more frequently. Moreover, the separation can be performed at room temperature; the modular membrane surface can be easily adjusted to the wastewater flows and various industrial membranes are now available (JIN et.al. [22]; PELIZZETTI & PRAMAURO [23]; HERNANDEZ et.al. [24]; AIHARA et.al. [25]; SAN ANDRES et.al. [26]; SAN ANDRES & VERA [27] ; WATANABE [28]).

We investigated the effect of surfactants and their concentration (Cs) on the Zn^{2+} via the flame atomic absorption spectrometry method. Three typical surfactants including ionic and non-ionic ones were explored and the optimized Cs for each one was identified.

2. Material and Methods

Reagents and solutions

In this study, analytical reagent grade chemicals were used. Deionized (DI) water was used in all experiments. The 1000 mgL^{-1} standard stock solution was prepared by dissolving appropriate amounts of $Zn(NO_3)_2 \cdot 6H_2O$ (Merck) in DI water. Working solutions were prepared daily by diluting suitable aliquots of standard stock solution with DI water. All standard solutions for FAAS instrument calibration were prepared in mixture of acetone-ethanol (1:1). SDS (Merck), CTAB (Aldrich), and TX100 (Riedel) were used as obtained from sources. To prepare 2% v/v of surfactant stock solutions were dissolved 2mL of concentrated solution in DI water. (Acetate buffer solution (1.0 M, pH 6.0)) was prepared by mixing an appropriate volumes of acetic acid and sodium acetate solution.

Apparatus and procedure

A Philips PU 9285 model flame atomic absorption spectrometer (FAAS) equipped with an air acetylene burner, deuterium background correction and a hollow cathode lamp (HCL) was used for the determination of zinc. Important instrumental parameters were listed as follows: wavelength: 213.9 nm, lamp current: 7 mA, bandpass: 0.5 nm and fuel flow rate: 1.2 $Lmin^{-1}$. All experiments were done in triplicate.

3. Results and discussions

Dependence of concentration readouts on surfactant concentration

The effect of surfactant on the analytical results irrespective of the kind of analyzer is a criticial parameter in micelle-mediated separation processes. Surfactants may bring about changes reaction rates and mechanisms, chemical equilibria and selectivity in reactions within the media (PRAMAURO & PELIZZETTI [29]). -Surfactants increase the absorption of analytes or inhibit the solubility of volatile species Thus; not only favoring the bulk solvent but also improving transport to the atomizer. - There have been many publications related to-(on) the use of surfactants in FAAS *nebulization* efficiencies (PEREZ-BENDITO & RUBIO [30]; FERNANDEZ DE LA

CAMPA et.al.[31]. Consequently, the influence of the surfactant concentration on the amount absorption of Zn^{2+} by FAAS was evaluated in seven different concentrations. The plots of apparent concentration of Zn^{2+} in a concentration of 1.961 ppm *vs*. surfactant concentration were shown in Figs. 1-a , 1-b and 1-c, respectively. Similar plots showing a typical decrease were obtained for the binary systems (Zn^{2+}-SDS, Zn^{2+}-CTAB and Zn^{2+}-TX100).
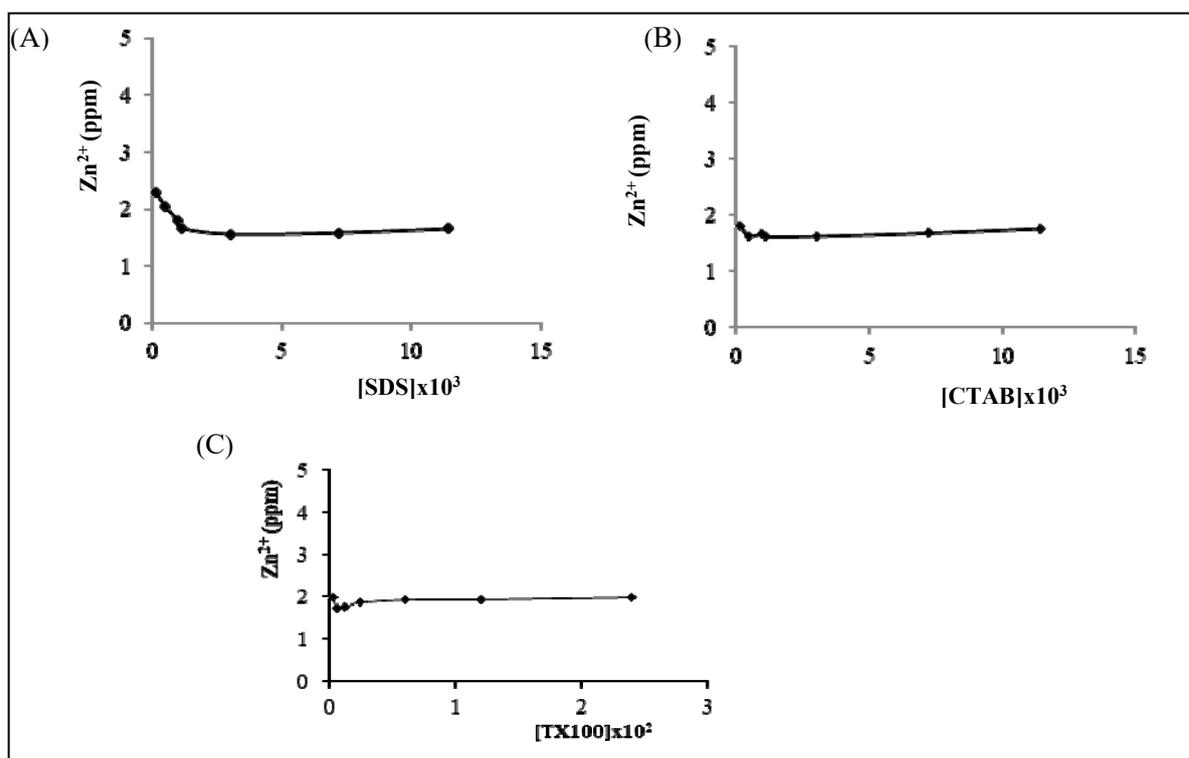

