

Spectrophotometric Determination of Trace Hg(II) in Cetyltrimethylammonium Bromide Media

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The simple and convenient determination of trace Hg(II) with its 2-mercaptobenzothiazole (MBT) complex in cetyltrimethylammonium bromide (CTAB) media has been studied. The UV-visible spectrum of Hg(II)-MBT complex in CTAB media had a good sensitivity and reproducibility. The Hg(II)-MBT complex in CTAB solution was very stable at pH 10.0 and could be quantitatively complexed if MBT were added to the sample solution more than 10 equivalent of Hg(II). The optimum concentration of CTAB was 0.001%. The calibration curve of Hg(II)-MBT complex with good linearity ($R^2 = 0.9985$) was obtained at the concentration range between 1.0×10^{-7} and 1.0×10^{-5} M in 0.001% CTAB media. The detection limit was 3.1×10^{-8} M (6.2 ng mL^{-1}). Hg(II) in the synthetic samples and in the wastewater of the university's wastewater tank and the industrial wastewater tank could also be determined. Based on the experimental results, this proposed technique could be applied to the simple and convenient determination of trace Hg(II) in real samples.

Key Words : Mercury, 2-Mercaptobenzothiazole, Cetyltrimethylammonium bromide (CTAB), UV-Visible spectrophotometry

Introduction

Mercury is so volatile that it could be exposed easily to human environment. It would cause a neurological damage and even result in death.¹ Generally, the concentrations of Hg in environmental samples are relatively low unless exposed in some industrial area. Total mercury concentrations in natural waters ranged from 0.2 to 100 ng L^{-1} ,² while methylmercury levels were known to even lower level, about 0.05 ng L^{-1} .³ However, mercury in contaminated environmental materials may exist at levels of micrograms per liter. The simple and convenient methods are required to permit the determination of Hg(II) in the contaminated samples. Techniques which can determine low concentration of mercury in water and biological materials have been developed, including inductively coupled plasma mass spectrometry,^{4,5} inductively coupled plasma atomic emission spectrometry,^{6,7} cold vapor atomic absorption spectrometry,^{8,9} and anodic stripping voltammetry.¹⁰

In some techniques, the preconcentration should be performed to determine ultratrace Hg(II). However, these procedures could reduce the accuracy of the determination and require a longer time in handling of sample. Among these preconcentration techniques, cold vapor atomic absorption spectrometry has widely been used^{11,12} with merits such as high sensitivity and little interference effects, but has somewhat poor precision and accuracy.¹³ Inductively coupled plasma-atomic emission spectrometry and inductively coupled plasma-mass spectrometry are useful in determining ultratrace Hg(II) without preconcentration.^{14,15} However, these instruments are very expensive and costly for the maintenance.

To determine trace Hg(II) with UV-visible spectrometry, various chelating agents such as dithizone,¹⁶ diphenyl-carbazone,¹⁷ and di- β -naphthylthiocarbazone¹⁸ have been used. This technique should be performed with solvent extractions that are time-consuming and tedious, have lower accuracy and precision, and usually involve harmful solvent. One of these widely used techniques is dithizone method. But this method has limitations due to the serious interference by Cu(II) as well as the photosensitivity of the mercury-dithizonate complex.¹⁹

Organic micellar media are very useful in analytical applications, including the improved analyte sensitivity in UV-visible spectrometric methods²⁰⁻²³ and in fluorescence methods and quenching processes.²⁴ Especially, the surfactants have been used to improve UV-visible spectrophotometric determination of metal ions with complexing agents. Generally, the metal-chelate complexes formed in the surfactant media are more stable than those formed in the absence of surfactant.²⁵

In the present study, the convenient and simple determination of trace mercury(II) was spectrometrically performed with its 2-mercaptobenzothiazole complex in cationic CTAB media without an extraction procedure.

Experimental Section

Instrumentation. A Hewlett-Packard 8453A single beam diode array spectrometer was used to measure the absorbance of Hg(II)-MBT complex in CTAB media. To determine Hg(II) in university's wastewater samples, a HP 4500 ICP-MS spectrometer was also used. To adjust the pHs and prepare the buffer solution, a Bantex model 300A digital pH meter equipped with a combined glass and calomel electrode was used.

