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Cloud Point Extraction and Preconcentration of Silver and Cadmium Using Schiff Base Prior to Flame Atomic Absorption Spectrometric Determination

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Cloud point methodology was successfully used for the extraction of trace amounts of silver and cadmium as a prior step to their determination by flame atomic absorption spectrometry. Silver and cadmium reacts with Schiff base benzyl*bis*-(thiosemicarbazone) as chelating agent in a surfactant solution yielding a hydrophobic complex, which then is entrapped in surfactant micelles. After phase separation, based on the cloud point the mixture and dilution of the surfactant-rich phase with methanol containing 0.1 M HNO_3, the enriched analytes were determined by flame atomic absorption spectrometry. After optimization of the complexation and extraction conditions and preconcentration 60 mL of sample in the presence of 0.17 % Triton-X-114 the enhancement factors of 140 and 60 and detection limits of 0.04 ng mL^{-1} and 0.08 ng mL^{-1} were obtained for silver and cadmium, respectively. The proposed method was applied satisfactory to the determination of Ag and Cd in natural water samples.

Key Words: Cloud point extraction, Silver, Cadmium, Preconcentration.

INTRODUCTION

Cadmium is known to be highly toxic for animals, plants and humans even at low concentrations and can be accumulated in several organs[1]. It also causes high blood pressure and destruction of red blood cells. Experimental and epidemiological studies has provided substantial evidence that low levels of long-term exposure to cadmium can attribute to an increased risk of cancer[2].

Silver enters the environment in industrial waters because it often occurs as impurity in copper, zinc, arsenic and antimony ores[3]. Low level exposure to silver compounds is widespread due to the use of soluble silver compounds to disinfect water used for drinking[4]. On the other hand, recent

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information about the interaction of silver with essential nutrients, especially selenium, copper, vitamin E and B_{12}, have focused attention on its potential toxicity[4,5].

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. This procedure is attractive when flame atomic absorption spectrometry (FAAS), a relatively simple and available technique in many laboratories, is used.

In recent years, a methodology of separation and preconcentration based on cloud point extraction are becoming an important and practical application of the use of surfactants in analytical chemistry[6]. Cloud point extraction is a simple and powerful technique for separation and preconcentration of metal ions[7-10].

Aqueous solutions of many non-ionic surfactant micellar systems become turbid when the temperature has been changed and this temperature is named 'cloud point'. Above the cloud point, the solution separates into two phases: the surfactant-rich phase with very small volume and the bulk aqueous solution, containing surfactant monomers. The use of micellar systems as an alternative to other techniques of separation offers several advantages including low cost, safety and high capacity to concentrate a wide variety of analytes of widely varying nature with high recoveries and concentration factors[11-13].

Several ligands such as 1-(2-pyridylazo)-2-naphthol (PAN), 4-(2-pyridylazo)resorcinol[14], 8-hydroxylquinoline[15], calixarenes[16] and dithizone[17], have been used in cloud point extraction of metal ions. Schiff base as a chelating agent has been used for the first time for preconcentration and speciation of chromium[8].

Schiff base is a strong and selective ligand, as spectrophotometric reagents for several ions[18,19]. These compounds also have sufficient hydrophobicity to use as a compleaxing agent in cloud point extraction technique[7,8].

The aim of this work was to optimize the use of a newly synthesized Schiff base benzyl*bis*(thiosemicarbazone) as a chelating agent and to assess its application to the preconcentration of silver and cadmium prior to flame atomic absorption spectrometric determination.

EXPERIMENTAL

All the chemicals used were of analytical reagent grade, free from Ag and Cd traces. Stock solutions of Ag(I) and Cd(II) were prepared by dissolving appropriate amounts of their respective salts in double distilled water. Working standard solutions were obtained by appropriate dilution of the stock standard solutions.

