Flame atomic absorption spectrometric determination of trace quantities of cadmium in water samples after cloud point extraction in Triton X-114 without added chelating agents

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Abstract

A new micell-mediated phase separation method for preconcentration of ultra-trace quantities of cadmium as a prior step to its determination by flame atomic absorption spectrometry has been developed. The method is based on the cloud point extraction (CPE) of cadmium in iodide media with Triton X-114 in the absence of any chelating agent. The optimal extraction and reaction conditions (e.g., acid concentration, iodide concentration, effect of time) were studied, and the analytical characteristics of the method (e.g., limit of detection, linear range, preconcentration, and improvement factors) were obtained. Linearity was obeyed in the range of 3–300 ng mL^{-1} of cadmium. The detection limit of the method is 1.0 ng mL^{-1} of cadmium. The interference effect of some anions and cations was also tested. The method was applied to the determination of cadmium in tap water, waste water, and sea water samples.
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1. Introduction

Because of the toxicity of cadmium to plants and humans, its determination in the environment is increasingly important. Cadmium is known to damage organs such as kidneys, liver and lungs [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. The maximum contaminant level (MCL) allowed by the American Environmental Protection Agency (US EPA) in standard drinking water is 10 μg L^{-1} to provide ample protection of human health [2].

Aqueous solutions of certain surfactants display the so-called cloud point phenomenon in which the aqueous surfactant solution (surfactant above the critical micelle concentration) suddenly becomes turbid because of a decrease in the solubility of the surfactant in water [3]. This clouding phenomenon is usu-

ally induced by an increase in temperature. The result is the formation of two distinct phases: a surfactant-rich phase and an aqueous phase with concentration of surfactant close to the critical micellar concentration [4,5]. It has been demonstrated that the surfactant-rich phase, thus separated under the cloud point conditions, is able to extract and preconcentrate a wide range of organic and inorganic compounds from the aqueous phase.

The use of cloud point extraction, offers an interesting alternative to the conventional extraction systems. Compared with conventional solvent extraction, CPE uses water and avoids the use of large amounts of expensive, toxic and flammable organic solvents. In addition, CPE can lead to higher recovery efficiency and a large preconcentration factor because the presence of surfactant can minimize losses of analytes due to their adsorption onto the container [6]. The CPE method has been used for the preconcentration of metal ions, after the formation of sparingly water-soluble complexes, as a prior step to their determination by FAAS [7–15].

Several reports have been published on the preconcentration of cadmium by CPE method prior to its determination. In all reported works cadmium has been preconcentrated by CPE method after the formation of sparingly water-soluble com-

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plexes with a suitable chelating agent such as dithizone [8], 1-(2-thiazolylazo)-2-naphthol (TAN) [12], 1-(2-pyridylazo)-2-naphthol (PAN) [16], diethyldithiocarbamate (DDTC) [17], 8-hydroxyquinoline [18] and *O,O*-diethyldithiophosphate (DDTP) [7,11,19] and. Although, to the best of our knowledge there is no report on the CPE after the formation of its iodo complexes, but there are several reports on the conventional liquid–liquid extraction of cadmium after complexation by iodide [20].

In this work, we report on the results obtained in a study of the CPE of Cd^{2+}, after the formation of a complex with iodide using Triton X-114 as surfactant followed by analysis by FAAS.

2. Experimental

2.1. Apparatus

A water bath with a good temperature control within $\pm 1\,°C$ and a centrifuge with 10 mL calibrated centrifuge tubes (Superior, Germany) were used to achieve and accelerate the phase separation process, respectively. A Shimadzu model 670 atomic absorption spectrometer with flame atomization and cadmium hallow-cathode lamp was used for the determination of cadmium. The operating parameters were set as recommended by the manufacturer. Atomic absorption measurements were carried out in an air-acetylene flame. The following conditions were used—absorption line: Cd: 228.8 nm; slit widths: 0.6 nm; and lamp currents: 4 mA. The ratio of the flow rate of air to that of acetylene was 8:1.8. All measurements were carried out without background correction.

