

Spectrophotometric Determination of Mercury with Iodide and Rhodamine B

(Penentuan Spektrofotometri untuk Merkuri dengan menggunakan Rhodamine B dan Iodida)

AU YOONG YOW LOO*, YAP PEI LAY, MURALITHRAN G. KUTTY, OLAF TIMPE, MALTE BEHRENS & SHARIFAH BEE ABD HAMID

ABSTRACT

Spectrophotometric methods for the trace amount determination of Hg(II) via extraction and polyvinylalcohol (PVAI) water stabilization was explored. The methods are based on the formation of ion-association complex of Hg(II) with Rhodamine B, $[(HgI_4)^2-][(Rhodamine\ B)^+]_2$ in highly acidic solution. Extraction using benzene showed the Beer's law was obeyed for mercury(II) in the range of 5 to 27 $\mu\text{g Hg(II) / 20 mL}$ of sample and molar absorptivity, $\epsilon = 17.68 \times 10^4 \text{ L mole}^{-1}\text{cm}^{-1}$. For polyvinylalcohol (PVAI) stabilization method, Beer's law showed the validity range of 10 to 120 $\mu\text{g Hg(II) / 10 mL}$ of sample and molar absorptivity, $\epsilon = 16.84 \times 10^3 \text{ L mole}^{-1}\text{cm}^{-1}$. The benzene-extraction method has been applied in assessing the performance of copper sulfide ion-exchanger in removing Hg(II). The result was comparable to the result obtained using cold vapor atomic absorption spectrometry (CVAAS).

Keywords: Aqueous mercury analysis; Hg complexation; Rhodamine B; UV-Visible spectrophotometry

ABSTRAK

Kaedah spektrofotometri untuk menentukan Hg(II) melalui pengekstrakan dan penstabilan di dalam air dengan menggunakan polivinilalkohol (PVAI) telah dikaji. Kaedah tersebut berdasarkan pada pembentukan kompleks gabungan ion Hg(II) dengan Rhodamine B, $[(HgI_4)^2-][(Rhodamine\ B)^+]_2$ dalam larutan berasid. Pengekstrakan dengan menggunakan benzen mematuhi hukum Beer dalam lingkungan Hg(II) antara 5 hingga 27 $\mu\text{g Hg(II) / 20 mL}$ sampel dengan pemalar serapan, $\epsilon = 17.68 \times 10^4 \text{ l mol}^{-1}\text{cm}^{-1}$. Untuk kaedah penyetabilan dengan menggunakan polivinilalkohol (PVAI), hukum Beer's menunjukkan julat kesahihan antara 10 hingga 120 $\mu\text{g Hg(II) / 10 mL}$ sampel dengan pemalar serapan, $\epsilon = 16.84 \times 10^3 \text{ L mol}^{-1}\text{cm}^{-1}$. Kaedah pengekstrakan menggunakan benzen telah dilakukan untuk mengkaji prestasi penukar ion kuprum sulfida untuk mengekstrak Hg(II). Keputusannya adalah setanding dengan keputusan yang diperolehi menggunakan spektrometri serapan atom wap sejuk (CVAAS).

Kata kunci: Analisis merkuri akueus; Hg pengkompleksan; Rhodamine B; UV-Visible spektrofotometri

INTRODUCTION

Rhodamine B, is a basic xanthone dye which occurs in the form of amphoteric salt in aqueous solution. The existence of different protonated species in aqueous solution have been shown in the literature (Hasanin et al. 2010; Moreno-Villoslada et al. 2006; Ramette & Sandell 1956). Equilibrium between these species is highly pH dependent. In addition, the type of Rhodamine B species can also be altered with different type of solvent used (Elderfield 1950; Gahlmann et al. 2005; Golkowska & Pszonicki 1973).