The non-ionic surfactant Triton-X-114 (Fluka Chemie AG, Switzerland) was used without further purification. Nitric acid (Merck) and methanol (Merck) were used. The chelating agent solution was prepared by dissolving 0.356 g, Schiff's base in 100 mL of methanol 99.5 %. The Schiff base benzyl*bis*(thiosemicarbazone) (Fig. 1) was synthesized and purified as described in literature[20]. The pipettes and vessels used for trace analysis were kept in nitric acid (10 % v/v) for at least 1 h and subsequently washed four times with water.

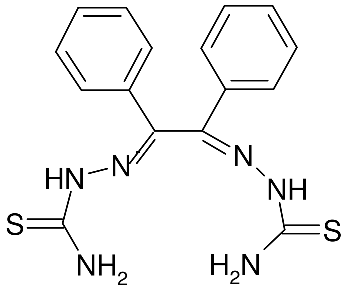


Fig. 1. Structure of Schiff base

A Shimadzu model 680 atomic absorption spectrometer equipped with deuterium background correction and Ag and Cd hollow cathode lamp as the radiation source was the manufacture's recommendations.

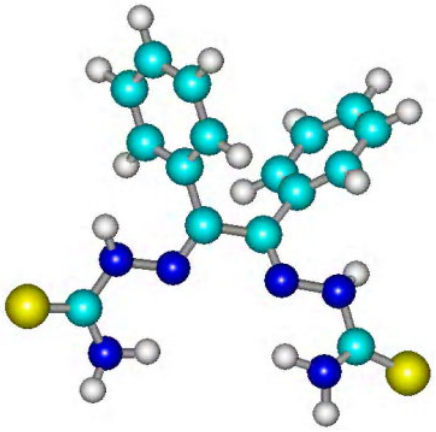
A thermostat bath (Tokyo Rikakikai Ltd., Japan) model UA-1, maintained at the desired temperatures was used for cloud point temperature experiments and phase separation was assisted using a centrifuge (Hettich, Universal). The pH of solutions was controlled with a metrohm pH meter model 713.

For the cloud point extraction, an aliquots of 60 mL of the cold solution containing the analytes, 0.17 % (w/v) Triton-X-114 and, 3×10^{-4} M Schiff base was adjusted to the appropriated pH value (pH = 11.5) with NaOH. The mixture was kept for 10 min in the thermostatic bath at 50 °C. Subsequently, the phase separation is accelerated by centrifugating at 3500 rpm for 10 min. The phases were cooled in an ice-bath in order to increase the surfactant-rich phase viscosity. Then, the bulk aqueous phase was easily decantated.

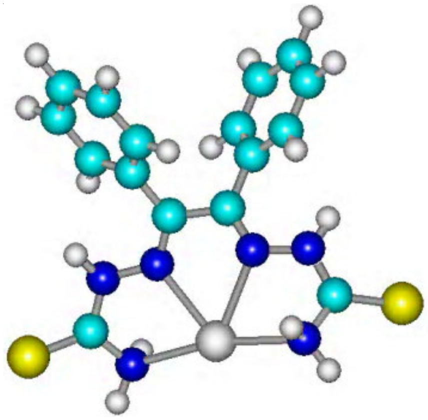
Later, in order to decrease the viscosity and facilitate sample banding, 800 μL of a solution of methanol containing 0.1 M HNO_3 was added to the surfactant-rich phase. The samples (*ca.* 1.0 mL) were introduced into the flame by conventional aspiration.

