A novel and simple spectrophotometric method for micro determination of mercury(II) in presence of micellar medium using new azobenzothiazol reagents

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ABSTRACT

A simple, selective and highly sensitive method has been developed for the determination of mercury(II) spectrophotometrically in presence of micellar medium using new three azobenzothiazol reagents, 2-amino-6-(thiazole-2-ylazo)-3-pyridinol [R_1], 8-hydroxy-7-(thiazole-2-ylazo)quinoline-5-sulfonic acid [R_2] and 1-hydroxy-4- (thiazole-2-ylazo)-2-naphthoic acid [R_3]. The optimization of experimental conditions for the procedure has been studied. For the enhancement determination of mercury(II), Tween 80 and cyproheptadiene are used as micellar medium to increase the sensitivity of the procedure. The absorbance is measured at λ_{max} of 617, 633 and 554 nm using universal buffer solution of pH 6.00, 7.13 and 4.97 for R_1, R_2 and R_3 complexes with Hg(II) respectively. Beer's law was obeyed in the ranges 1-10, 1-13 and 1-5 μg mL^{-1} for R_1, R_2 and R_3 complexes with Hg(II) respectively. The molar absorptivity, Sandell's sensitivity, detection and quantification limits were calculated. The interference of various ions has been studied in detail and the statistical evaluation of the experimental results is reported. The proposed methods have been successfully applied for the determination of trace amount of mercury(II) in environment water and food samples.

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1. Introduction

The development of the new determination methods is among the subject of the analytical chemists. Speciation information of heavy metal ions is very important for their toxicity and biological role of a particular element vary greatly depending on its chemical form. For this reason extensive research has been focused on the developing sensitivity, relative simplicity, accurate, speed and costly effective methods for determination of metals which have industrial importance and affect human health [1, 2].

Speciation studies of heavy metal ions are generally focused on mercury, lead, zinc, arsenic, antimony, etc. Mercury is a serious environmental pollutant because of its toxic effects on all living organisms [3]. Mercury and its compounds cause serious diseases such as leukemia [4]. Mercury compounds can be present as a result of anthropogenic activities in various environmental samples [5]. They are usually present in natural waters at trace levels [5, 6].

The lakes, rivers in vicinity of the industrial areas are the important indicators for mercury pollution. So, it needs to develop new, selective, effective, cheap methods for determination of mercury [7]. A serious problem in the determination of mercury is related to low concentrations of target species. The main species of mercury in natural waters are inorganic mercury (Hg_2^{2+}, Hg^{2+}) and methyl mercury (CH_3Hg^+). Recent reports estimate that total mercury concentration is in the range of (0.2-100) $\times$ 10^{-3}µg L^{-1} and methyl mercury concentrations are lower (Ca. 5×10^{-5}) µg L^{-1}in natural waters [8].

Numerous analytical and sophisticated techniques such as inductively coupled plasma mass spectrometry [ICP-MS] [9,10], inductively coupled plasma atomic emission spectrometry [ICP-AES] [11,12], cold vapor atomic absorption spectrometry [CV-AAS] [13,15], neutron activation analysis [NAA] [16], x-ray

fluorescence spectrometry [XRF] [17], atomic fluorescence spectrometry [AFS] [18,19], and spectrophotometry [20-23] have been developed to determine Hg(II) at trace level. Each of the mentioned techniques has its own merits, but each method also offers some problems such as poor reproducibility and limited sample adaptability. [ICP-AES] and [ICP-MS] are useful for trace determination without any preconcentration. However, these instruments are very expensive to purchase and operate. Moreover, these techniques have some inherent interference [9,12]. [CV-AAS] is a suitable and widely used technique for accurate determination of mercury due to its simplicity. But, its usage is limited because of a narrow linear range and spectral interference from volatile species [14,24,25].

Therefore, those techniques are not directly applicable to environmental and biological samples in view of low analyte contents and they require preconcentration steps to enhance the sensitivity. A number of photometric reagents have been used for spectrophotometric determination of Hg(II). Dithizone, which forms a water-insoluble complex, is the most commonly used [20-23, 25]. The formed complex is extracted either in CCl_4 or $CHCl_3$before photometric determination [26, 27].

In the present work, three types of azo dyes have been prepared and used for direct spectrophotometric determination of Hg(II) ions based on the absorbance measurements of the formed complexes in presence of surfactants against the reagent blank. The azo dyes which have been used are 2-amino-6-(thiazole-2-ylazo)-3-pyridinol [R_1], 8-hydroxy-7-(thiazole-2-ylazo)quinoline-5-sulfonic acid [R_2] and 1-hydroxy-4-(thiazole-2-ylazo)-2-naphthoic acid [R_3]. The methods were applied successfully to the determination of Hg(II) ions at trace levels in environmental samples. The advantages of these methods are simplicity, selectivity, sensitivity, cheapness, wide linear range and applicability to real samples. The proposed methods use only a conventional spectrophotometer after

simple procedure. All essential equipment for the proposed methods can be provided in almost every laboratory.