2.2. Reagents

All chemical reagents used were of analytical reagent grade, and triply distilled water was used throughout the experiments. Stock Cd(II) solution was prepared by dissolving appropriate amounts of $Cd(NO_3)_3 \cdot 4H_2O$ (Merck) in watery. Triton X-114 stock solution (2%, v/v) was prepared by dissolving 2 mL of concentrated solution (Merck) in hot distilled water. Iodide solution was prepared from KI (Merck) and sulfuric acid solution was prepared by appropriate dilution of its concentrated solution (Merck).

2.3. Procedure

A solution containing 30–3000 ng Cd^{2+} ion was transferred to a 10 mL centrifuge tube with a graduation line. After adding iodide, sulfuric acid and Triton X-114 the solution was diluted to 10 mL with water. The sample was shaken and left to stand in a thermostated water bath for 20 min at 60 °C before centrifugation. Separation of two phases was achieved heating and accelerated by centrifugation for 5 min at 3800 rpm. The mixture was cooled in an ice bath to increase the viscosity of the surfactant-rich phase, and the aqueous phase was easily decanted by simply inverting the tube. The micellar extract of this procedure was diluted to 0.5 mL with ethanol and its cadmium content was determined by flame atomic absorption at 228.8 nm against a

blank solution. Calibration was carried using different standard solutions of cadmium submitted to the same preconcentration and determination procedures. Blank solution was submitted to the same procedure and measured in parallel to the samples.

3. Results and discussion

Cadmium iodide solutions are known to contain the following ionic and molecular species: Cd^{2+}, CdI^+, CdI_2, CdI^-, $CdI_2{}^{2-}$ and I^-. The simple cadmium and iodide ions are probably found only in negligible amounts, since cadmium iodide is a weak electrolyte, except in very dilute solutions. The iodide complexes of cadmium present in the following decreasing order of abundance: $CdI_4{}^{2-}$, $CdI_3{}^-$, CdI_2 and CdI^+ [20].

We observed that the produced complexes can be extracted by CPE method without adding any chelating agent probably as neutral complex of CdI_2 and/or as ion pairs of $[2H^+, CdI_4{}^{2-}]$, $[H^+, CdI_3{}^-]$. Therefore, the method is suitable for preconcentration of cadmium.

3.1. Effect of variables

To take full advantage of the procedure, the reagent concentrations and reaction conditions must be optimized. Various experimental parameters were studied in order to obtain an optimized system.

At point zero for concentration of Triton X-114, H_2SO_4 and I^-, no extraction of cadmium was performed and therefore, the absorbance was zero.

The concentration of surfactant that is used in CPE is critical factor. To obtain the optimal concentration of Triton X-114, the effect of surfactant concentration on the preconcentration of cadmium was investigated in the range 0.04–0.44% (v/v). As Fig. 1 shows, the absorbance of the cadmium in surfactant-
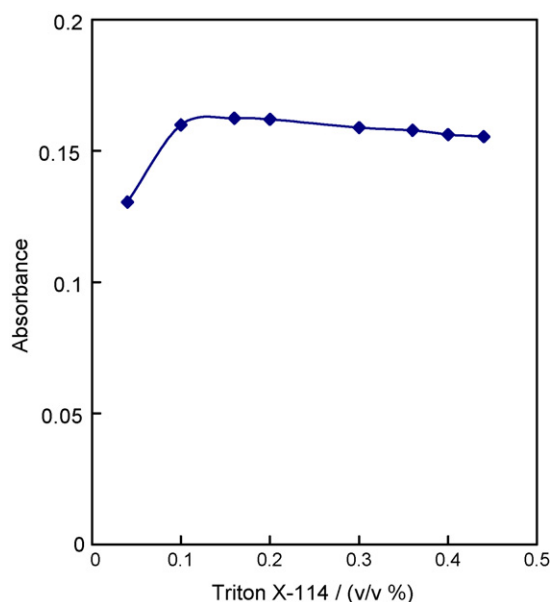

Fig. 1. Effect of Triton X-100 concentration on the extraction of cadmium. Conditions: Cd^{2+}, 100 ng mL^{-1}; sulfuric acid, 1 mol L^{-1}; iodide, 0.017 mol L^{-1}.

rich phase at 228.8 nm increased by increasing the Triton X-114 concentration up to 0.10% (v/v) and remained nearly constant at higher concentrations. Surfactant concentrations smaller than 0.1% (v/v) lead to a reduction of the analytical response due to incomplete partitioning of the analytes in the surfactant micelles. Therefore, 0.20% (v/v) Triton X-114 was used in the proposed method.

