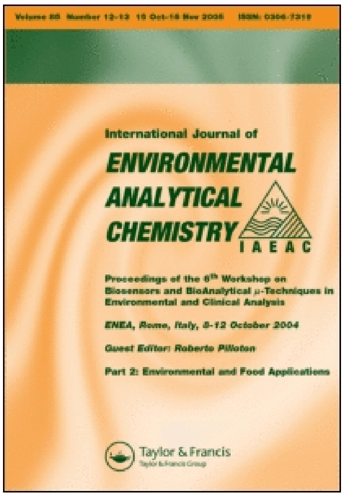

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Highly selective determination of trace quantities of mercury in water samples after preconcentration by the cloud-point extraction method

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Highly selective determination of trace quantities of mercury in water samples after preconcentration by the cloud-point extraction method

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A cloud-point extraction method for preconcentration of ultra-trace quantities of mercury ions as a prior step to its determination by spectrophotometry. The method is based on the cloud-point extraction of mercury in iodide media with Triton X-114. The preconcentrated mercury was then determined spectrophotometrically by measuring the absorbance of the surfactant rich phase at 300 nm and also by cold-vapour atomic absorption spectrometry (CVAAS). Linearity was obeyed in the range of 0.40–40.0 ng mL^{-1} by CVAAS and in the range of 10.0–400.0 ng mL^{-1} by spectrophotometry. The detection limit is 3.0 ng mL^{-1} by spectrophotometry and 0.10 ng mL^{-1} by CVAAS. The interference effect of several anions and cations was also tested. The method was used to determine mercury in water samples.

Keywords: Mercury determination; Cloud-point extraction; Spectrophotometry; CVAAS

1. Introduction

Mercury is one of the most toxic metals [1]. Although it is found at low concentrations, its toxicity can be dangerous. The interesting chemical and physical properties of mercury have led to wide uses in different industrial sectors such as catalysis, amalgams, electrodes, lamps, batteries, thermometers, fungicides, and pigments. Once introduced into the environment, Hg becomes involved in many transformation, transportation, and bioassimilation processes. Owing to its high toxicity, mobility, and wide usage, mercury has caused serious environmental pollution worldwide [2–7]. Therefore, the determination and monitoring of mercury in various types of samples is of vital importance.

Several methods have been reported for mercury determination. These include titrimetry [8], spectrophotometry [9], HPLC [10, 11], isotope dilution inductively coupled plasma mass spectrometry [12], atomic absorption spectrometry with cold vapour [13–15], and inductively coupled plasma mass spectroscopy [16].

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One of the routes of incorporation of mercury into the human body is drinking water. Hence, mercury determination in this type of sample has become very important. However, mercury is at such low concentrations in this kind of sample that the analyte needs to pre-concentrated before the aforementioned techniques are used.

The use of cloud-point extraction (CPE) [17] offers an interesting alternative to conventional extraction systems. Compared with conventional solvent extraction, CPE uses aqueous reagent solutions and obviates the need to use large amounts of expensive, toxic, and flammable organic solvents. In addition, CPE can lead to higher recovery efficiency and a large pre-concentration factor because the presence of surfactant can minimize losses of analytes due to their adsorption onto the container.

The CPE method has been used to pre-concentrate metal ions after the formation of sparingly water-soluble complexes, as a prior step to their determination [18–28]. In one method [27], mercury was pre-concentrated by CPE prior to inductively coupled plasma optical emission spectrometry coupled to a flow injection with a cold-vapour generation system. The mercury was extracted as mercury-2-(5-bromo-2-pyridylazo)-5-diethylaminophenol [Hg(II)-(5-Br-PADAP)] complex, at pH 9.2, mediated by micelles of the non-ionic surfactant polyethyleneglycolmono-*p*-nonylphenylether (PONPE 5). The calibration graph was linear at levels near the detection limits up to at least $50\,\mu g\,L^{-1}$, and the detection limit (DL) was $4\,ng\,L^{-1}$. In another method [28], mercury was pre-concentrated by CPE method as a mercury–dithizone complex in Triton X-100 micellar media. The calibration is linear over the range of $0.05–0.5\,\mu g\,mL^{-1}$ and the limit of detection was $0.014\,\mu g\,mL^{-1}$.