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Reagents and solutions. All chemicals, such as $\text{Hg}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ (Fisher Co.) and 2-mercaptobenzothiazole (MBT) (Wako Co.), were analytical or guaranteed-grade reagents. Standard $\text{Hg}(\text{II})$ was made from 10^{-2} M stock solution. The stock solution of $\text{Hg}(\text{II})$ was made in 0.1 M HNO_3 , and stored at less than pH 2.0. A 0.01% (w/v) cetyltrimethylammonium bromide (CTAB) (BHD Co.) solution was prepared by dissolving 0.01 g of CTAB in a 100 mL volumetric flask with stirring; MBT solution was prepared by dissolving in ethyl alcohol to give a 10^{-3} M solution. Borax buffer (pH 10.0) was prepared by mixing 0.025 M borax and 0.1 M NaOH. To investigate the interfering effects by various species, 1.0×10^{-2} M stock solutions were used. Deionized water prepared by a Barnstead system (Barnstead Co.) was used throughout all experimental procedures.

Calibration curve. Standard $\text{Hg}(\text{II})$ solutions were prepared in the range of 1.0×10^{-7} M~ 1.0×10^{-5} M. Several aliquots of $\text{Hg}(\text{II})$ standard solutions were taken in 10 mL volumetric flasks, and 0.3 mL of 10^{-3} M MBT and 1.0 mL of 0.01% CTAB were added to each flask. Then it was filled to the mark with borax buffer solution (pH 10.0). After 30 minutes of leaving it as it stood, a calibration curve of $\text{Hg}(\text{II})$ was constructed by a UV-visible spectrophotometer. The regression equation was obtained with the method of least squares. Using this linear equation, we determined the correlation coefficient (R^2) and the detection limit. The detection limit is defined as the sample concentration giving a signal equal to the blank average signal plus three times the standard deviation of the blanks.²⁶

Applications to real samples. The university wastewater and the industrial wastewater were taken as a real sample after suspended matter or particles were filtered out with a glass filter (1-G-1). A synthetic sample was prepared so that the concentration of $\text{Hg}(\text{II})$ was 4.0×10^{-6} M, that of NaNO_3 was 5.0×10^{-4} M, and that those of $\text{Cu}(\text{NO}_3)_2$, $\text{Cd}(\text{NO}_3)_2$, $\text{Ni}(\text{NO}_3)_2$, $\text{Bi}(\text{NO}_3)_3$ and $\text{Pb}(\text{NO}_3)_2$ were 1.0×10^{-5} M. To determine $\text{Hg}(\text{II})$ with the method of standard addition, several 5.0 mL aliquots of the university wastewater, the industrial wastewater and the synthetic samples were taken in 10 mL volumetric flasks. Exactly 0.0, 0.2, 0.4, 0.6, 0.8, and 1.0 mL of a standard solution containing 5.0×10^{-5} M of $\text{Hg}(\text{II})$ were also added to each flask. Then, 0.3 mL of 10^{-3} M EDTA, 0.3 mL of 10^{-3} M MBT and 0.1 mL of 0.01% CTAB were added, and the flask was filled to the mark with borax buffer (pH 10.0).

Results and Discussion

Absorption spectra of $\text{Hg}(\text{II})$ -MBT complex. After $\text{Hg}(\text{II})$, MBT and CTAB were taken in a 10 mL volumetric flask so that their concentrations were 3.0×10^{-6} M, 3.0×10^{-5} M and 0.001%, respectively, the solution was diluted to the mark with borax buffer (pH 10.0). Then, the absorption spectrum of $\text{Hg}(\text{II})$ -MBT complex was obtained (Figure 1). The analytical sensitivity and the reproducibility in this spectrum were good in CTAB media. The phenomenon