The efficiency of the preconcentration process depends on the acid concentration. The effect of this variable was investigated in the range 0.10–1.50 mol L^{-1}. The results showed that the absorbance for cadmium in the surfactant rich phase at 228.8 nm increased by increasing sulfuric acid concentration up to 1 mol L^{-1}. Increasing the absorbance by increasing sulfuric acid up to 1 mol L^{-1} can be due to the increase in the concentration of extractable ion pairs. But higher concentrations of acid prevents cloud formation in the solution. Therefore, 1 mol L^{-1} sulfuric acid was selected as optimal.

The effect of iodide concentration was investigated in the range 4.2–34.0 mmol L^{-1}. As Fig. 2 shows the absorbance for cadmium in the surfactant-rich phase at 228.8 nm increased by increasing iodide concentration up to 25×10 mol L^{-1} and remained constant at higher concentrations. By increasing iodide concentration the concentration of iodide complexes of cadmium increases and causes more extraction efficiency. A 30 mmol L^{-1} iodide concentration was used as optimal.

The effect of equilibration temperature and incubation time was investigated. It is desirable to employ the shortest incubation time and the lowest possible equilibration temperature, which compromise efficient separation of the phases. The results showed that at constant incubation time of 5 min equilibration temperature of 40 °C is sufficient for maximum recovery of the cadmium.

As the surfactant-rich phase was very viscous, ethanol was added to the surfactant-rich phase after CPE to facilitate its transfer into flame. The amount of 0.40 mL ethanol was chosen to have an appropriate amount of sample for transferring and measuring the sample absorbance.

3.2. Analytical parameters

From measurements made under the optimum conditions described above, the calibration graph was linear in the range 3.0–300.0 ng mL^{-1}. The calibration equation is $A = 2.20 \times 10^{-3}C + 4.0 \times 10^{-4}$ with a correlation coefficient of 0.9997 ($n = 11$), where A is the atomic absorbance for cadmium in the surfactant rich phase at 228.8 nm and C is the concentration of Cd^{2+} in the sample solution in ng mL^{-1}. The limit of detection, defined as $C_L = 3S_B/m$ [21], where C_L, S_B and m are the limit of detection, standard deviation of the blank and the slope of the calibration graph, respectively, was 1.0 ng mL^{-1}.

To evaluate the accuracy and precision of the method, a series of independent standard samples was used. The results are given in Table 1. As Table 1 shows, the R.S.D. for the determination of different concentrations of Cd^{2+} was in the range 0.8–3.0% and the absolute value of the relative error was ≤3%.

The preconcentration factors, f_c, defined as the ratios of the cadmium concentration in the surfactant-rich phase to that in the bulk phase initially, will remain constant in the same surfactant solutions, regardless of the initial cadmium concentration.

$$f_c = C_s/C_0$$

where C_s is cadmium concentration (ng mL^{-1}) in the surfactant-rich phase after phase separation (0.1 mL surfactant-rich phase) and C_0 is the initial concentration of cadmium (ng mL^{-1}). The preconcentration factor was obtained as 55.6 ± 1.3 ($n = 3$).

As for the determination of the absorbance for cadmium in the surfactant-rich phase, micellar extract (0.1 mL) was diluted to 0.5 mL, the preconcentration factor for the proposed method is 11.1 ± 0.26.

The improvement factor, defined as the ratio of the slope of the calibration graph for the CPE method to that of the calibration graph in micellar media without preconcentration, was 14.7.

