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Spectrophotometric Determination of Mercury Ion After Liquid-Liquid Extraction with Toluidine Blue-O

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A simple and highly sensitive extraction-spectrophotometric determination of mercury is described. The ion-associate formed between the HgI_4^{2-} and toluidine blue-O is extracted with dichloromethane at pH 6. The absorption maximum of the extracted species occurs at 593 nm, the molar absorptivity being 1.42×10^5 L mol^{-1} cm^{-1}. The calibration curve was linear in the concentration range of 0.1-2.5 µg mL^{-1} of Hg^{2+} with a correlation coefficient of 0.9995. The limit of detection (LOD) is 0.021 µg mL^{-1}. The relative standard deviation (RSD) at 0.6 and 1.2 µg mL^{-1} of mercury were 2.12 and 3.08 % (n = 8), respectively. The method was applied for measuring the amount of mercury in water samples.

Key Words: Extraction-spectrophotometry, Mercury, Toluidine blue-O, Potassium iodide, Ion associate.

INTRODUCTION

Extraction is a useful separating methods[1,2]. Solvent extraction of precious metal is widely employed in chemistry and industry for many years[3]. Normally, it is difficult for metals such as palladium, platinum, rhodium, *etc*., to form complex with extractant at the room temperature, while at a high temperature the water-insoluble complex can form easily and rapidly. Ion association systems, in a more general way, could be said to result from the interaction of charged particles such as metal cations or complexes with oppositely charged ions. Such complexes were made to associate with anionic ligand in order to be extractable from aqueous solutions[4].

Different liquid-liquid extraction[5,6], ICP-MS[7,8] and electrochemical[9] methods are used for trace quantitative determination of Hg^{2+}. Present paper shows a extraction-spectrophotometric method for $(HgI_4^{2-}-TBO^+)$ ion-associate in to the interface between aqueous and dichloromethane phase by liquid-liquid extraction method (here TBO is toluidine blue-O). The method proposed has been successfully applied to the determination of Hg cation in different water samples.

EXPERIMENTAL

The absorption spectra were recorded on a Shimadzu model 160A UV-vis. A Metrohm model 691 pH meter with a combined glass electrode was for pH measurements.

Unless otherwise stated, all commercial reagents used were of analytical grades without further purification. 20 µg mL^{-1} stock solution of Hg^{2+} was prepared by dissolving 0.162

g of $Hg(NO_3)_2$ (Merck) in freshly distilled water and diluting to the mark in a 100 mL volumetric flask. Stock solution of toluidine blue-O (1×10^{-4} mol L^{-1}) was prepared by dissolving 0.00306 g of toluidine blue-O (Fluka) in distilled water and diluting to 100 mL in a flask. Stock solution of KI (1×10^{-1} mol L^{-1}) was prepared by dissolving 1.66 g of KI (Merck) in distilled water and diluting to 100 in a flask. Stock solution of NaCl (1×10^{-1} mol L^{-1}) was prepared by dissolving 0.584 g NaCl in distilled water and diluting to 100 mL in a flask. Phosphate buffer solution in the pH range of 6 was made by mixing 250 mL of 0.1 mol L^{-1} solution of acid or salt with appropriate volumes of 0.1 mol L^{-1} solution of sodium hydroxide.

Recommended procedure: Transfer an aliquot of a sample solution containing 1 mL of 20 µg mL^{-1} of Hg^{2+} into a 25 mL volumetric flask, 6.0 mL of 1×10^{-1} mol L^{-1} of KI, 2.0 mL of 1×10^{-4} mol L^{-1} of toluidine blue-O, 1.5 mL of 1×10^{-1} mol L^{-1} of NaCl, 2 mL of buffer 6, diluted to the mark with distilled water and left for 5 min. Then transfer the flask content to a 100 mL separatory funnel containing 3 mL of dichloromethane and shake vigorously the mixture for 60 s and then allow standing for 10 min for separation of organic phase from aqueous phase. The $(HgI_4^{2-}-TBO^+)$ ion associate (colour liquid) floats under the aqueous phase. The absorbance of extracted coloured ion associate (organic layer) was measured at 593 nm in 1 cm cells against a reagent blank. All the experiments were carried out at room temperature. The proposed procedure has been applied to the determination of Hg^{2+} in water samples containing.