Figure 1. The dependence of the apparent concentration of Zn^{2+} solution in a concentration of 1.961 ppm on surfactant concentration SDS (A), CTAB (B), TX100 (C)

The maximum shifts were determined as 0.378, 0.289 and 0.241 ppm SDS,CTAB and TX100, respectively. It was observed that micelle solution prepared with concentrations of critical micellization concentration (CMC) to 10-fold CMC did not significantly *a*ffect the apparent concentration of Zn^{2+}. Thus, an appropriate value for initial surfactant concentration was $10 \times$ CMC for effective determination of Zn^{2+} in the presence of surfactant.

Calibration graphs and selection of the surfactant

We performed comprehensive tests for a relationship between nature, concentration of surfactants and analytical result of Zn^{2+} with 90 values. Experiments were performed in triplicate. First step, calibration was done with zinc solutions containing surfactant (Fig. 2; 2). Each standard mixtures were prepared as follows: 6.0×10^{-3} M of surfactant and appropriate amounts of the Zn^{2+} ion solution were added to 10 mL voltametric flask and made up to the mark with deionized water. Different amounts of zinc were added from 1000 mgL^{-1} solution of the metal ion. The Zn^{2+} concentrations in these mixtures were in the range of 0.56-3.36 ppm. The absorbance measurements were made at 213.9 nm against a reagent blank.

The next step involves calibrating the aqueous solutions (Fig.2.;1). Finally, the apparent concentration of Zn^{2+} were plotted versus its actual concentration in the presence of 6.0×10^{-3} M surfactant and then determined the ion concentration in feed solution (Fig. 3). An optimum surfactant-to-metal (S/M) ratio has been observed to be 10-400 for MEUF system. For this reason, samples were prepared with 200 S/M ratio.
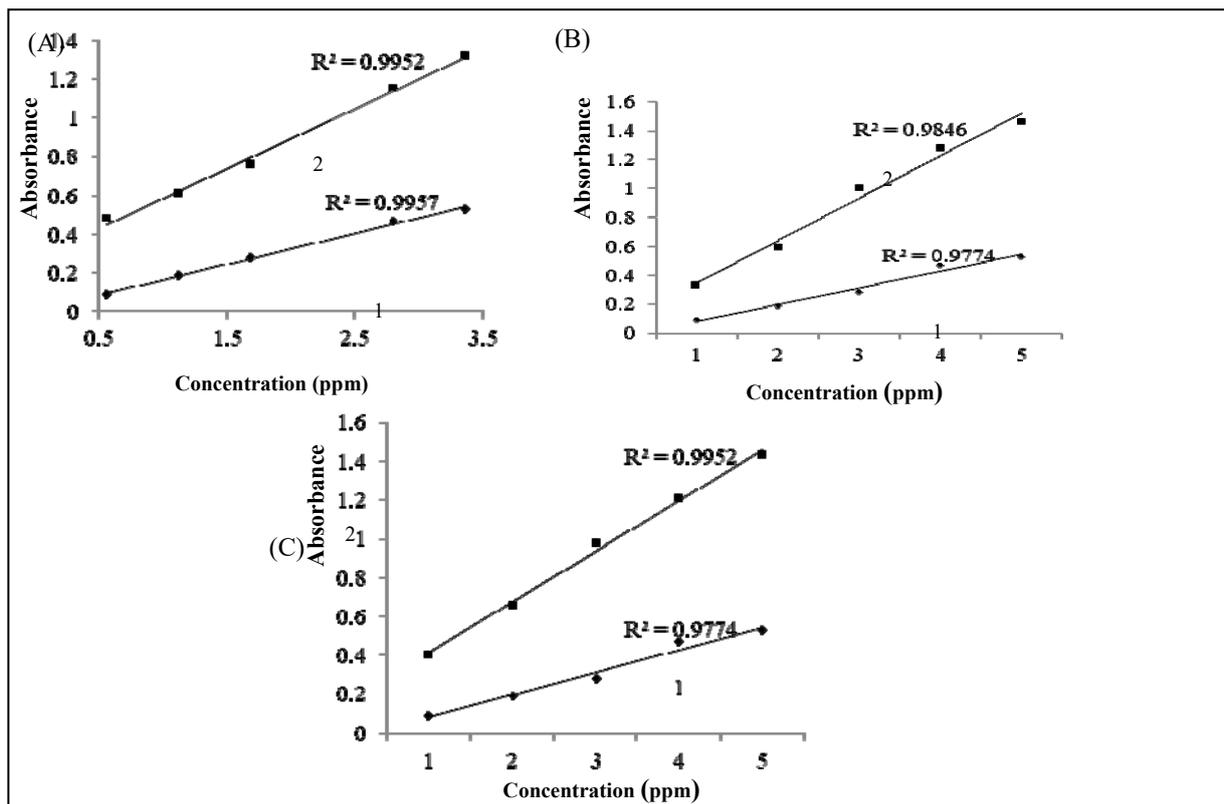
Figure 2. Calibration curves for aqueous solutions (1)
and zinc solutions containing surfactant (2); (A) SDS, (B) CTAB, (C) TX100