3.3. Effect of foreign ions

The effect of foreign ions on the determination of Cd^{2+} by the proposed method was investigated. An ion was considered
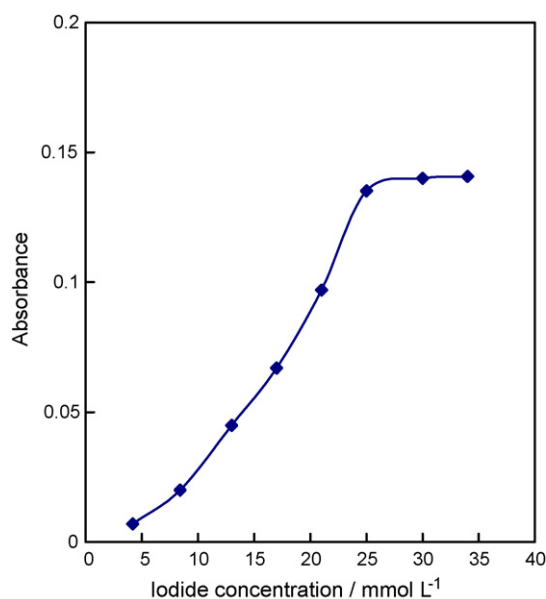

Fig. 2. Effect of iodide concentration on the extraction of cadmium. Conditions: Cd^{2+}, 70.0 ng mL^{-1}; sulfuric acid, 1 mol L^{-1}; Triton X-114, 0.2% (v/v).

Table 1
Accuracy and precision of the method

Cadmium concentration (ng mL^{-1})		Relative error (%)	R.S.D.[a] (%, $n = 3$)
Taken	Found		
15.0	14.6	−2.7	3.0
25.0	24.3	−2.8	2.4
40.0	41.2	+3.0	1.7
80.0	79.6	−0.5	1.6
100.0	98.3	−1.7	1.3
200.0	200.0	0.0	0.8

[a] Relative standard deviation.

Table 2
Determination of cadmium in water samples

Sample	Cadmium concentration (ng mL^{-1})		Recovery (%, $n = 3$)
	Taken	Found	
	–	5.21 ± 0.26	–
Waste water	5.0	10.03 ± 0.15	96.4
	10.0	15.32 ± 0.10	101.1
	15.0	20.45 ± 0.33	101.6
Sea water (Persian gulf)	–	4.42 ± 0.14	–
	5.00	9.73 ± 0.21	106.2
	10.00	14.58 ± 0.25	101.6
	15.00	19.26 ± 0.08	98.9
River water	–	ND	–
	10.00	10.15 ± 0.23	101.5
	15.00	14.80 ± 0.38	98.7
	20.00	19.00 ± 0.18	95.0

ND: not detected.

as interferent, when it caused a variation in the absorbance of the sample greater than $\pm 5\%$. The following ions did not interfere at 1.0×10^5 ng mL^{-1} in the preconcentration and determination of 80 ng mL^{-1} Cd^{2+}: Na$^+$, K$^+$, Li$^+$, Ca^{2+}, Mg^{2+}, Ba^{2+}, Sr^{2+}, Cr^{3+}, Ni^{2+}, Co^{2+}, Zn^{2+}, Cu^{2+}, Pb^{2+}, Cl$^-$, Br$^-$, SO$_4^{2-}$, NO$_3^-$, PO$_4^{3-}$, SiO$_3^{2-}$, Be^{2+}, Bi^{3+}, Hg^{2+}, V(V), As(III) and Fe^{3+}.

As the results show large excess amounts of common cations and anions do not interfere on the determination of trace quantities of cadmium.

3.4. Applications

In order to evaluate the analytical applicability of the proposed method, it was applied to the determination of cadmium in several water samples. The water samples were filtered to remove the suspended solids and their cadmium concentration were determined by the proposed method. The results are given in Table 2. The recovery for the addition of different concentrations of cadmium to water samples, were in the range 95.0–104.3%. The results show that the proposed method is suitable for determination of Cd^{2+} in such water samples.

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