2. Experimental

2.1. Instrumentation

All the absorption spectral measurements are made using V-530 (UV-Vis) spectrophotometer (Japan) with scanning speed 400 nm/min, bandwidth 2.0 nm and equipped with 10 mm matched quartz cells. The pH of all solutions was adjusted to the required value using pH-meter type HI 8014 HANA instruments.

2.2. Chemicals

All the chemical reagents employed were analytical grade and the solutions were prepared with bidistilled water. A stock solution of 10^{-2} M mercuric chloride solution were prepared by weighing 0.6787 g of ($HgCl_2.2H_2O$, Merck) and dissolve it in least amount of water and then completed in a 100 mL measuring flask to the mark with bidistilled water. The stock solution is then standardized by EDTA titration using xylenol orange as an indicator [28]. All the working solutions were prepared by diluting appropriate volumes of the stock solution. The solution is stable for a month, at ambient temperature. Universal buffer solution were prepared, according to the previous procedure of Britton [29]. Different surfactants were used such as Tween 80 [0.5% (v/v)], Triton X-100 [0.5% (v/v)], cyproheptadiene [0.5% (w/v)] and sodium dodecyle sulphate (SDS) [0.5% (w/v)] because of their commercial availability in a high-purified homogeneous form, low toxicological properties and cost. Tween 80 and Triton X-100 were prepared by adding 0.5 mL of the surfactant to 50 mL distilled water and then completed to 100 mL with distilled water to obtain 0.5% (v/v) solution. . In case of sodium dodecyl sulphate (SDS) and Cyproheptadiene a solution of 0.5 % (w/v) was prepared by

dissolving 0.5 g from the surfactant in 50 mL distilled water then the volume was completed in 100 mL measuring flask with distilled water.

2.3. Synthesis of reagents

The azo compounds in the present work have been prepared by the following procedure. Three different solutions of 0.1 mole (10.014 g) 2-aminothiazole (Aldrich) were prepared in 1:1 HCl (Aldrich) and cooled in ice bath to – 5.0 ˚C. To these solutions a cold solution of sodium nitrite (Merck) (6.903 g, 0.1 M) was added and mixed with vigorous stirring and kept in an ice bath at 0-5˚C for 20 mins [29]. The cold diazonium salt solution was used for coupling with an equivalent amount of cold solutions of 2-amino-3-hydroxypyridine (11.01 g), 8-hydroxyquinoline-5-sulphonic acid (26.125 g) and 1-hydroxy-2-naphthoic acid (18.81 g) which dissolved in 10% NaOH (Merck). The azo compounds formed were kept for 30 mins in an ice bath at -5.0 ˚C then filtered off, washed by distilled water and dried. The crude material was recrystallized using ethanol [Fig. 1]. The compounds were tested by measuring the melting point, IR and ^{1}H-NMR spectra and the reaction yields were in ranges (75-85%). The reagent solutions were prepared by dissolving (0.11, 0.033 and 0.148 gm) in 100 ml ethanol to obtain (5×10^{-3}, 1×10^{-3} and 5×10^{-3} M) of R_1, R_2 and R_3, respectively.

Fig. 1

2.4. General procedure

An appropriate volume of the sample containing 10^{-3} M of Hg(II) was placed in a 10 mL- measuring flask. Universal buffer of (pH 6.0, 5mL), (pH 7.13, 4mL) and (pH 4.97, 4mL) were added to the sample with (1 mL of 5×10^{-3}M)R_1, (2.0 mL of 1×10^{-3}M)R_2 and (1mL of 1×10^{-3}M)R_3, respectively. (1.0 mL of tween [0.5%(v/v)]), (1.5 mL of cyproheptadiene [0.5%(w/v)]) and

(0.5 mL of tween [0.5%(v/v)]) were transferred into the measuring flask containing the sample in case of R_1, R_2 and R_3, respectively. A blank solution containing all the reagents except Hg(II) was prepared and treated in the same way as the sample. Allow the mix to stand at room temperature (25 ˚C). The absorbance difference between the sample and its corresponding blank, was measured as described above at wavelength (617, 633 and 554 nm) for R_1, R_2 and R_3, respectively. The optimum time was detected by measuring the absorbance at different time after preparation of the sample.