Among the different forms of Rhodamine B in aqueous solution, only the singly protonated species is responsible in forming the ion association compound with metal anionic complexes (Hosseini & Naseri 2003). In the past, use of Rhodamine B has been tried in determining metal ions such as gallium, uranium, thallium, palladium, and mercury (Hasegawa et al. 1983; Hernandez-Córdoba et al. 1984; Hosseini & Naseri 2003; Lopez-Garcia et

al. 1986; Moeken & Van-Neste 1967; Ramakrishna et al. 1976). In comparison with the more expensive and sophisticated instrument *i.e* inductively couple plasma mass spectrometry (ICP-MS) or atomic absorption spectrometry (AAS), the use of spectrophotometric complexing agent in metal ion detection has provide a non-destructive route especially for those who are dealing with little amount of sample where further sample analysis is still needed. Herein, the aim of this work was to present a simple and reasonably cheaper methods for determination of trace amount of Hg(II). The methods employed coloured Rhodamine B and iodide anion in complexing with Hg(II). The use of iodide in Hg(II) complexation is comparable to the use of thiocyanate (Hernandez-Córdoba et al. 1984). In our case, the ion association compound formed can either be extracted into benzene or stabilized by polyvivylalcohol in water which can be determined spectrophotometrically.

MATERIALS AND METHODS

All solutions were prepared using chemicals of analytical-reagent grade (Merck, Germany). Doubly deionized water was used throughout the experiments. Standard Hg(II) solution, mostly 1000 ppm, was prepared in deionized water. Working solutions were prepared daily by suitable dilution of the standard stock solution. 5×10^{-3} M of Rhodamine B solution and 0.15 M KI solution was prepared in 100 mL of water, respectively. Further dilution of Rhodamine B solution to 5×10^{-4} M was also carried out during the preparation. About 10.8 M of H_2SO_4 solution was prepared by diluting 95-97% commercial H_2SO_4 . Polyvinylalcohol (PVAI) of MW = 15000 was used as 1% (w/v) aqueous solution. Dichloromethane and benzene were used without further purification. Perkin-Elmer (Lambda 25 or 35) spectrophotometer and 10 mm quartz cells were used for absorption spectra collection. Mercury Analyzer (CVAAS, NIC-MA-2000) using SnCl_2 as reductant is used to measure the concentration of Hg(II) for comparison with spectrophotometric method.

The Rhodamine B-Hg(II) iodide complex, $[(\text{HgI}_4)^{2-}][(\text{Rhodamine B})^+]_2$ in aqueous solution. An aliquot of solution (10 mL) containing not more than 120 μg of Hg(II) was transferred to a 25 mL volumetric flask. One milliliter of 10.8 M H_2SO_4 , followed by 1 mL of 0.15 M KI was added into the solution. After shaken for 1 min, the mixture was added with 1 mL of 5×10^{-4} M of Rhodamine B. Finally, the mixture solution was added with 5 mL of 1% PVAI solution, diluting to calibration mark and left it to stabilize for 10 min. The absorbance of this solution was measured against water at 590 nm.

The Rhodamine B-Hg(II) iodide complex, $[(\text{HgI}_4)^{2-}][(\text{Rhodamine B})^+]_2$ in organic solvent. Pipette 20 mL of sample solution containing not more than 25 μg of Hg(II) into a separating funnel. One milliliter of 10.8 M H_2SO_4 , followed by 1 mL of 0.15 M KI was added into the solution

and shaken vigorously for 1 min. After that, 1 mL of 5×10^{-3} M of Rhodamine B was added and again shaken vigorously for 1 min. The resulting red-violet solution was then extracted with 10 mL of benzene or dichloromethane for 3 min. Allowing the phases to separate, the absorbance of the organic layer was measured against the benzene and dichloromethane at 565 and 556 nm, respectively.

Performance assessment of copper sulfide in Hg(II) removal. One hundred milliliter of 100 ppm HgCl_2 was added with 0.1 g of copper sulfide powder and stirred under magnetic stirrer. Sampling was collected each hour for the duration of 4 h. The sample collected was then analyzed spectrophotometrically using benzene extraction method and well established cold vapor atomic absorption spectrometry (CVAAS) method.

RESULTS AND DISCUSSION

The reaction of Hg(II) with Rhodamine B and iodide occurs through the formation of $[(\text{HgI}_4)^{2-}][(\text{Rhodamine B})^+]_2$ under the highly stable tetraiodomercurate(II) ($\log K = 29.689$) and singly charged Rhodamine B. However, a major problem of gradual precipitation of the violet ternary $[(\text{HgI}_4)^{2-}][(\text{Rhodamine B})^+]_2$ complex is observed during the reaction. Therefore, the complex is either extracted into a stable solvent system or stabilized in the solution by protective water soluble polymer before spectrophotometric determination.

