

SPECTROPHOTOMETRIC METHOD FOR Hg(II) DETERMINATION IN AQUEOUS ENVIRONMENT USING ZINC-DITHIZONATE COMPLEX

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ABSTRACT

This article described the use of zinc-dithizonate for spectrophotometric determination of Hg(II) in aqueous environment. Zinc dithizonate was found to react selectively with Hg(II) to give a reddish yellow complex with optimum absorbance at pH 1.0. This complex was found to be useful for spectrophotometric determination of aqueous Hg(II) in the concentration range of 1.0 – 12.0 ppm. This method was also found to be reproducible with calculated relative standard deviation, RSD of 1.08%. At 1:1 mole ratio, interfering ions such as CH_3COO^- , Pb^{2+} and Ag^+ were found to interfere at degree of interference of more than 10.0%.

1. INTRODUCTION

Mercury, Hg(II) and its complexes are considered as the most harmful metal pollutant to human health because it is wide-spread in the lithosphere and water^{1,2}. Hg(II) could also disturb the nerves system and caused psychology and physical symptom³. Exposure to a small amount of Hg(II) vapour could lead to other complication like mental distability etc.

Standard methods for Hg(II) determination include cold vapour atomic absorption spectrophotometry^{4,5}, which based on the absorption of ultraviolet radiation at a wavelength of 253.7 nm by mercury vapour. Another method is interference-free determination of Hg(II) using a gold-plated piezoelectric crystal detector⁵, energy dispersive x-ray fluorescence⁶, atomic emission spectrometry⁷ and gas chromatography⁸. Some of the latest techniques reported in the literatures include the use of thiamine for Hg(II) florescence optosensing⁹, the use of graphite plate-filtration-electrothermal atomic absorption spectrometry for direct Hg(II) determination in atmospheric particulate matter¹⁰, total Hg determination by using electro-thermal vaporisation-inductively coupled plasma mass spectrometry¹¹ and the use of Hg(II) selective membrane electrode¹².

Dithizon is the main sulphophilic reagent that frequently been used for heavy metal detection¹³. It was chosen in this study because of its selectivity towards heavy metals and the reaction could be observed through significant colour changes¹⁴. Unfortunately, dithizone solution is not thermal- and photostable¹⁵ and therefore was left abandon for years until 1925 when Helmut Fischer found an application of this reagent for determination of some trace metals. One of the method used to overcome the problem of photo and thermal instability of dithizone is by complexing the reagent with metal such as zinc, Zn(II). The use of Zn(II)-dithizonate complex which is pink in colour, has been reported in the literature^{16,17,18}.

Our main interest is in immobilising Zn(II)-dithizonate complex on suitable solid supports for use as a reagent phase in the development of optical fibre sensor for aqueous Hg(II) determination. In our study, we found that in the presence of Hg(II), the immobilised complex was able to change its colour as in solution and could be used for Hg(II) concentration determination when coupled to the distal end of a glass optical fibre¹⁹. Since the use of the Zn(II)-dithizonate complex solution for Hg(II) determination has not been reported in the literature, we present in this paper a study which has been carried out by using this complex solution for spectrophotometric determination of Hg(II) in aqueous environment.

2. EXPERIMENT

2.1 Instrumentation

All absorbance measurements were carried out by using Shimadzu UV-Visible Spectrophotometer Model UV-260 with 1 cm quartz cells.

2.2 Chemicals and solution

Stock solution of Hg(II), 1000 µg/mL was prepared by dissolving 0.1618 g mercury (II) nitrate, $\text{Hg}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ in 0.2 M nitric acid and made the volume to 100.00 mL in volumetric flask. Lower concentration of Hg(II) solutions was obtained by serial dilution of the stock solution.

Dithizone 0.01% (w/v) was prepared by dissolving 0.0100g of dithizone in carbon tetrachloride and made up to 100 mL. The complex of zinc dithizonate was prepared by mixing 100 mL of 0.01% dithizone with 100 mL 1% zinc sulphate solution. The mixture was stirred using mechanical stirrer for 30 minutes.

Buffer solution pH 6.0 was prepared by following the standard method²⁰ where 500.00 mL 0.1 M potassium dihydrogen phosphate was mixed with 56.00 mL 0.1 M NaOH. The pH value of this solution was adjusted to pH 6.0 (or smaller pH values) by adding required amount of concentrated HCl. The pH of the solution was measured by using Corning pH meter Model 155.