Pappas and Powell [29] reported a spectrophotometric method for mercury determination in the range $0.5–5.0 \times 10^{-5}\,mol\,L^{-1}$, based on its complexation with iodide.

In the present work, we proposed a CPE method for pre-concentration of Hg^{2+} ions as a prior step to its determination by CVAAS and spectrophotometry. Hg^{2+} is pre-concentrated in the presence of iodide in acidic media using Triton X-114 as a non-ionic surfactant.

2. Experimental

2.1 *Apparatus*

A water bath with a good temperature control and a centrifuge with 10 mL calibrated centrifuge tubes (Superior, Germany) were used to accelerate the phase-separation process. A Shimadzu model 670 atomic absorption spectrophotometer equipped with a mercury vaporizer unit (figure 1) was employed. The mercury vaporizer unit was operated in the closed circulation mode. UV–visible absorbance spectra were recorded on a Perkin-Elmer Lambda 45 UV–vis spectrometer spectrophotometer using 1 cm quartz cells (0.5 mL).

2.2 *Reagents*

All chemical reagents used were of analytical reagent grade, and triply distilled water was used throughout the experiments. Stock Hg(II) solution was prepared by

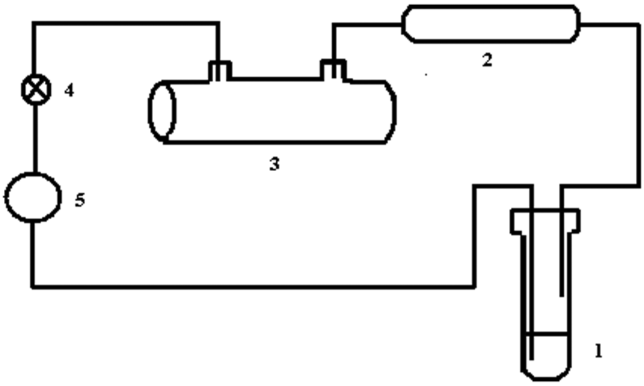

Figure 1. Mercury vaporizer unit. (1) Reaction vessel (a tube with 1 cm i.d. and 7 cm length), (2) calcium chloride tube, (3) atomic absorption flow through cell (from mercury vaporizer unit MVU-1A, Shimadzu), (4) selection valve, and (5) vacuum pump.

dissolving the appropriate amount of $HgCl_2$ (Merck) in water. 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 sulphuric acid solution was prepared by appropriate dilution of its concentrated solution (Merck). A 0.4% (w/v) sodium borohydride in 0.2 mol L^{-1} NaOH solution was prepared daily.

2.3 *Sample collection*

Water samples were collected immediately before use and filtered to remove the suspended solids.

2.4 *Procedure*

An aliquot of the solution containing the appropriate amount of Hg(II) (100–4000 ng for spectrophotometry and 4–400 ng for CVAAS) was transferred to a 10 mL graduated centrifuge tube. After adding 1 mL of 0.25 mol L^{-1} iodide solution, 1 mL of 5.0 mol L^{-1} sulphuric acid solution, and 1 mL of 2.0% Triton X-114 solution, the solution was diluted to 10 mL with water. The sample was shaken and left to stand in a thermostatically controlled water bath for 20 min at 60°C before centrifugation. Separation of two phases was achieved 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 used for the determination of its mercury content by CVAAS or spectrophotometry.

For the determination of mercury by CVAAS, the diluted micellar extract was transferred into the reaction vessel of the mercury vaporizer unit. Then, 0.2 mL of 0.4% sodium borohydride in 0.20 mol L^{-1} sodium hydroxide was added, and the vessel was plugged with the rubber plug. The pump was started, and the atomic absorbance of the mercury was measured at 253.7 nm.

For the mercury determination by spectrophotometry, the solution was transferred into a 0.5 mL quartz cell to measure its absorbance at 330 nm. A blank solution was submitted to the same procedure and measured in parallel with the samples.

