

Short communication

Spectrophotometric determination of mercury in water samples after cloud point extraction using nonionic surfactant Triton X-114

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ABSTRACT

A cloud point extraction process using the nonionic surfactant Triton X-114 for extracting mercury from aqueous solutions was investigated. The method is based on the complexation reaction of Hg(II) with Thio-Michler's Ketone (TMK) and micelle-mediated extraction of the complex. The optimal extraction and reaction conditions (e.g., pH, reagent concentration, effect of time) were studied, and the analytical characteristics of the method (e.g., limit of detection, linear range) were obtained. Linearity was obeyed in the range of 5.0–80.0 ng mL⁻¹ of Hg(II) ion. The detection limit of the method was 0.83 ng mL⁻¹ of Hg(II) ion. The interference effect of some anions and cations was also tested. The method was applied to the determination of mercury in water samples.

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1. Introduction

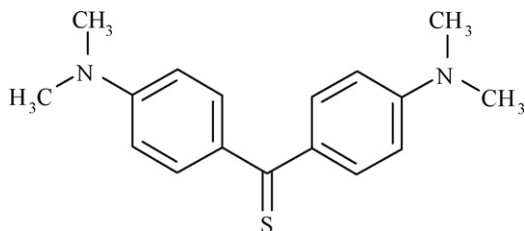
Mercury is one of the most toxic heavy metals. It enters the environment as metallic, inorganic and organic mercury compounds through various industries like pulp and paper industry, gold and silver mining, electrical industry, paints fungicides and pharmaceuticals. The toxicity of mercury depends on its chemical species and it is found that organomercurials are more toxic than inorganic mercury compounds [1,2]. Various determination methods of trace mercury have been continuously developed not only for monitoring the component but also for controlling its presence in the environment [3,4]. Different methods including cold vapour generation-atomic spectrometry (CV-AAS) [5], cold vapour generation-atomic fluorescence spectrometry (CV-AFS) [6], inductively coupled plasma optical emission spectrometry (ICP-OES) [7], inductively coupled plasma mass spectrometry (ICP-MS) [8] and electrothermal atomization atomic absorption spectrometry (ETAAS) [9] have been reported for determination of mercury. Usually a preconcentration step has been needed for mercury determination in several environmental samples [10]. A scheme of preconcentration can thus be proposed mediated by surfac-

tants instead of liquid–liquid extraction mediated by organic solvents.

Micellar extraction with nonionic surfactants at cloud point is a highly effective method for microcomponents preconcentration, which has been developed, intensively in recent years [11–15]. The aqueous solutions of some nonionic surfactants exhibit cloud point or turbidity above a certain temperature. The temperature at which this phenomenon occurs is called cloud point temperature and the methodology is known as cloud point extraction [16,17]. When solutions containing nonionic surfactants are heated above the cloud point temperature, two phases are formed. The first one is a surfactant-rich phase containing high concentration of surfactant and the analyte, the other one is the aqueous phase containing low concentration of surfactant. The surfactant-rich phase containing the analyte is separated, diluted with small volume of a solvent and the analyte is determined by suitable techniques. Cloud point extraction procedure is an easy, safe rapid and inexpensive methodology which has been designed for the separation, purification and preconcentration of a variety of substances including metal ions and organic compounds [18–21].

This paper describes a novel and sensitive cloud point extraction and spectrophotometric methods for the determination of mercury in water samples [22]. The method is based on the micelle-mediated extraction of the complex of Hg²⁺ with TMK (Scheme 1). A nonionic surfactant, Triton X-114, was chosen as the extraction agent.

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Scheme 1. Chemical structure of Thio-Michler's ketone.

2. Experimental

2.1. Apparatus

A Hewlett-Packard 8453 diode array spectrometer controlled by a Hewlett-Packard computer and equipped with a 1-cm path length quartz cell. A Horiba M-12 pH meter furnished with a combined glass-saturated calomel electrode was calibrated with at least two buffer solutions at pH 3.00 and 9.00. A centrifuge (Sigma 3K30) was used to accelerate the phase separation process. A thermostated bath maintained at the desired temperature was used for the cloud point temperature experiments.