2.3 Procedures

The absorption spectra for dithizone 0.01% solution, zinc dithizonate solution and Hg(II) dithizonate were recorded by using UV-Visible spectrophotometer. Hg(II)-dithizonate complex solution was prepared by mixing 5.00 mL Zn(II)-dithizonate solution with 5.00 mL of Hg(II) stock solution, 50.00 ppm. The aqueous phase was separated from the organic phase. The absorbance spectrum of the Hg(II)-dithizonate complex in the organic phase was recorded by using UV-Visible Spectrophotometer in the wavelength range of 350 – 700 nm.

The optimum pH for the Hg(II)-dithizonate complex formation was studied by mixing 2.50 mL Hg(II) stock solution in 50.00 volumetric flask and made to volume with buffer solution (pH 1.0 – 6.0). About 10.00 mL of this solution was taken and mixed with 10.00 mL of Zn(II)-dithizonate solution to form a Hg(II)-dithizonate complex. After removal of aqueous phase, the organic phase was analysed for absorbance measurement at wavelength of 488.8 nm.

For reproducibility studies, Hg(II) concentration of 50.00 ppm was used throughout the experiment. To this solution, 10.00 mL of Zn(II)-dithizonate solution was added. After shaking, the aqueous phase was removed and the organic phase was analysed using UV-Visible Spectrophotometer at wavelength of 488.8 nm. This experiment was repeated for 10 times using the same Hg(II) concentration but from different preparation.

An interference from some foreign ions was studied by introducing definite amount of interfering ions at 1:1 mole ratio, to the aqueous Hg(II) solution. The degree of interference of these ions was evaluated by measuring the absorbance of the complex in the presence and absence of the interfering ions.

Dynamic range of Hg(II) concentration was studied by using different concentration of Hg(II) i.e. 0.1, 0.3, 0.5, 0.7, 1.0, 3.0, 5.0, 7.0, 10.0, 30.0, 70.0 and 100.0 ppm. For each solution, 10.00 mL was taken and added to 10.00 mL of Zn(II)-dithizonate solution in volumetric flask. After shaking the content, the aqueous phase was removed and the organic phase was analysed by using UV-Visible Spectrophotometer.

The usefulness of the proposed method in real sample analysis was evaluated by determining the content of Hg(II) in river water samples. The river water samples were collected from Langat River and filtered with filter paper for suspended solid removal. Since the content of Hg(II) in the water sample was not detectable with the proposed method, the water samples were spiked with Hg(II) at three different concentration level i.e. 5 ppm, 7 ppm and 10 ppm before the analysis was carried out. The analysis of each concentration levels was repeated for three times.

3. RESULTS AND DISCUSSION

Figure 1 shows the absorption spectrum of dithizone alone and its complex with Zn(II). As shown, dithizone alone produced two absorption peaks, each at wavelength of 450.6 nm and 618.4 nm. This result is actually with a good agreement with what have been reported by Sandell & Onishi³ and Burger²¹ which reported absorption peak at around 450 nm and 620 nm. These two peaks are expected due to the tautomeric form of the reagent. Absorption peak at wavelength of 618.4 nm is correspond to the presence of keto structure whereas enol structure absorbed light at wavelength of 450.0 nm.

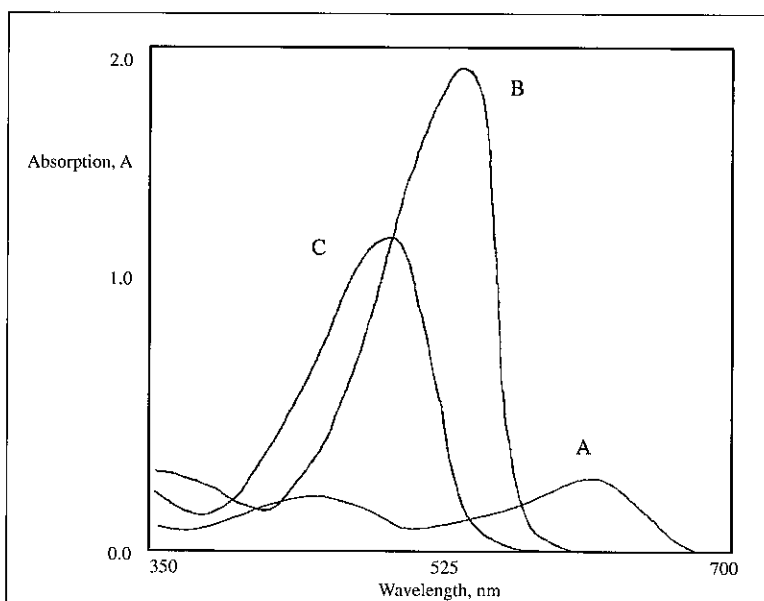


Figure 1: Absorption spectra of dithizone (A), Zn(II)-dithizonate complex (B) and Hg(II)-dithizonate (C).