3. Results and discussion

In acid media and in the presence of excess iodide, Hg(II) forms HgI_3^- and HgI_4^{2-} complexes [29]. The HgI_4^{2-} ion, which has an absorption maximum at 323 nm ($\varepsilon = 2.34 \times 10^4$), is the principal mercury-containing species present in 1.0 mol L^{-1} aqueous potassium iodide [30].

We observed that the produced complexes can be extracted by the CPE method probably as a neutral complex of HgI_2 and/or as ion pairs of $[2H^+,HgI_4^{2-}]$, $[H^+,HgI_3^-]$. Therefore, the system can be used to preconcentrate trace quantities of mercury.

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 to obtain an optimized system. The effects of variables were studied spectrophotometrically.

The concentration of surfactant used in CPE is a critical factor. To obtain the optimal concentration of Triton X-114, the effect of surfactant concentration on the pre-concentration of mercury was investigated in the range of 0.04–0.44% (v/v). As figure 2 shows, the absorbance of the surfactant rich phase at 330 nm increased by increasing the Triton X-114 concentration up to 0.16% (v/v) remained constant at 0.16–0.24% and slowly decreased at higher concentrations. Therefore, 0.20% (v/v) Triton X-114 was used in the proposed method.

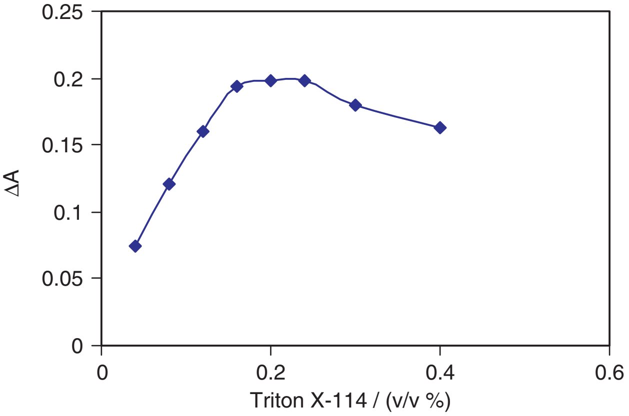

Figure 2. Effect of Triton X-114 concentration on the extraction of mercury. Conditions: Hg^{2+}, 165.0 ng mL^{-1}; sulphuric acid, 0.5 mol L^{-1}; iodide, 0.017 mol L^{-1}.

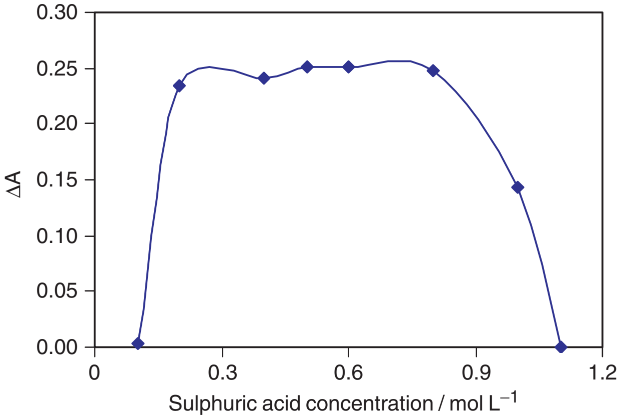

Figure 3. Effect of sulphuric acid concentration on the extraction of mercury. Conditions: Hg^{2+}, 200.0 ng mL^{-1}; Triton X-114, 0.2% (v/v); iodide, 0.017 mol L^{-1}.

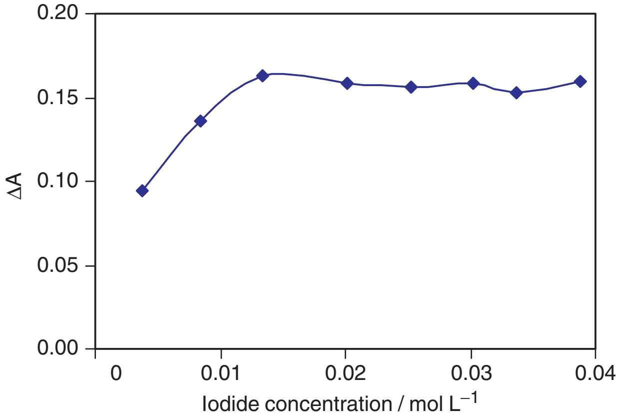

Figure 4. Effect of iodide concentration on the extraction of mercury. Conditions: Hg^{2+}, 130.0 ng mL^{-1}; sulphuric acid, 0.5 mol L^{-1}; Triton X-114, 0.2% (v/v).