2.2. Reagents

All reagents were of analytical reagent grade. The water utilized in all studies was double-distilled and deionized. Stock solution of Hg(II) ($1000 \mu\text{g mL}^{-1}$) was prepared by dissolving appropriate amounts of their corresponding salts in deionized water. Triton X-114 (Fluka, Buches, Switzerland) was used without further purification. Stock solution $1.1 \times 10^{-3} \text{ mol L}^{-1}$ of Thio-Michler's Ketone (TCI, Shanghai, China) was prepared by dissolving the reagent in acetone (Merck, Darmstad, Germany). Aqueous 5% (w/v) solution of Triton X-114 was prepared by dissolving 5 g in 100 mL of distilled water. A buffer of pH 3 was prepared by using sodium acetate (0.1 mol L^{-1}) and hydrochloric acid (Merck, Darmstad, Germany) at appropriate concentrations.

2.3. Procedure

For cloud point extraction, 1.2 mL Triton X-114 5%, 1 mL TMK $1.1 \times 10^{-3} \text{ mol L}^{-1}$ and 5 mL of buffer acetate (pH 3), in a 50 mL flask were added and a proper amount of mercury was added to it, and diluted to 50 mL by distilled water, then, the whole of solution transport to 50 mL tube. The tubes were kept for 15 min in the thermostatic bath at 50°C . Subsequently, separation of the phases was achieved by centrifugation for 10 min at 4000 rpm. The phases were cooled down in an ice bath in order to increase the viscosity of the surfactant-rich phase. The bulk aqueous phase was easily decanted by tilting the tube. The surfactant-rich phase in the tube was made up to 1.5 mL by adding ethanol. The absorbance was measured at the wavelength of maximum absorbance of the complex, 570 nm.

2.4. Analysis of water samples

Prior to the preconcentration procedure, all the water samples were filtered through a $0.45 \mu\text{m}$ pore size membrane filter to remove suspended particulate matter and then were stored at 4°C in the dark.

3. Results and discussion

Fig. 1 shows the absorption spectra for the individual metal complex in surfactant-rich phase against reagent blank. The mercury

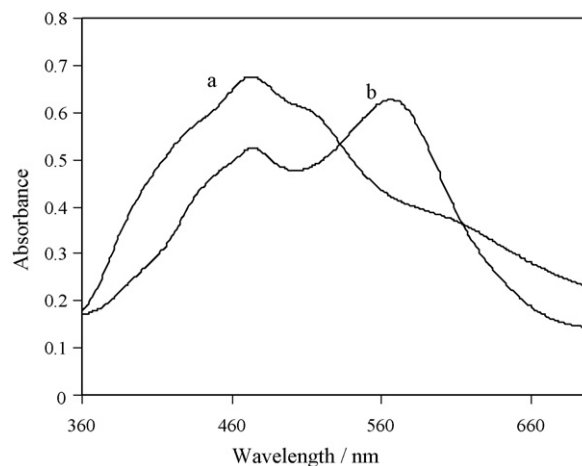


Fig. 1. Absorption spectra of (a) $2.2 \times 10^{-5} \text{ mol L}^{-1}$ of TMK and (b) its complex with 60 ng mL^{-1} of mercury at pH 3.0 after cloud point extraction.

complex of TMK is insoluble in water but easily dissolved in micelles such as Triton X-114.

3.1. Cloud point extraction method

3.1.1. Effect of pH

The separation of mercury ion by cloud point 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. pH plays a unique role on metal-chelate formation and subsequent extraction. Fig. 2 shows the influence of pH on the absorbance of the mercury complex at 570 nm. As can be seen, at pH 3 maximum extraction efficiency was obtained. Hence, pH 3 was chosen as the working pH.

3.1.2. Effect of TMK concentration

The effect of concentration of TMK on analytical response is shown in Fig. 3. As it is seen for mercury complex, the signal increases up to a known concentration of TMK, reaching a plateau, which is considered as complete extraction. A concentration of $2.2 \times 10^{-5} \text{ mol L}^{-1}$ of TMK was chosen as the optimum.