2.5. Determination of molecular structures using mole ratio method

In the mole ratio method, described by Yoe and Jones [31], the concentration of metal ion is kept constant (1×10^{-4} M) while that of the ligand is regularly varied ($0.2 - 2.4 \times10^{-4}$) M. The absorbances of the solutions prepared were determined at optimum wavelength. The absorbances values were then plotted versus the mole ratio [ligand/metal]. The intersection of any two straight lines obtained shows the mole ratio of the most stable complex.

2.6. Determination of Mercury (II) in Food samples

The accuracy and validity of the proposed method was checked by applying the determination of mercury concentration in various food samples. The sample was dried in a forced-draft oven at 70 ˚C to constant mass and then ground to a fine powder. A suitable aliquot was weighed (2.0 gm dry material) into a 100 mL claisen distilling flask and 10 mL of HNO_3 was added. After that, the flask was put into a model MDS-81D microwave oven and digested for 5.0 min at 50% power and continuously for 15 min at 100% power. Then the flask was taken out and

cooled to ambient temperature before another 10 mL of HNO_3 and 1.0 mL of H_2O_2 were added and left to stand for 20 min. the flask was placed in the microwave oven and irradiated for 40 min at 100% power. Then the flask was taken out and cooled to ambient temperature. The final 1.0 mL of HNO_3 was added and again the flask was left to stand for 10 min. The final solution was neutralized to pH 8.0-9.0 with solid Na_2CO_3 and transferred into a 25 mL calibrated flask. The solutions were further treated as given in general procedure. Standard addition method was used in order to calculate recovery values and check correctness of results [32].

2.7. Determination of Mercury (II) in water samples

A choice of water samples in and around the Shobra-El-Qhema and Benha cities has been made. Each filtered environmental water sample is evaporated nearly to dryness with a mixture of 5.0 mL concentrated H_2SO_4 and 10 mL concentrated HNO_3 in a fume cupboard and then cooled to room temperature. The residue is then heated with 10.0 mL of deionized water, in order to dissolve the salts. Th solution is cooled and neutralized with dilute NH_4OH. The resulting solution is filtered and quantitatively transferred into a 25 mL calibrated flask and made up to the mark with deionized water. A known aliquot o the above sample solution is taken into a 25 mL separating funnel and the mercury content is determined as described in the general procedure [32].

3. Results and discussion

Mercury(II) forms a pink complex with R_1, R_2 and R_3 at the optimum condition. Figs. 2 shows the absorption spectra of Hg(II)–R_1, Hg(II)–R_2 and Hg(II)–R_3 complexes with λ_{max} at 617, 633 and 554 nm respectively, where there are a shift to bathochromic direction compared with free reagents that absorbed at

557, 563 and 477 nm, respectively. Investigations were carried out to establish the most favorable conditions to give a highly color intensity and to achieve maximum color development in the quantitative determination of mercury. The influences of each of the following variables on the complexation reactions were tested.

Fig. 2

3.1. Effect of pH

The pH is a critical factor affecting both the reaction between Hg (II) and reagent molecules. In order to determine the optimum pH, a universal buffer system in range of 2.7-12.0 was used. As shown from Fig. 3, the maximum absorbance was obtained at pH 6.0, 7.13 and 4.97 for Hg(II)-complexes with R_1, R_2, and R_3, respectively. Moreover, the effect of buffer volume on the analytical band was studied in the range 0.5-6 mL (in final volume of 10 mL), the highest analytical absorbance was obtained with buffer volume of 5.0 mL for R_1-Hg(II) and 4.0 mL in case of R_2-Hg(II) and R_3- Hg(II) complexes.

3.2. Effect of reagent concentration

The effects of R_1, R_2 and R_3 concentration on the analytical response are shown in Fig. 4. As shown for R_1-Hg(II) and R_3-Hg(II) complexes, absorbance increases up to a known concentration of R_1 and R_3. A concentration of 5×10^{-4} M of R_1 and R_3 was chosen as the optimum value. Similarly, the absorbance increases with R_2 concentration and reaches its maximum value in 2×10^{-4} M. Therefore, a 2×10^{-4} M of R_2 was chosen as the optimal concentration.

3.3. Effect of surfactant volume

According to the obtained results, Tween 80 is the most suitable for the R_1 and R_3 complexes, while the suitable one for R_2 complex is cyproheptadiene. A volume of 1.0 mL and 0.5 of 0.5% (v/v) Tween-80 were the optimum for Hg(II) complexed with R_1 and R_3, respectively. For Hg (II)-R_2 complex a 1.5 mL of 0.5% (w/v) was the optimum to give highly absorbance values.