As both the complex and ion-pair formations depend on the concentration of acid, the efficiency of the pre-concentration process depends on the acid concentration. Hydrochloric acid, nitric acid, and sulphuric acid were tested, and sulphuric acid was found to be the best. Nitric acid oxidizes iodide to iodine, and hydrochloric acid prevents extraction of mercury. The effect of sulphuric acid was investigated in the range of 0.10–1.10 mol L^{-1}. As figure 3 shows, the absorbance of the surfactant rich phase at 330 nm increased by increasing the sulphuric acid concentration up to 0.2 mol L^{-1}, remained constant at 0.20–0.80 mol L^{-1}, and decreased at higher concentrations. The decrease in absorbance at higher concentrations is due to the prevention of cloud formation in the solution. Therefore, 0.5 mol L^{-1} of sulphuric acid was selected as optimal.

The effect of iodide concentration was investigated in the range 0.0037–0.0388 mol L^{-1}. As figure 4 shows, the absorbance of the surfactant rich phase at 330 nm increased by increasing iodide concentration up to 0.0134 mol L^{-1} and remained constant at higher concentrations. A 0.025 mol 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 a constant incubation time of 5 min, an equilibration temperature of 40°C is sufficient for maximum recovery of the mercury.

As the surfactant-rich phase was very viscous, ethanol was added to the surfactant-rich phase after CPE to facilitate its transfer into the spectrophotometric cell. The surfactant-rich phase was diluted to 0.50 mL with ethanol to obtain an appropriate amount of sample for transferring and measuring the sample absorbance.

3.2 *Analytical parameters*

Under the optimum conditions described above, a calibration graph was constructed by CVAAS and spectrophotometry. The calibration graph obtained by CVAAS was linear in the range of 0.40–40.00 ng mL^{-1}. The calibration equation was $A = 0.014C + 0.003$ with a determination coefficient of 0.9987 ($n = 15$), where A is the absorbance of the sample at 253.7 nm corrected against blank solution, and C is the concentration of Hg^{2+} in the sample solution in ng mL^{-1}.

The calibration graph obtained by spectrophotometry was linear in the range of 10.0–400.0 ng mL^{-1}. The calibration equation was $\Delta A = 1.20 \times 10^{-3}C – 1.80 \times 10^{-3}$ with a determination coefficient of 0.9995 ($n = 15$), where ΔA is the difference between the absorbance of the sample and blank surfactant rich phase at 330 nm, and C is the concentration of Hg^{2+} in the sample solution (ng mL^{-1}).

The limit of detection, defined as $C_L = 3S_B/m$, [31] where C_L, S_B, and m are the limit of detection, standard deviation of the blank, and slope of the calibration graph, respectively, was 0.10 ng mL^{-1} for CVAAS and d 3.0 ng mL^{-1} for spectrophotometry. S_B was obtained from 10 determinations of the blank solutions in both CVAAS and spectrophotometry.

The preconcentration factor, f_c, defined as the ratios of the mercury 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 mercury concentration:

$$f_c = C_s/C_0$$

where C_s is the mercury 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 mercury (ng mL^{-1}). The preconcentration factor was obtained for the initial concentration of 5 ng mL^{-1} as 97.44 ± 0.8 ($n = 3$).

As for the determination of mercury in the surfactant-rich phase, the micellar extract (0.1 mL) was diluted to 0.5 mL, and the preconcentration factor for the proposed method is 19.5 ± 0.16 ($n = 3$).

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 10.0.