3.1.3. Effect of Triton X-114 concentration

The nonionic surfactant Triton X-114 was chosen because of its commercial availability in a high purified homogenous form,

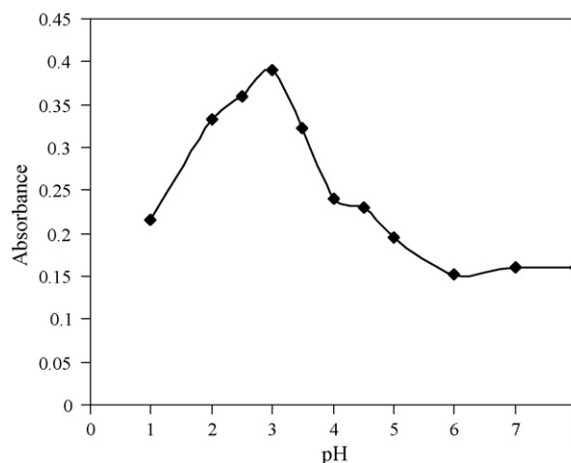


Fig. 2. Effect of pH on the absorbance of the complex. Conditions: 0.12% (w/v) Triton X-114, $2.2 \times 10^{-5} \text{ mol L}^{-1}$ TMK and 25 ng mL^{-1} of mercury.

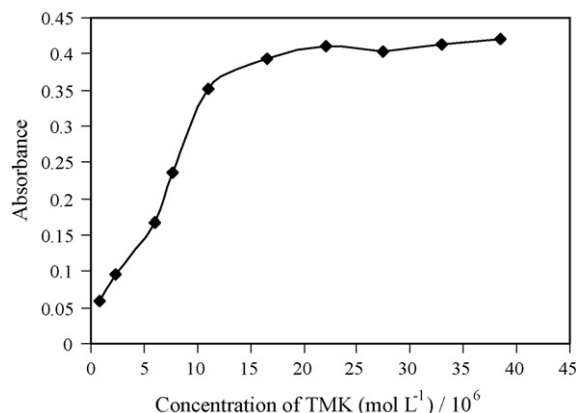


Fig. 3. Effect of TMK concentration on the absorbance of the complex. Conditions: 0.12% (w/v) Triton X-114 and 25 ng mL⁻¹ of mercury at pH 3.

low toxicological properties and cost. Also, the high density of the surfactant-rich phase, facilitates phase separation by centrifugation. Additionally the cloud point (~25–30 °C) of Triton X-114 permits its use in the extraction and/or preconcentration of a large number of molecules and chelate. According to the carried investigation, for this determination, Triton X-114 is more suitable than Triton X-100. The variation of absorbance at λ_{\max} of complex Hg(II)–TMK as a function of the concentration of Triton X-114 is shown in Fig. 4. A concentration of 0.12% (w/v) was chosen as optimum concentration for the determination of mercury. At lower concentrations, the extraction efficiency of complex is low probably because of the inadequacy of the assemblies to entrap the hydrophobic complex quantitatively.

3.1.4. Effect of the equilibrium temperature and time

It was desirable to employ the shortest equilibrium time and the lowest possible equilibrium temperature, as a compromise between completion of extraction and efficient separation of phases. The dependence of extraction efficiency upon equilibrium temperature and time was studied over ranges of 25–70 °C and 2–30 min, respectively. The results showed that an equilibrium temperature of 50 °C and an equilibrium time of 10 min were adequate to achieve quantitative extraction.

3.1.5. Effect of centrifugation time

A centrifugation time of 10 min at 4000 rpm was selected as the optimum, since complete separation occurred at this time, and

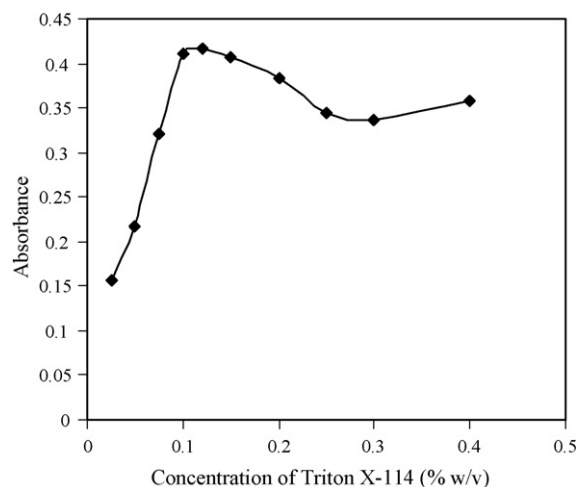


Fig. 4. Effect of Triton X-114 concentration on absorbance of the complex. Conditions: 2.2×10^{-5} mol L⁻¹ TMK and 25 ng mL⁻¹ of mercury at pH 3.

no considerable improvement was observed for longer periods of time.