Since dithizone is not stable and undergone photochromism process when exposed to light, the reagent has been complexed with Zn(II) in this study and this complex was found to be more stable than the reagent alone. The use of metal dithizonate complex was first suggested by Spevackova & Krivanek²². They reported that cations with extraction constant value of greater than metal-dithizonate complex, could replace the metal. By applying this concept, ion Zn(II) ion has been used for Zn(II)-dithizonate complex formation and the complex was later immobilised on a styrene-divinylbenzene copolymer¹⁴, hydrophobic gel¹⁷ and also silica gel surface²³. The column packed with immobilised Zn(II)-dithizonate gel functioned in a similar way as column packed with immobilised dithizone since Zn(II)-dithizonate gel could be easily converted to dithizone gel by passing 1.0 M mineral acid to the column. Lee *et al*¹⁶ on the other hand reported the use of immobilised Zn(II)-dithizonate on styrene-divinylbenzene for sub-ppm determination of Hg(II). The immobilised reagent was packed in the column and the acidified sample solution was introduced to the column. This method could be applied for environmental sample analysis.

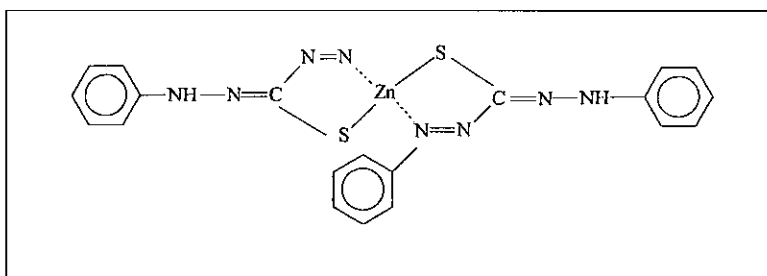
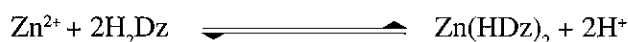
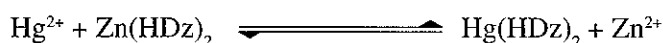


Figure 2: Chemical structure of Zn(II)-dithizonate complex.

As shown in Figure 1, Zn(II)-dithizonate complex gives a very intense absorption intensity at wavelength of 530.0 nm. Figure 2 shows the chemical structure of Zn(II)-dithizonate complex. According to Mawby & Irving²⁴, this complex consists of two dithizone ions which are coordinated in tetrahedral form to Zn(II) ion via two sulphur atoms and two nitrogen atoms. The chemical reaction between dithizone and Zn(II) to form Zn(II)-dithizonate complex is as follows:



According to Sandell & Onishi¹³, reaction between Zn(II)-dithizonate complex and Hg(II) ion will produce primer dithizonate complex i.e. Hg(II)-dithizonate complex which is red-yellowish in colour. As shown in Figure 1 Hg(II)-dithizonate complex absorbed strongly at wavelength of 488.8 nm. Sandell & Onishi¹³ reported that solution of primer Hg(II)-dithizonate complex in CCl_4 , absorbed at wavelength between 485.0 – 490.0 nm. Hg(II)-dithizonate complex is having the same chemical structure as for Zn(II)-dithizonate complex. The chemical reaction involved in the formation of Hg(II)-dithizonate complex is shown below:



The effect of pH to the complex formation in solution is summarised in Figure 3. The range of pH studied was pH 1.0 - 6.0. Complex formation at higher pH was not studied because of the tendency that Hg(I) ion will also be present and forming secondary dithizonate complex which having almost the same colour as for Hg(II). As can be seen in Figure 3, the optimum pH for the Hg(II)-dithizonate complex formation is pH 1.0. With this finding, buffer solution with pH 1.0 will be used for all preparation of Hg(II) solution.

Grant & Grant²⁵ defined reproducibility as a limit at which experimental results remain the same within experimental error when the experiment was carried out by different operators. In this experiment, reproducibility refers to the error generated when the same reagent solution was used to analyse different Hg(II) solution with the same concentration (50.0 ppm). For 10 different measurements, the result was shown in Figure 4. Statistical analysis carried out for these data revealed that the relative standard deviation, RSD for this experiment was 1.08%. The low RSD value indicates a very good reproducibility when the method is used for Hg(II) determination.