EXTRACTION INTO ORGANIC SOLVENT

The pre-described $[(\text{HgI}_4)^{2-}][(\text{Rhodamine B})^+]_2$ complex was first extracted into dichloromethane and benzene. Figures 1 and 2 show the absorbance spectra of the dichloromethane and benzene extracted Hg(II) sample. Comparing the contribution of absorbance of reagent blank, benzene solvent seems to be a better solvent. The

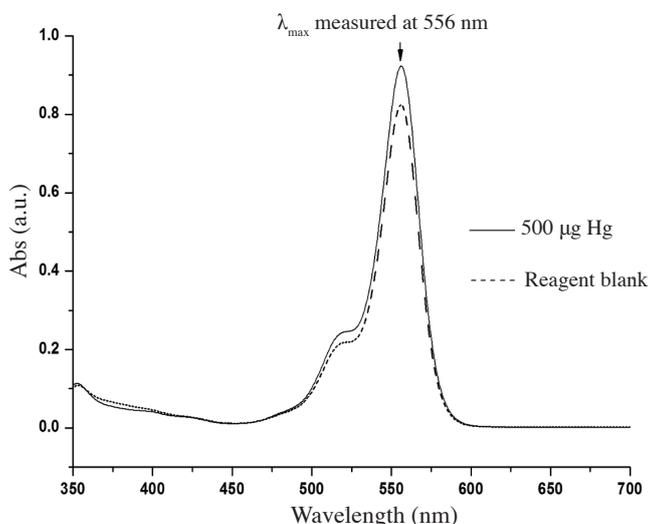


FIGURE 1. Absorbance spectra of dichloromethane extracted Hg(II) sample and reagent blank

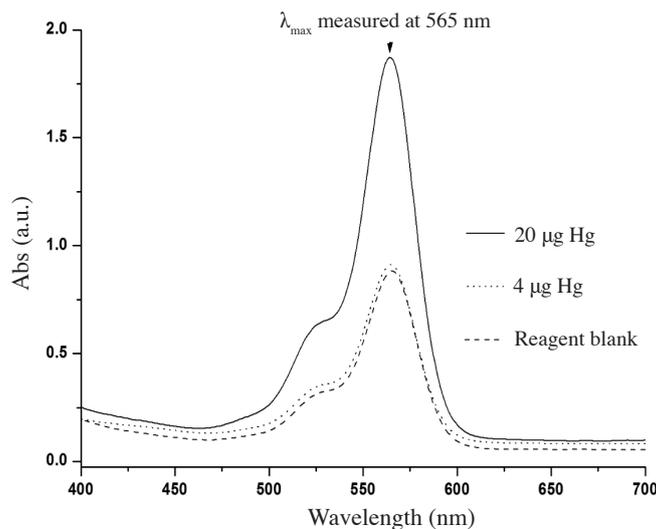


FIGURE 2. Absorbance spectra of benzene extracted Hg(II) sample and reagent blank

contribution by ion associates of Rhodamine B-sulfate, Rhodamine B-Iodide, and Rhodamine B-chloride in the extracted blank are lowered in benzene, giving lower value of absorbance, thus a lower limit of detection (L.O.D). From this observation, we deduce that the uses of more polar solvents lead to higher values of reagent blank being measured. If the polarity is too low, the colourless form of the dye predominates in the organic layer which results in a relatively lower reagent blank value measured (Lopez-Garcia et al. 1986).

Graph of absorbance against amount of Hg(II) is shown in Figure 3. The graph shows that the Beer's law validity ranged from about 5 µg to 27 µg Hg(II). Above the limit, Beer's law started to deviate due to high analyte concentration or fluorescence interferences. For a given method, molar absorptivity (absorption coefficient), ϵ ,

greater than $1 \times 10^3 \text{ L mole}^{-1}\text{cm}^{-1}$ is regarded as sensitive (Marczenko & Balcerzak 2000). Therefore, this method seems to be sensitive with molar absorptivity at 565 nm = $17.68 \times 10^4 \text{ L mole}^{-1}\text{cm}^{-1}$ and limit of detection value (LOD) was approximately 5 µg of Hg(II).