3.1.6. Effects of added electrolyte

The cloud point of Micellar solutions can be controlled by addition of salts, alcohols, nonionic surfactants and some organic compounds (salting-out effects). To date, most of the studies conducted have shown that ionic strength has no appreciable effect on the extraction efficiency. An increase in the ionic strength in the cloud point extraction does not seriously alter the efficiency of extraction of the chemical forms. Moreover, the addition of a salt can markedly facilitate the phase-separation process, as demonstrated with some nonionic surfactant system, since it alters the density of the bulk aqueous phase [23]. It was observed that the addition of NaNO₃ within the interval of 0.1–1.0 mol L⁻¹ had no significant effect on the cloud point extraction efficiency.

3.2. Selectivity studies

TMK is known to be fairly selective for mercury at pH 3, and only palladium and gold can be interfered [24]. Interferences by palladium and gold just depend on TMK concentration. The concentration of palladium and gold is usually very low in most water samples and thus they have no interference in the extraction and determination mercury.

3.3. Analytical characteristics

Table 1 summarizes the analytical characteristics for with and without CPE, including regression equation, linear range, and limit of detection, reproducibility and preconcentration and improvement factors. The limit of detection, defined as $C_L = 3S_B/m$ (where C_L , S_B and m are the limit of detection, standard deviation of the blank and the slope of calibration graph, respectively), was 0.83 ng mL⁻¹. Because the amount of mercury in 50 mL of sample solution is measured after preconcentration by cloud point extraction in a final volume of 1.5 mL (0.5 mL surfactant-rich phase and 1.0 mL ethanol), the solution is concentrated by a factor of 33.3. The improvement factor defined as the ratio of the slope of the calibration graph for CPE method to that the calibration graph in micellar media without preconcentration, was 11. The relative standard deviation (R.S.D.) for three replicate measurements of 5 ng mL⁻¹ of mercury was 0.27%.

3.4. Determination of mercury in water samples

In order to validate the proposed methodology, the developed procedure was applied to the determination of mercury in tap water, river water, well water and waste water samples. For this purpose, 10 mL of each of the samples were preconcentrated with 0.12% (w/v) Triton X-114 and a TMK concentration of 2.2×10^{-5} mol L⁻¹, following the proposed procedure. The results are shown in Table 2. Also, water samples are analyzed by cold vapor method and the

Table 1

Analytical characteristics of the proposed method with CPE and without CPE.

Parameters	CPE	Without CPE
Concentration range (ng mL ⁻¹)	5.0–80.0	50.0–120.0
Slope	0.0055	0.0005
Intercept	0.2661	0.2855
Correlation coefficient (<i>r</i>)	0.9948	0.9968
R.S.D. (%) (<i>n</i> = 3)	5 (0.27) ^a	50 (0.41) ^a
LOD (ng mL ⁻¹)	0.83	12.3

^a Values in parentheses are R.S.D.

Table 2
Determination of mercury in the water samples by proposed method (ng mL^{-1}).

Sample	Mercury added	Mercury found (proposed method)	Recovery (%)	Mercury found (Cold vapor method)	Recovery (%)
Tap water	–	n.d. ^a	–	n.d.	–
	35	34.3 ± 0.2^b	98.0	34.8 ± 0.1	101.4
Well water	–	10.6 ± 0.1	–	10.2 ± 0.1	–
	40	49.6 ± 0.3	97.5	50.3 ± 0.2	100.2
River water	–	n.d.	–	n.d.	–
	40	42.3 ± 0.3	105.8	40.6 ± 0.1	101.5
Waste water	–	32.8 ± 0.2	–	33.0 ± 0.2	–
	50	85.6 ± 0.4	105.6	82.9 ± 0.2	99.8

^a Not detected.

^b Mean \pm S.D. ($n=3$).

results are given in Table 2. As it is seen, the results of proposed method and cold vapor technique are the same.

4. Conclusion

The combined advantages of the cloud point methodology (easy, safe, rapid and inexpensive) and the use of TMK as a selective and sensitive chromogenic reagent for mercury was utilized for their determination in water samples. The method gives a very low limit of detection and good R.S.D. values. The results of this study clearly show the potential and versatility of this method, which could be applied to monitoring mercury spectrophotometrically in various water samples.

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