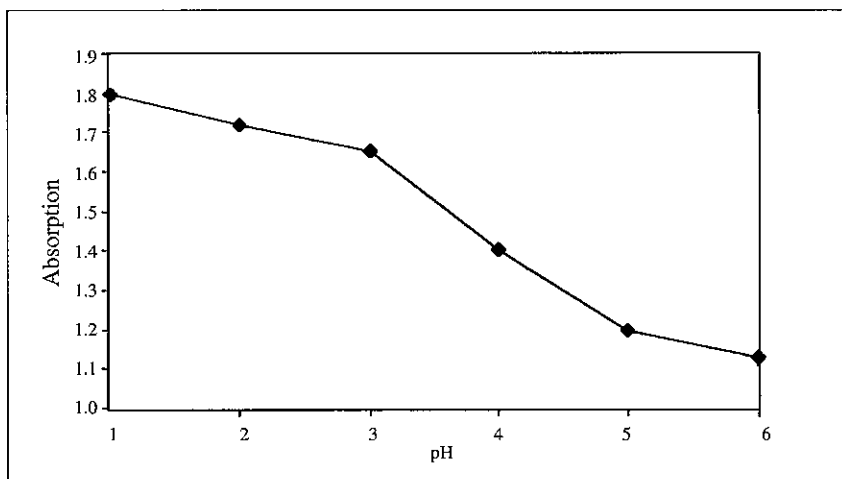


Figure 3: The effect of pH to the absorption intensity of Zn(II)-dithizonate complex solution.

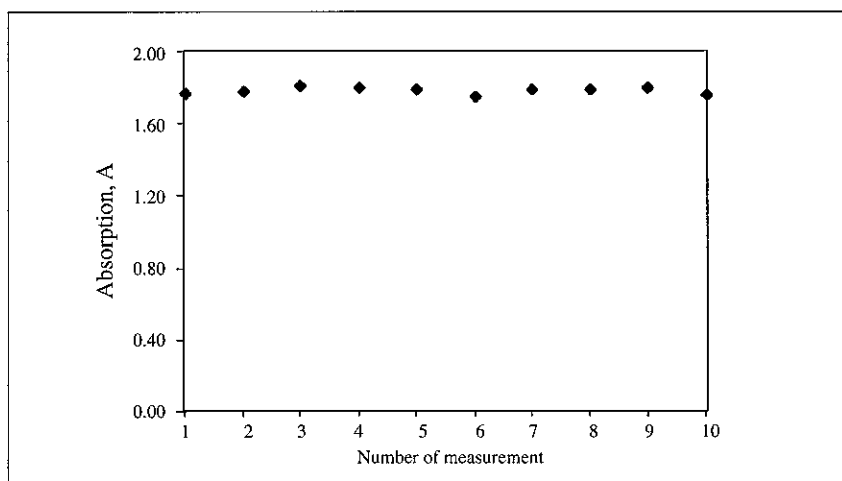


Figure 4: The reproducibility of the method for determination of the same concentration (50.0 ppm) of Hg(II).

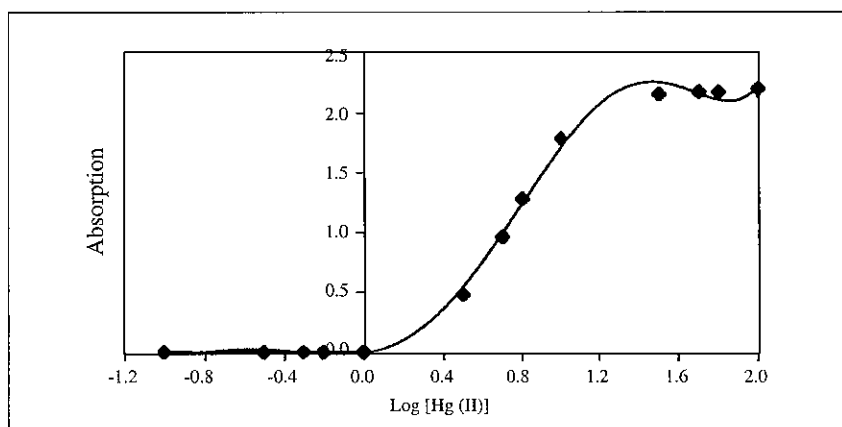


Figure 5: The response of the method over Hg(II) concentration range of 0.1 - 100.0 ppm.