The accuracy of the method was evaluated by studying the analytical recovery, since no certified reference material was available. To evaluate the accuracy and precision of the method, a series of independent standard samples was used. The concentration of standard mercury samples varied between 1.0 and 20 ng mL^{-1} in CVAAS and between 20.0 and 200.0 ng mL^{-1} in spectrophotometry. The results showed that the RSD for the determination of different concentrations of Hg^{2+} was in the range of 2.10–3.12% by CVAAS and in the range of 0.76–2.51.0% by spectrophotometry. The absolute value of the relative error was $\leq$5% by CVAAS and $\leq$4.3% by spectrophotometry.

3.3 *Selectivity*

The effect of foreign ions on the determination of Hg^{2+} by the proposed methods was investigated. The following ions did not interfere at 10 µg mL^{-1} in the preconcentration and determination of 0.10 µg mL^{-1} Hg^{2+} by spectrophotometry: Na^+, K^+, NH_4^+, Li^+, Ca^{2+}, Mg^{2+}, Ba^{2+}, Sr^{2+}, Cr^{3+}, Ni^{2+}, Co^{2+}, Zn^{2+}, Pb^{2+}, Cl^-, Br^-, SO_4^{2-}, NO_3^-, PO_4^{3-}, SiO_3^{2-}, SCN^-, NO_2^-, $S_2O_3^{2-}$, SO_3^{2-}, IO_3^-, ClO_4^-, $CH_3CO_2^-$, Be^{2+}, Bi^{3+}, V(V), As(III), and Fe^{3+}. The ions Cu^{2+}, Bi^{3+}, and Cd^{2+} produced positive interference. The interfering effect of Cu^{2+} up to 5 µg mL^{-1} was completely removed by the addition of 10 µg mL^{-1} of sodium thiosulphate to the solution. The interfering effects of these ions are due to the extraction of the iodine, produced by the reaction of iodide with Cu^{2+}, and complexes of Bi^{3+} and Cd^{2+} with iodide into the surfactant-rich phase that absorb at 330 nm.

As the results show, excessive amounts of common cations and anions do not interfere with the determination of trace quantities of mercury. The cations and anions investigated at 10 µg mL^{-1} did not interfere with the preconcentration and determination of 25 ng mL^{-1} of Hg^{2+} by CVAAS.

3.4 *Application*

The proposed method was applied to mercury determination in natural waters. The water samples were analysed, and none was found to contain mercury. To identify potential matrix effects of the water samples, they were spiked with Hg^{2+} at variable concentrations. Sodium thiosulphate solution was added to the samples to eliminate possible Cu^{2+} interferences. The results are given in table 1. The recoveries are close to 100% and indicate that there is no serious interference in such water samples.

4. Conclusion

The results show that although CVAAS offers more selectivity and lower limits of detection for the determination of preconcentrated mercury than spectrophotometry, the present method is cheaper, uses simpler instrumentation [27], and provides a higher

Table 1. Determination of mercury added to water samples.

Sample	Hg^{2+} concentration (ng mL^{-1}) Added	Found	Recovery (%, $n = 5$)
CVAAS			
Spring water	0	1.9 ± 0.03	–
	4	5.72 ± 0.05	96.5
	8	9.96 ± 0.08	101
	15	17.31 ± 0.02	103
	25	26.76 ± 0.05	99.6
Spectrophotometry			
Tap water	15	15.07 ± 0.65	100.5
	30	29.91 ± 0.25	99.7
	50	49.20 ± 0.68	98.4
	100	102.10 ± 0.54	102.1
Spring water	40	42.00 ± 0.23	105
	65	67.47 ± 0.37	103.8
	90	86.67 ± 0.49	96.3
	150	147.00 ± 0.51	98
River water	20	20.46 ± 0.32	102.3
	35	35.28 ± 0.16	100.8
	85	87.98 ± 0.24	103.5
	120	118.92 ± 0.32	99.1

selectivity and sensitivity [28] than others. The proposed low-cost procedure is suitable for the determination of trace quantities of mercury in real samples. The surfactant has been used for preconcentration of mercury in water, and thus toxic solvent extraction has been avoided.

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