RESULTS AND DISCUSSION

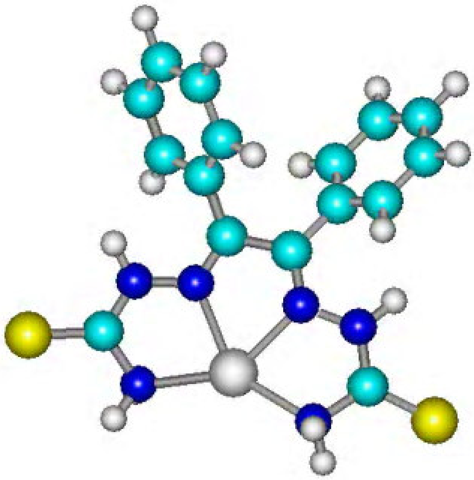
To obtain information about the optimized structures of the benzyl*bis*-(thiosemicarbazone) and its complexes with the Ag^+ and Cd^{2+} used, the molecular structure of uncomplexed ligand and its complexes with the Ag^+ and Cd^{2+} were built with the hyperchem program. The structure of free ligand was optimized using the 6.31 G* basis set at the restricted Hartree-Fock (RHF) level of theory. The optimized structure of the ligand was then used to find out the initial structure of its metal complexes. Finally, the structure of the resulting 1:1 complex was optimized using Lanl 2mb basis set at the RHF level of theory. No molecular symmetry constraint was applied; rather, full optimization of all band lengths, bond angles and torsion angles was carried out using the Gassian 98 program. The optimized structures are shown in Fig. 2.



(a) Benzyl*bis*(thiosemicarbazone) (Schiff base)



(b) Silver complex of Schiff base



(c) Cadmium complex of Schiff base

Fig. 2. Optimized structure of free ligand (a); complexed with silver (b) and cadmium (c)

In the resulting 1:1 complex, the two C=N groups and two NH_2 groups of the ligand are nicely involved in bond formation with the central metal ion, while the two sulfur atoms (C=S) and two NH groups will remain unattached. However, the introduction of the central metal ion will result in the formation of a 'pseudo cavity' in the molecule Fig. 2b and 2c so that only four donating atoms of the ligand molecule will be in suitable proximity of the central metal ion for maximum binding intractions.

The pH was the first critical parameter evaluated for its effect on the determination of the two species. Cloud point extraction (CPE) of Ag^+ and Cd^{2+} was performed in different pH. The separation of metal ions by the CPE method involves prior formation of a complex with sufficient hydrophobicity to be extracted into the small volume of surfactant-rich phase, thus obtaining the desired preconcentration. Extraction yield depends on the pH at which complex formation occurs.

Fig. 3 shows the effect of pH on the extraction of Ag^+ and Cd^{2+} complexes. It can be seen that for both Ag^+ and Cd^{2+} the signal increases after pH 8.0 and reaches maximum extraction efficiency up to 11.0. At lower pH values, ligand is protonated, so recoveries are decreased. Hence, pH 11.5 was chosen for both analytes.

The concentration of the chelating agent [benzyl*bis*(thiosemicarbazone)] was studied for its effect on the extraction of the Ag^+ and Cd^{2+} and the results were presented in Fig. 4. For this study, aliquots of 60 mL

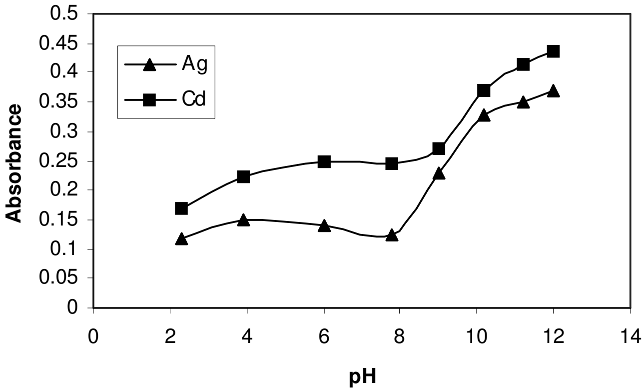


Fig. 3. Effect of pH on the absorbance of silver and cadmium; Conditions: Ag (10 ng mL^{-1}) and Cd (20 ng mL^{-1}); Triton-X-114, 0.17 % (w/v); Schiff base 3×10^{-4} M