Table 1 summarises the degree of interference measured from some foreign ions. At 1:1 ratio of Hg (II) to the interfering ion, the degree of interference was observed to be less than 20.00%. Interference from anions such as I⁻, Br⁻ and Cl⁻ are expected as they are chemically reactive to form metal halide compounds²⁶ whereas CH₃COO⁻ is known as a good electron donor. As shown in Table 1, CH₃COO⁻ gives the highest degree of interference whereas Fe³⁺ was found not to interfere at all during the analysis. Meanwhile EDTA was found to give a positive interference and this could be possibly due to the capability of EDTA to form a mixed ligand complex with unidentate ligand such as chloride which is available in the buffer solution. Formation of such complex has been reported in the literature²⁷. Except for Fe³⁺, all cations listed in Table 1 were reported to be capable of forming coloured metal dithizonate complex with the immobilised reagent¹³.

Table 1: The anions and cations interference during Hg(II) determination using Zn(II)-dithizonate complex solution.

Cations	Degree of Interference, %	Anions	Degree of Interference, %
Cu ²⁺	- 6.7	Cl ⁻	- 2.7
Pb ²⁺	- 15.8	Br ⁻	- 3.7
Ag ²⁺	- 10.2	I ⁻	- 2.9
Fe ²⁺	- 7.4	CH ₃ COO ⁻	- 18.9
Fe ³⁺	0.0	EDTA	+ 5.4

An attempt was also made in this study to determine the analytical working range of Hg(II) concentration when Hg(II)-dithizonate complex solution was used as a reagent. As shown in Figure 5, a linear relationship was obtained between the absorption intensity and the Hg(II) concentration in the range of 1.0 – 12.0 ppm. Using this calibration graph for determination of three known concentration of Hg(II) shows that this method having a relative error between -4.4% - +4.2%.

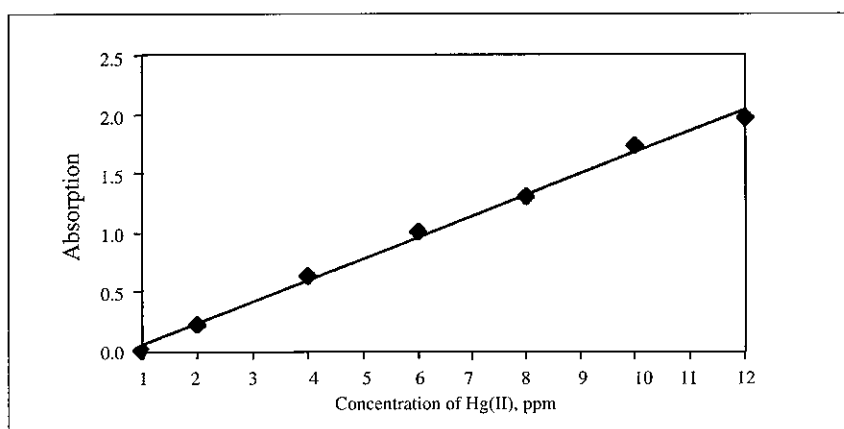


Figure 6: The dynamic range of Hg(II) concentration which produced linear response ($R = 0.9957$).

Table 2 shows the results obtained for determination of Hg(II) concentration in Langat River water. As can be seen, the spiked and the recovered values of the Hg(II) concentration are in good agreement. These are expected because the concentration of Hg(II) in Langat River was very small. Since the percent recovery is less than 100%, the proposed method might not be suitable for real sample analysis containing Hg(II) concentration less than 1 ppm.

Table 2: The use of the proposed method for Hg(II) determination in river water.

Langat River water sample	Hg(II) spiked (ppm)	Hg(II) recovered (ppm)	Recovery, %
1	5.0	4.8 ± 0.2	96.0%
2	7.0	6.9 ± 0.3	98.6%
3	10.0	9.7 ± 0.3	97.0%

4. CONCLUSION

The present work shows that Hg(II)-dithizonate complex solution could be used for determination of Hg(II) concentration in aqueous environment. The method was found to be reproducible with RSD value of 1.08% and optimum signal was obtained at pH 1.0. A linear relationship between absorption intensity and Hg(II) concentration was obtained in the concentration range of 1.0 -12.0 ppm.

5. ACKNOWLEDGEMENT

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