Experimental studies have shown that all studied surfactants enhance the analytical signal of Zn^{2+} was noted for the surface-active compounds. Presence of the surfactant on the interface reduces the surface tension, viscosity and droplet size of an aerresol and changes the oxidation/reduction characteristics of the flame, the charge distribution of molecule, the efficiency of excitation energy or electron transfer of molecules. The use of surfactants can also result in decreasing or increasing the reaction rate or changing the yield of reaction (19). The greatest extent is achieved when SDS is added to the analyte solutions. In this case, the weight fraction of surfactant is 0.2 wt% or 6.0×10^{-3} M.

A representative calibration graph is shown in Figure 3, from Zn^{2+}-6.0×10^{-3} M SDS. The calibration graphs are plotted for three systems, *i.e.,* Zn^{2+}-Triton X-100, Zn^{2+}-SDS, and Zn^{2+}-CTAB in the same manner. All obtained regression factors, R^2, are greater than 0.99.
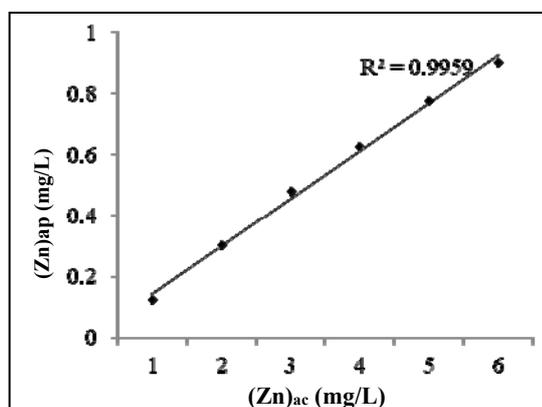

Figure 3. Dependence of the apparent concentration of Zn^{2+} determined by FAAS, on its actual concentration in the presence of 6.0×10^{-3} M SDS

Effect of foreign ions on the analytical signal for Zn^{+2}

The effect of various foreign ions which are generally associated with Zn^{+2} on its determination is studied by measuring the absorbance of the zinc. Among the studied ions Co^{2+}, Ca^{2+}, Mg^{2+}, Cu^{2+}, Ni^{2+}, Pb^{2+}, Cr^{3+} and their mixtures have an effect on the analytical signal for zinc.

Adding the surface-active compounds to analyte solutions eliminate the effect of the foreign ions and their sum for different ratios relative to Zn^{+2}, and also increases the analytical signal in proportion to the analyte concentration of zinc and the selectivity of zinc determination.

Atomic Absorption Determination of Zn^{+2} in Water Samples

The proposed method was applied to determine this concentration in distilled water samples. The results reported in Table 1 show that the proposed method is suitable for determination of Zn^{2+} in such water samples. Water samples were filtered using a 5000 Da pore size membrane filter to remove Zn^{2+}.

Table 1. Determination of zinc in environmental water samples

Sample	Zinc concentration (mgL^{-1}) Added	Found	Recovery (%, n=3)
Distilled water	-	-	BDL
	10.0	9.9±0.15	99.0
	20.0	20.1±0.10	100.5

BDL: Below Detection Limit

4. Conclusions

The method has shown good sensitivity, reliability, and easy preparation for estimation of Zn^{2+} from water samples. It was found that SDS increases the sensitivity and selectivity but decreases the detection limit for Zn^{2+}. The developed method was used to determinate the trace zinc in water samples with satisfactory results. This method also was utilized to determinate the copper, cadmium in water samples in our other experiments [32].

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