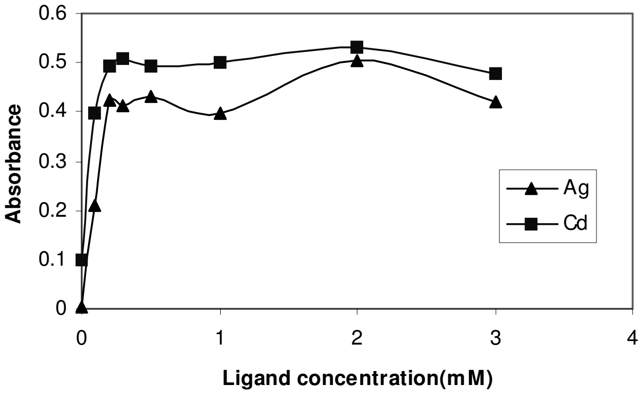


Fig. 4. Effect of concentration Schiff base on the extraction recovery of silver and cadmium. Conditions: Ag (10 ng mL^{-1}) and Cd (20 ng mL^{-1}); pH 11.5; Triton-X-114, 0.17% (w/v)

of the sample solution containing Ag^+ and Cd^{2+} in the presence of 0.17 % (w/v) Triton-X-114 with various amounts of Schiff base (at pH = 11.5) were subjected to the cloud point preconcentration process. As can be seen, the signal increases up to a concentration of 2×10^{-4} M, reaching a plateau, which is considered as complete extraction. Therefore, the concentration of 3×10^{-4} M was chosen as an optimum concentration for the subsequent experiments.

A successful cloud point extraction would be that which maximizes the extraction efficiency through minimizing the phase volume ratio, thus maximizing its concentrating ability. The variation in extraction efficiency within the Triton-X-114 range 0.05-0.25 % (w/v) was examined. Quantitative extraction was observed when the Triton-X-114 concentration was 0.17 %. Fig. 5 highlights the differences observed in the signals at different surfactant concentrations.

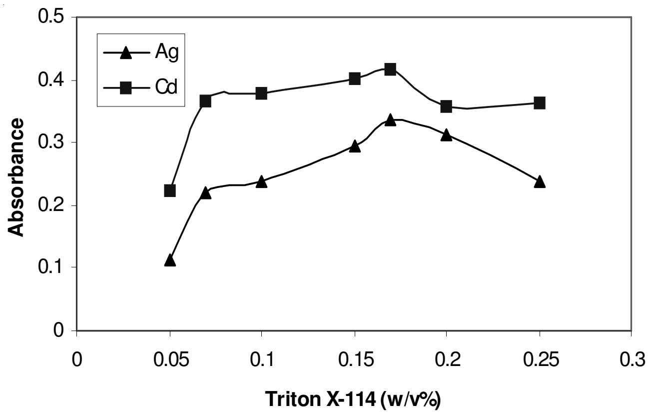


Fig. 5. Effect of Triton-X-114 concentration on the absorbance of silver and cadmium. Conditions: Ag (10 ng mL^{-1}) and Cd (20 ng mL^{-1}); pH 11.5; Schiff base 3 × 10^{-4} M

At lower concentration, the extraction efficiency of the complexes is low, probably because of an inadequacy in the assemblies to entrap the hydrophobic complex quantitatively. With the increase of Triton-X-114 concentration above 0.20 %, the signals decrease beacause of the increment in the volumes and the viscosity of surfactant phase. The optimum surfactant concentrations are same for both analytes. An amount of 0.17 % Triton-X-114 was chosen in order to achieve the greatest analytical signal and thereby the highest extraction efficiency.

To achieve easy phase separation and preconcentration as efficient as possible, optimal incubation time and temperature are necessary to complete reactions. The effect of the equilibration temperature was investigated from 25 to 80 ºC. It was found that the CPE efficiency reach maximum in the rang of 40-60 ºC. Over 60 ºC, the CPE efficiency decreased probably due to stability problems for chelates and chelating agent[21]. So, an equilibration temperature of 50 ºC was used.

The effect of the incubation time on extraction efficiency was studied for a time span of 5-25 min. An incubation time of 10 min was chosen to be the optimal to achieve quantitative extraction.