3.4. Effect of sequence of addition

The effect of sequence of additions (reagent (R), metal (M), buffer (B) and surfactant (S) on the complex formation was studied by measuring the absorbance of sample solution prepared using different sequences of additions against blank solution prepared by the same manner except of metal solution. The best sequence of addition was determined from the highest absorbance value. The optimal sequence of addition for each metal complex and other optimal conditions are shown in Table (1).

3.5. Effect of temperature and time

The dependence of the proposed methods upon temperature and time was studied over ranges of 25-70 ˚C and 5-50 min, respectively. The results showed that the optimum temperature is 25 ˚C for R_1-Hg(II), R_2-Hg(II) and R_3-Hg(II) complexes. All of these complexes give their highest absorbance instantaneously except that of R_1, it gets its highest value of absorbance after 10 mins from its formation. Optimum time and temperature for other complexes are recorded in Table (1).

3.6. Stoichiometric ratio

Molar ratio method was used in order to define the stoichiometry of Hg (II)-R_{1-3} complexes. The best wavelength absorbance for each complex was at 617 nm for R_1, 633 nm for R_2, and 554 nm for R_3. The results showed that the molar ratio

curves reaches a maximum value of absorbance in same molar ratio (1:1) for R1 and R2 complexes. This proves that a single complex compound is formed for these two systems, having a (Hg-R_1) and (Hg-R_2) composition. In the case of R_3, the results showed that its molar ratio curve reaches two maximum value with molar ratio (1:1) and (1:2). This proves that two complex compounds are formed in the system, having a (Hg-R_3) and (Hg-$[R_3]_2$) compositions.

3.7. Interference studies

In view of the high selectivity provided by spectrophotometry at the characteristics absorption wavelengths of 617, 633 and 554 nm for Hg^{2+}complexed with R_1, R_2 and R_3, respectively. The tolerance limits were determined for a maximum error of ±3.0 % and the results are given in Table (2). In order to perform this study, interfering ions in different concentrations were added to a solution containing 2 µg mL^{-1} of Hg(II). These results demonstrate that, the common coexisting ions did not have significant effect on the determination of analyte ions. Co(II), Ni(II) and Mn(II) ions were found to interfere at tolerance limits ranging from 1 to 20. Sodium borate, sodium tungstate and sodium chloride have no interference in the detection process of mercury(II) ions. Moreover, the concentrations of these ions are usually very low in most water and food samples thus these methods can therefore be applied to determine Hg(II) species in environmental water and food samples.

3.8. Analytical characteristics

Table (3) summarizes the analytical characteristics such as linear range, limits of detection and quantification limits. The limits of detection and quantification were (0.051 and 0.156) µg mL^{-1} for R_1 , (0.150 and 0.450) µg mL^{-1} for R_2 and (0.26 and 0.785) µg mL^{-1} for R_3. These concentrations intervals are appropriate for measured mercury ion concentrations in water and food samples. The R.S.D for six

replicate measurements of 2 μgL^{-1} of mercury (II) with R1 was 2.88% while with R2 was 3.42% and 6.64% with R3.

3.9. Determination of mercury species in water samples

The accuracy and validity of the proposed method was checked by applying the determination of mercury concentration in various water samples and food samples. The method was applied to four different water samples and five different food samples. The results found are in good agreement based on standard addition curve approach. The accuracy was verified by the student's-test according to this test, the calculated t values (in the range of……..) are less than the theoretical value (2.77,n: 5) at a confidence level of 95%. In addition, the statistical F-test was also applied for comparing the precision of the spectrophotometric R1 method with those of the R2 method. The $F_{4,2}$- test value at 95% confidence level did not exceed the theoretical value (6.39, n:8) with a value ranging from (…….)for F-test, indicating no significant difference between the performance of methods. The results can be seen in Table (4).

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4. Conclusion

In the present study, three detection methods were developed for trace mercury ions, R_1, R_2 and R_3 were used as chelating ligands. The absorbance of the complexes was measured at 617, 633 and 554nm, respectively. These procedures allow determination of Hg(II) at very low concentration, [1:10 µg/mL] for R_1, [1:13 µg/mL] for R_2 and [1:5 µg/mL] for R_3. The detection limits of proposed methods, [0.051 µg /mL] for R_1, [0.150 µg /mL] for R_2 and [0.26 µg /mL] for R_3. The methods were successfully applied in the determination of mercury in environmental water and food samples, the results are statistically in good agreement with each other in terms of accuracy and precision. The methods have the following advantages: simple, rapid, reproducible, sufficient sensitivity, wide

linear range, and low analysis cost. These methods can be applied to trace mercury determination in every analysis laboratory having a conventional spectrophotometry without needing any expensive instrument Table (5).