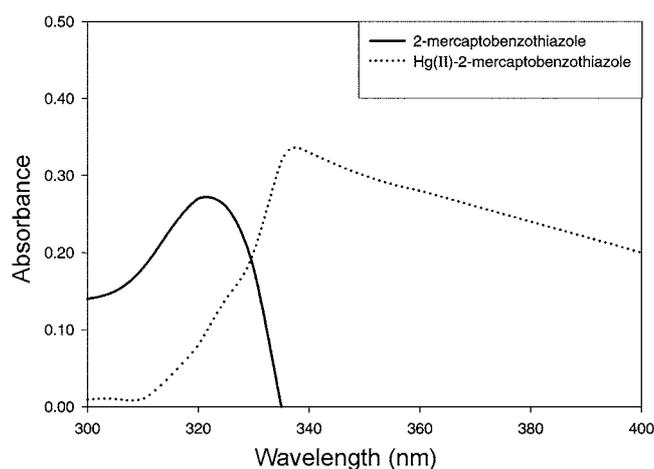


Figure 1. UV-Visible spectra of $\text{Hg}(\text{II})$ - 2-mercaptobenzothiazole (3.0×10^{-6} M) and 2-mercaptobenzothiazole (1.0×10^{-5} M) in 0.001% CTAB media at pH 10.0.

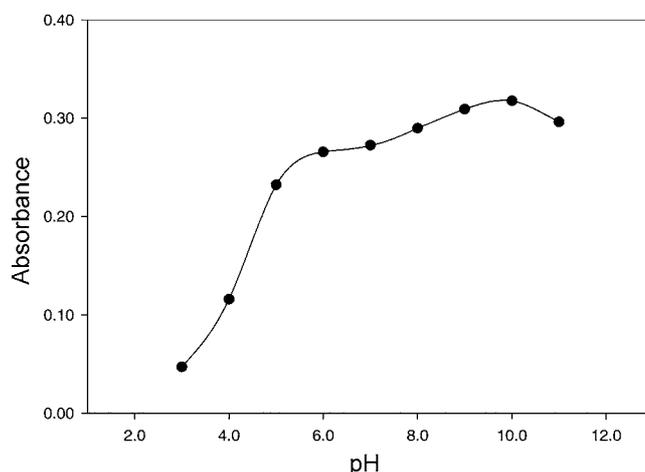


Figure 2. Effects of pH on the absorbance of $\text{Hg}(\text{II})$ - 2-mercaptobenzothiazole (3.0×10^{-6} M) in 0.001% CTAB media.

seems to have been caused by the electrostatic and hydrophobic interactions between $\text{Hg}(\text{II})$ -MBT complex and surfactant.²⁷ And after 10 mL chloroform solution of 10^{-3} M MBT was added to 10 mL of 3.0×10^{-6} M $\text{Hg}(\text{II})$ solution which was buffered at pH 10.0 in a 100 mL separatory funnel, it was shaken for 30 min. Unfortunately, the reproducible absorption spectra of $\text{Hg}(\text{II})$ -MBT in chloroform could not be obtained.

pH effect. The influence of pH on the absorbance of $\text{Hg}(\text{II})$ -MBT (3.0×10^{-6} M) complex in 0.001% CTAB media was investigated (Figure 2). $\text{Hg}(\text{II})$ -MBT complex showed the maximum absorption at pH 10.0. From this result, we realize that $\text{Hg}(\text{II})$ -MBT complex was quantitatively formed and well dissolved in CTAB media at pH 10.0. We assume that the reaction to form this complex could have competed against hydroxide precipitation above pH 10.0 and at acidic pH, as the sulfur atom in the chelating site of MBT has more affinity power with proton at a higher concentration of protons.

Concentration of MBT. It is known that $\text{Hg}(\text{II})$ is

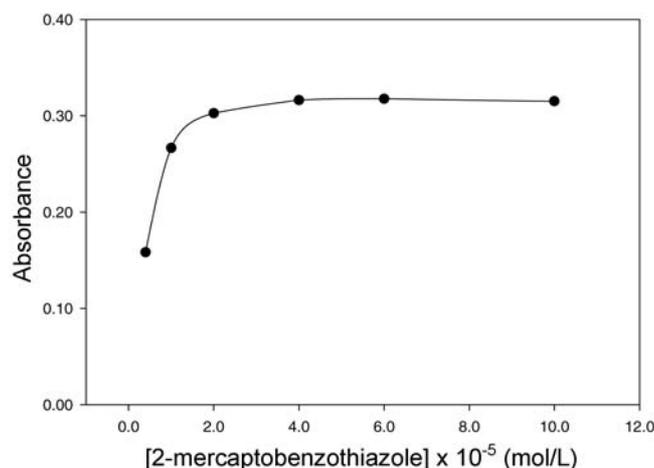


Figure 3. The absorbance changes of Hg(II) – 2-mercaptobenzothiazole (3.0×10^{-6} M) on the concentration of 2-mercaptobenzothiazole in 0.001% CTAB media at pH 10.0.