RESULTS AND DISCUSSION

The preliminary investigation indicated that interaction of Hg^{2+} with I^- and toluidine blue-O$^+$ can form a liquid ion associate which is insoluble in aqueous phases. The absorption spectra of (HgI_4^{2-}-TBO$^+$) ion associate in dichloromethane showed a maximum absorbance at 593 nm. Among organic solvents tested (CH_2Cl_2, CCl_4, $CHCl_3$), CH_2Cl_2 showed good characteristics. The volume effect of the CH_2Cl_2 on the extraction process was examined in the range of 1.5-8.0 mL. 3 mL was used as optimum dichloromethane volume. The influence of pH on the liquid extraction of (HgI_4^{2-}-TBO$^+$) ion associate was studied by varying the pH in the range of 2-11, before the organic phase addition (Fig. 1). The pH was adjusted to the desired value using phosphate buffer. The maximum extraction was observed at pH = 6. The effect of I^- ligand concentration used for the extraction of Hg^{2+} was examined by varying the amounts of I^-. The absorbance increased with increasing I^- concentration up to 0.024 mol L^{-1} of I^- in the final solution and concentrations greater than 0.024 mol L^{-1} have no effect on the extraction of the ion associate.
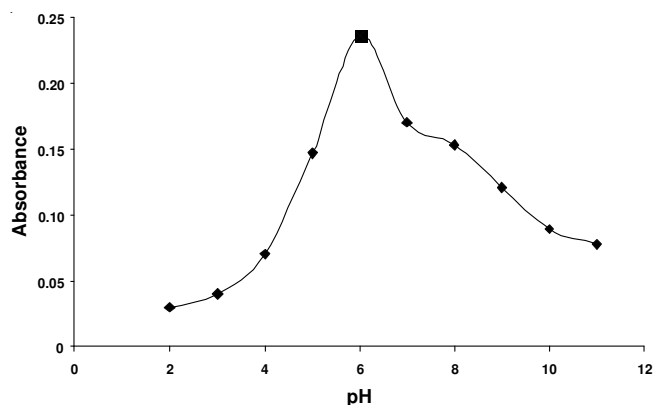

Fig. 1.   Influence of pH on the extraction of (HgI_4^{2-}-TBO$^+$) ion associate. Conditions: Hg^{2+}, 0.8 µg mL^{-1}; I^-, 0.024 mol L^{-1}; toluidine blue-O, 8.0×10^{-6} mol L^{-1}; λ_{max} = 593 nm

The results are shown in Fig. 2 and so 0.024 mol L^{-1} of I^- anionic ligand for Hg^{2+} extraction process. The effect of toluidine blue-O concentration used for the extraction of Hg^{2+} was examined by varying the amounts of toluidine blue-O dye. The absorbance of ion associate increased with increasing toluidine blue-O concentration up to 8.0×10^{-6} mol L^{-1} of toluidine blue-O in the final solution and decreases at more concentrations. 8.0×10^{-6} mol L^{-1} of toluidine blue-O in the final solution was chosen as the optimum concentration of toluidine blue-O for Hg^{2+} extraction process. The results are shown in Fig. 3.

The effect of standing time on the formation of (HgI_4^{2-}-TBO$^+$) ion associate was studied over the time period 2-10 min for 0.8 µg mL^{-1} of Hg^{2+}, 0.024 mol L^{-1} of I^-, 8.0×10^{-6} mol L^{-1} of toluidine blue-O and 6.0×10^{-3} mol L^{-1} of NaCl concentration at optimum pH (pH = 6) of solution and then by measuring the absorbance at 593 nm after liquid extraction. The maximum absorbance was obtained at 5 min. The effect of electrolyte concentration on the formation of (HgI_4^{2-}-TBO$^+$) ion associate was examined by various amounts of 6.0×10^{-3}

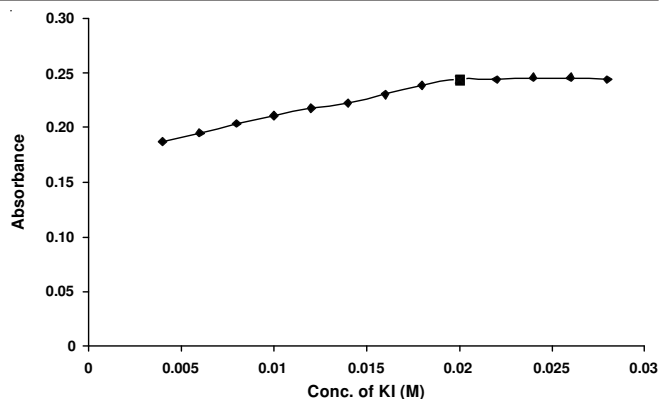Fig. 2.   Effect of I^- ligand concentration on the extraction of Hg^{2+}. Conditions: Hg^{2+}, 0.8 µg mL^{-1}; toluidine blue-O, 8.0×10^{-6} mol L^{-1}; pH = 6; λ_{max} = 593 nm
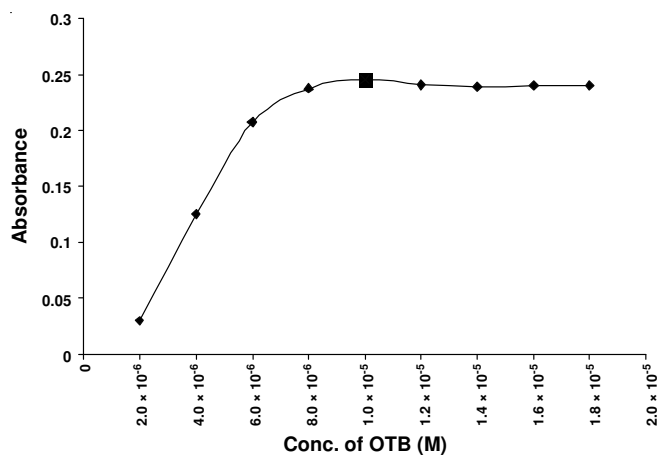