STABILIZATION IN WATER USING POLYVINYLALCOHOL (PVAI)

Preliminary studies showed that concentration of Rhodamine B needed to be decreased from $5 \times 10^{-3} \text{ M}$ to $5 \times 10^{-4} \text{ M}$ to get a satisfactory result for this method. The former gives a very high reagent blank that contribute to the entire system. Detail analysis of Figure 4 shows that a new peak evolution at about 590 nm corresponds to $[(\text{HgI}_4)^2][(\text{Rhodamine B})^+]_2$ is observed. Further investigation

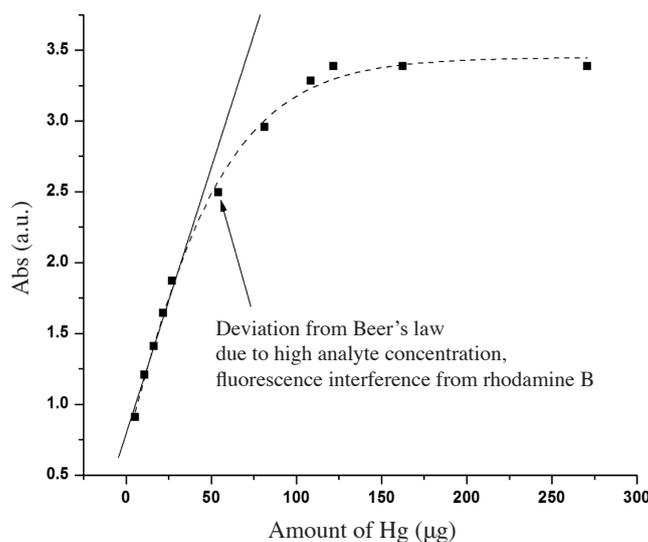


FIGURE 3. Measurement of different concentration benzene extracted Hg(II) sample and reagent blank

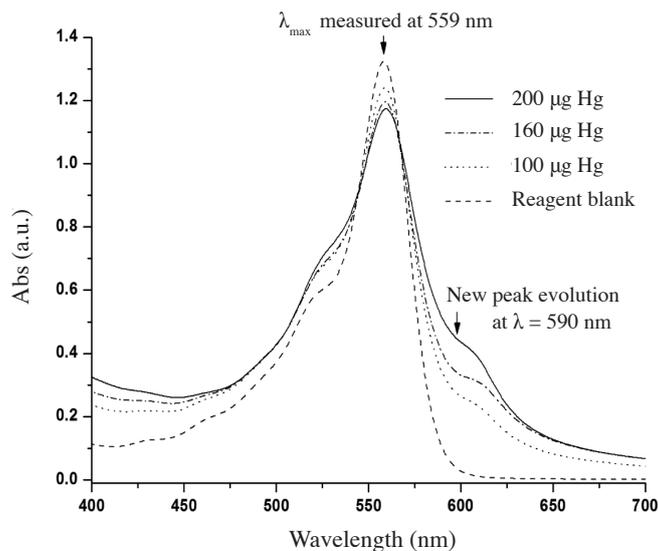


FIGURE 4. Absorbance spectra of PVAI stabilized Hg(II) sample and reagent blank

was carried out at this wavelength for different Hg(II) concentration sample.

The results of the measurements is shown in Figure 5. This method is applicable in the range of about 10 µg to 120 µg of Hg(II). Above the limit, Beer's law started to deviate due to high analyte concentration and fluorescence interference. Molar absorptivity (absorption coefficient) measured, ϵ is $16.84 \times 10^3 \text{ L mole}^{-1}\text{cm}^{-1}$ and limit of detection value (LOD) is approximately 10 µg of Hg(II). Compared to the benzene extraction method, this method seems to be less sensitive due to the lower ϵ and higher LOD value. However, this method does not require an extra step of extraction which is time-consuming and imposing higher experimental error.