stoichiometrically combines with MBT to form 1:2 complex.²⁸ For a metal complex to be formed quantitatively, however, one must add more chelating agent to the sample solution. Figure 3 shows how the absorbance of Hg(II)-MBT complex changes with the concentration of MBT. We found that when MBT was added to more than 10 equivalent of Hg(II), the absorbance was high and constant

Concentration of CTAB. When the concentration of CTAB surfactant exceeds its critical micelle concentration, the homogeneous micelle solution is formed at a point where Hg(II)-MBT complex can be well dissolved. Due to high viscosity, the concentrated CTAB media was hard to handle, whereas those with low viscosity under diluted conditions could not form a micelle or make a homogeneous solution of complex as the polarity of aqueous solution was not lowered.

With the concentration of CTAB varying from 0.0005% to 0.05% at pH 10.0, the absorbance of Hg(II) (3.0×10^{-6} M) complex was investigated and the results are shown in Figure 4. The maximum absorbance was obtained when the

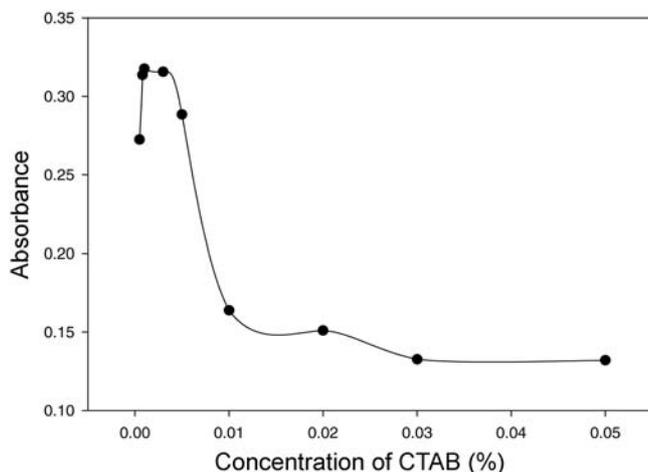


Figure 4. Effect of the concentration of CTAB on the Hg(II) – 2-mercaptobenzothiazole (3.0×10^{-6} M) complex at pH 10.0.

concentration of CTAB was 0.001% to 0.003%. We assumed that although the concentrations of these CTAB were somewhat less than critical micelles concentration (0.0013 M, 0.047%),²⁹ Hg(II)-MBT complex was homogeneously dissolved in surfactant media. Here, the selected concentration of CTAB was 0.0001%.

To investigate the effect of types of surfactants, Triton X-100 as nonionic and sodium dodecylsulfate as anionic surfactant were used. In given concentration range (1.0×10^{-7} M~ 1.0×10^{-5} M), calibration curve of Hg(II)-MBT could not be obtained in both nonionic Triton X-100 and anionic sodium dodecylsulfate media. Cationic surfactants have been used rather than anionic or nonionic surfactants to determine metal ions by UV-Vis spectrophotometry.³⁰ Because a metal ion is a cation, the electrostatic attractive interaction between a metal ion and cationic surfactant is not present, and the complex-forming process is not affected.

To investigate the stability of Hg(II)-MBT complex in CTAB media at pH 10.0, the absorbance was measured as the function of time. The absorbance decreased slowly from the beginning of measurement to 30 min (0.0013 absorbance unit/min.) and after 30 min, the variation of absorbance was not observed. It is assumed because the time that reached at dynamic equilibrium between Hg(II)-MBT complex and CTAB surfactant was relatively slow in incomplete micelle solution.