Fig. 3.   Effect of toluidine blue-O dye concentration on the extraction of Hg^{2+}. Conditions: Hg^{2+}, 0.8 µg mL^{-1}; I^-, 0.024 mol L^{-1}; pH = 6; λ_{max} = 593 nm

mol L^{-1} of NaCl solution. The results showed that the absorbance of ion associate increases with increasing NaCl concentration up 6.0×10^{-3} mol L^{-1} of NaCl in the final solution and remains constant at higher concentration of electrolyte (salting out). A constant concentration of 6.0×10^{-3} mol L^{-1} of NaCl was used throughout as optimum electrolyte concentration.

The extraction of the ion associate may also be influenced by the shaking time, because of increase in the active surface of the gas-liquid interface. Maximum absorbance was obtained at 60 s shaking time. The stoichiometry of the ion pair was determined using the continuous variation method. The mol ratio of Hg^{2+}:I^-:TBO$^+$: in the ion associate was 1:4:2.

Quantitative results: A calibration graph for the determination of Hg^{2+} was constructed under optimum experimental conditions described above. Beer's law was obeyed over the concentration range of 0.1-2.5 µg mL^{-1} of Hg^{2+} with a correlation coefficient of 0.9995 at 593 nm.

The regression equation obtained by the least square method is $A = 0.274C_{Hg} - 0.0265$ for 0.1-2.5 µg mL^{-1} of Hg^{2+}, where A is the absorbance and C_{Hg} shows the concentration of Hg^{2+} in µg mL^{-1}. A path length of 1 cm, the conditional molar absorptivity was 1.42×10^5 L mol^{-1} cm^{-1} at the above wavelength. The relative standards deviation (RSD) for 0.6 and 1.2 µg mL^{-1} of Hg^{2+} were 2.12 and 3.08 % (n = 8), respectively. The limit of detection (LOD) was 0.021 µg mL^{-1} based on $3S_b$ [10]. The method exhibits a good repeatability.

Effect of interferences: In order to study the influence of various cations and anions on the determination of Hg^{2+}, a fixed concentration of Hg^{2+}, 1 µg mL^{-1}, was taken with different amounts of foreign ions and the recommended procedure was followed. A relative error of ± 3 % with respect to the absorbance difference for the Hg^{2+} solution was considered tolerable. Telorance limits are as follows: $C_2O_4^{2-}$ (2000 folds), CH_3COO^- (1500 folds), HPO_4^{2-}, Fe^{2+} (1200 folds), HCO_3^-, NO_3^-, Ba^{2+}, Mn^{2+}, Ca^{2+} (1000 folds), NH_4^+, Cr^{2+} (600 folds), Zn^{2+}, Cu^{2+}, Pb^{2+}, Li^+ (500 folds), Cl^- (450 folds), Br^-, Ni^{2+} (400 folds), Co^{2+}, Cd^{2+} (300 folds), Sn^{2+} (100 folds).

Application: The proposed method was applied to the determination of Hg^{2+} in water samples. The results are shown in Table-1. The validity of the method is good.

TABLE-1
DETERMINATION OF Hg^{2+} IN WATER SAMPLES

Sample No.	Hg^{2+} (µg mL^{-1})* added	Hg^{2+} (µg mL^{-1}) found	Recovery
1	–	0.294	–
2	0.3	0.594	100
3	0.6	0.890	99
4	0.9	1.185	98
5	1.2	1.505	101

*Average of three determinations.

Conclusion

The proposed method is simple, rapid, reproducible and highly sensitive and can be applied for quality control of Hg^{2+} in water samples. Method shows good sensitivity due to high molar absorptivity character of toluidine blue-O dye and gave a wide linear dynamic range with respect to reported methods. The limit of detection of the proposed method seems to be good.

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