APPLICATION IN ACCESSING THE PERFORMANCE OF COPPER SULFIDE IN Hg(II) REMOVAL

The applicability of the benzene extraction method has been tried in studying the performance of Hg(II) removal using copper sulfide ion-exchanger. The use of copper sulfide in removing aqueous Hg(II) has been reported (Phillips & Kraus 1965; Wu & Yang 1976). Table 1 shows the measurement of performance using the benzene extraction method in UV-Vis spectrophotometry and well established cold vapor atomic absorption spectrometry method (CVAAS). As shown in Table 1, the percentage concentration difference measured by benzene extraction method compare to CVAAS are ranging from 9.5% to

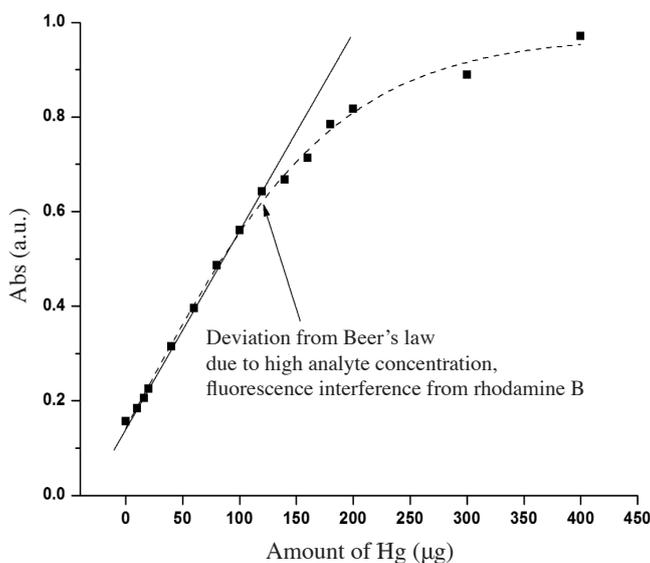


FIGURE 5. Measurement of different concentration PVAI stabilized Hg(II) sample and reagent blank

TABLE 1. Comparison of the results obtained from benzene extraction method using UV-Vis spectrophotometry and CVAAS method

Time (Hour)	Benzene extraction method (ppm)	CVAAS (ppm)	% Concentration difference
1	34.02 ± 3.76	37.61 ± 6.80	9.54
2	34.08 ± 3.67	36.67 ± 6.82	7.06
3	33.25 ± 3.63	36.36 ± 6.65	8.56
4	31.04 ± 3.56	35.61 ± 6.21	12.83

12.4% and this result are comparable to the concentration measured using CVAAS. Therefore, this method is apparently applicable in determining the aqueous Hg(II) with satisfactory results.

CONCLUSION

The reaction between Rhodamine B and tetraiodomercurate(II) produces an ion-associates that were unstable in water. Spectrophotometric determination of this complex can either be done by extraction into benzene or stabilized by protective colloid polymer i.e. polyvinylalcohol (PVAL) in water aqueous system. Both of the proposed methods are regarded as sensitive with molar absorptivity, ϵ , $17.68 \times 10^4 \text{ L mole}^{-1}\text{cm}^{-1}$ for benzene extraction and $16.84 \times 10^3 \text{ L mole}^{-1}\text{cm}^{-1}$ for PVAL stabilization. In comparison between the two methods, the applicable ranges for benzene extraction seem to be lower than PVAL stabilization with 5-27 μg and 10-120 μg respectively. On the other hand, the examination of the benzene extraction method has been tested in assessing the performance of Hg(II) removal using copper sulfide ion-exchanger. The performance testing results obtained using the benzene extraction method is comparable to the well established cold vapor atomic absorption (CVAAS) method. This further confirmed the applicability of this method in determining Hg(II) in water aqueous system.

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- Au Yoong Yow Loo*, Yap Pei Lay,
Muralithran G. Kutty & Sharifah Bee Abd Hamid
COMBICAT Laboratory
Nanotechnology & Catalysis Research Centre (NANOCEN)
University of Malaya

50603 Lembah Pantai, Kuala Lumpur
Malaysia

Olaf Timpe & Malte Behrens
Fritz-Haber-Institut der Max-Planck-Gesellschaft
Faradeweg 4-6
14195, Berlin
Germany

*Corresponding author; email: yowloo@yahoo.com

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