Interference effect. MBT combines with several metal ions such as Cu(II), Bi(III), Ni(II) and so forth to form a stable and slightly soluble metal complex in aqueous solution. So, when Hg(II) is determined with MBT, the other metal ions in real samples may interfere with Hg complex-forming. The possible interference effects of concomitant ions on the determination of Hg(II) were investigated under the optimum conditions given above and are shown in Table 1. Cu(II) and Bi(III) were interfered with more strongly than any other ions, and unfortunately, this interference could be partially (~85%) eliminated by adding EDTA to be 3.0×10^{-5} M. However, when EDTA was added to be above 3.0×10^{-5} M, the releasing effect was diminished. It is assumed that at pH 10, Hg(II) forms an MBT complex that is more stable than the corresponding EDTA complex and the EDTA complexes of Bi(III) and Cu(II) is more stable than their MBT complexes.

Application to real samples. This proposed technique is

Table 1. Tolerance limits^a for interfering ions in 3.0×10^{-6} M Hg(II) solution

Mole ratio of interfering ion to Hg(II)	Ions
100	SCN ⁻ , NH ₃ ,
50	S ₂ O ₃ ²⁻ , Cl ⁻
25	Cd(II), Zn(II), Br ⁻
10	Ni(II), Co(II), Pb(II), CN ⁻ , I ⁻
5	Cu(II), Bi(III)

^aTolerance limit is the maximum mole ratio of interfering ion to Hg(II) in which the effect on the absorbance is less than 5%.

Table 2. Analytical data of Hg(II) in real and synthetic samples by the standard addition method

Samples	Measured (M) ^a		Recovery yield (%)
	This proposed method	ICP/MS	
University wastewater	$2.52(\pm 0.08) \times 10^{-7}$	$2.43(\pm 0.09) \times 10^{-7}$	
	$3.75(\pm 0.08) \times 10^{-7}$	$3.68(\pm 0.09) \times 10^{-7}$	
Industrial wastewater	$1.83(\pm 0.08) \times 10^{-7}$	$1.78(\pm 0.09) \times 10^{-7}$	
	$2.02(\pm 0.09) \times 10^{-7}$	$1.97(\pm 0.09) \times 10^{-7}$	
Synthetic sample (4.00×10^{-6} M)	$4.09(\pm 0.09) \times 10^{-6}$		102.3

^aThe average values were obtained from seven samples.

simpler and more easily applicable in determining Hg(II) in a solution than dithizone liquid extraction technique. A calibration curve was constructed at optimum conditions according to calibration curve procedure in experimental section. The dynamic range of Hg(II) was 1.0×10^{-7} M to 1.0×10^{-5} M and the regression equation was $1.046(\pm 0.008) \times 10^5 x + 0.002(\pm 0.001)$. The correlation coefficient (R^2) was 0.9985, showing a good linearity of calibration curve. Based on the signals of twenty-five blank solutions and the slope of calibration curve, it was found that the detection limit was 3.1×10^{-8} M (6.2 ng mL^{-1}).

The standard addition method was used to determine Hg(II) in real samples because of the incomplete release due to the interfering effects. Hg(II) in the wastewater at the university's wastewater tank and the industrial wastewater tank and in the synthetic sample were determined by this proposed technique and the results are shown in Table 2. The relative standard deviations representing the reproducibility were less than 5.0% in these measurements. Hg(II) in the university wastewater samples and the industrial wastewater samples were also determined by ICP-MS spectrometry. At 95% confidence level, no difference between results from the proposed and ICP-MS methods had been established. Therefore, this proposed technique could be applied to the determination of a ppb level of Hg(II) in real samples.

Conclusions

By using of Hg(II)-MBT in CTAB bromide media, a ppb level of Hg(II) could be determined simply, conveniently and reproducibly. Results from the proposed method and ICP-MS method were slightly different. In comparison with dithizone extraction method that was time-consuming, tedious and using harmful solvent, this technique had not those limitations but showed higher sensitivity. Detection limit and relative standard deviation of the measured data were 3.1×10^{-8} M (6.2 ng mL^{-1}) and less 5.0%, respectively. The proposed technique could be applied to the determination of Hg(II) in real samples.

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