The influence of ionic strength was examined by studying the response for KCl concentration in the range 0.0-0.5 M. Ionic strength had no appreciable effect upon extraction efficiency and sensitivity up to 0.5 M. This is in agreement with the results reported in the literature which demonstrate that increases in ionic strength in micelle mediated systems do not seriously alter the extraction efficiency of the analyte[22,23].

The effect of centrifugation time upon extraction efficiency was studied for the range, 5-20 min. A centrifugation time of 10 min at 3500 rpm was selected as optimum, since complete separation occurred for this time and no appreciable improvement were observed for longer time.

A calibration curve was obtained by preconcentrating 60 mL of sample standard solutions containing known amounts of analyte under the optimization conditions of the method.

Table-1 shows the analytical characteristics of the method. Under the optimum experimental conditions, the calibration curve for silver and cadmium was linear from 0.1 to 50 and 0.2 to 83 ng mL^{-1}, respectively.

TABLE-1
ANALYTICAL CHARACTERISTICS OF THE METHOD

Parameter	Analytical feature	
	Ag	Cd
Enhancement factor[a]	140	60
LOD[b] (ng mL^{-1})	0.04	0.08
RSD % (n = 5)[c]	2.3	2.1
Correlation coefficient (r)	0.9988	0.9971
Regression equation, C (ng mL^{-1})	5.4×10^{-2} C + 0.012	2.4×10^{-2} C+ 0.032
Linear range (ng mL^{-1})	0.1-30.0	0.2-63.0

[a] Calculated as the ratio of absorbance of preconcentrated samples to that obtained without preconcentration.
[b] Limit of detection defined as three times the signal-to- noise ratio.
[c] Silver and cadmium concentration were 20 ng mL^{-1} for which the RSDs were obtained.

The enhancement factors calculated as the ratio of absorbance of preconcentrated samples to that obtained without preconcentration, were 140 for silver and 60 for cadmium. The limit of detections was sufficiently low as compared to those attained by FAAS without preconcentration and lie around 0.04 and 0.08 ng mL^{-1} for silver and cadmium.

The effect of foreign ions on the determination of Ag^+ and Cd^{2+} by the proposed method was investigated. An ion was considered as interferent, when it caused a variation in the absorbance of the sample greater than ± 5 %. Commonly encountered alkali and alkaline earth elements generally do not form stable complexes and are not CPE-extracted. The following ions did not interfere at 1.0×10^4 ng mL^{-1} in the preconcentration of 10 ng mL^{-1} Ag^+ and Cd^{2+}: Co^{2+}, Ni^{2+}, Fe^{3+}, Al^{3+}, Pb^{2+}, Cr^{3+}, Cr^{6+}, Hg^{2+}, Zn^{2+}, Mn^{2+}, Cu^{2+}, Cl^-, Br^-, SO_4^{2-}, NO_3^- and PO_4^{3-}.

As the results show large amounts of common cations and the anions do not interfere on the determination of trace quantities of Ag^+ and Cd^{2+}.

The proposed method was applied to the preconcentration and determination of Ag^+ and Cd^{2+} in several water samples. Water samples were filtered using a 0.45 μm pore size membrane filter to remove suspended particulate matter. As shown in Table-2, the proposed method could be applied successfully for the preconcentration and determination of trace amounts of silver and cadmium in water samples.

TABLE-2
RECOVERY OF SILVER AND CADMIUM FROM 60 mL OF DIFFERENT WATER SAMPLES

Sample	Added (ng mL^{-1})		Determined (ng mL^{-1})	
	Ag	Cd	Ag	Cd
Tap water	0.0	0.0	ND	ND
	10.0	10.0	10.08 ± 0.20[a]	10.11 ± 0.21
	20.0	20.0	19.90 ± 0.20[a]	20.50 ± 0.50[a]
River water	0.0	0.0	ND	ND
	10.0	10.0	10.12 ± 0.19	9.95 ± 0.23
	20.0	20.0	20.60 ± 0.50	20.02 ± 0.45

[a] Mean of three extraction ± SD.

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