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REMOVAL OF TRACE AMOUNTS OF MERCURY(II) USING ALUMINIUM HYDROXIDE AS THE COLLECTOR

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ABSTRACT

A method for the removal of trace amounts of mercury (II) using aluminium hydroxide as the collector.. Dithizone in carbon tetrachloride was used for the extraction of mercury. The amount of Hg (II) was varied from 40 mg to 100 mg. The sample volume was varied until 50ml and the level of extraction of mercury was recorded. It was found that the recovery was satisfactory until a sample volume of 25 ml, beyond which the recovery gradually decreased. The effect of interfering ions was studied at different concentrations of mercury and was found to be minimum.

Key words: Mercury (II), Collector, Aluminium hydroxide, Dithizone

RESUMEN

Un método para remover trazas de mercurio (II) usando hidróxido de aluminio como colector. Ditizona en tetracloruro de carbono fue usado para la extracción del mercurio. La cantidad de Hg (II) varió desde 40 µg hasta 100 µg. La muestra, en volumen, varió hasta 50 ml y el nivel de extracción del mercurio fue registrado. Se encontró que la recuperación fue satisfactoria hasta una muestra de un volumen de 25 ml, más allá de lo cual la recuperación decrecía gradualmente. El efecto de la interferencia de iones fue estudiada a diferentes concentraciones de mercurio y se encontró que era mínima.

Palabras clave: mercurio (II), colector, hidróxido de aluminio, ditizona.

INTRODUCTION

Science and technology has conferred many benefits on mankind, in terms of rapid transport and communication, relief to labor, new and better materials to improve the standard of living and prolongation of life. However, ecological imbalances and environmental pollution have accompanied scientific progress. This emphasizes the importance of analytical chemistry, which serves to establish the concentration of various pollutants, and thus helps to control the environment. In our undergraduate Analytical chemistry course, the students are taught various separation techniques like GC, column adsorption chromatography, HPLC, solvent extraction, etc. Considerable emphasis is given to the application of these separation techniques for the removal of pollutants from wastewater. These include toxic heavy metals like Hg (II), Pb (II), etc. and organic contaminants such as dyes and other Polycyclic Aromatic Hydrocarbons (PAH). These separation techniques are then coupled with a suitable instrumental method of analysis.

The objective of this study was to develop a simple and rapid method for the removal of trace amounts of mercury. Literature survey revealed that most of the heavy metals are removed only by adsorption methods. Hence co-precipitation was considered as an alternative procedure.

AIM AND SCOPE OF THE PRESENT INVESTIGATION

The aim of the present investigation is to develop a simple and rapid method for the removal of trace amounts of mercury. The method is based on the coprecipitation of Hg (II) using Aluminium Hydroxide as collector. The coagulated precipitate enriched with mercury can be easily separated from their aqueous environment by filtration.

Co-precipitation for the Pre-concentration of trace metal ions in water(1)

There are 4 distinct mechanisms for precipitate contamination i.e co-precipitation. They are:

a. Surface adsorption

b. Isomorphic inclusion (mixed-crystal formation)

c. Non-isomorphic inclusion (solid-solution formation)

d. Occlusion (ion entrapment)

Surface adsorption

If a precipitate is formed from two ions of opposite charge and of the two if one is present in excess, the precipitated particles will tend to carry an excess of these ions on the surfaces, and thus will be charged. Electrostatic forces will then hold other ions of the opposite charges there. Colloidal hydrous oxides of iron, aluminium and certain other cations are precipitates that strongly adsorb heavy metals by this mechanism, the excess ions on the particle surface being hydroxide ions.

Isomorphic Inclusion (mixed-crystal formation)

Here the co-precipitated ion has dimensions and chemical composition such that it can fit into the crystal structure of the precipitate without causing appreciable strain or distortion. Sometimes both ions can be co-precipitated.

Non-isomorphic inclusion

Here the bulk material being precipitated acts as a solid solvent for the trace components. The trace metal ions are first complexed with an organic reagent.

Occlusion (ion entrapment)

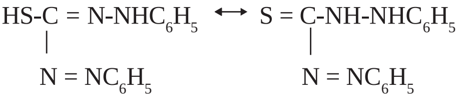
The precipitate is formed so fast that ions are physically engulfed in the solid before they can diffuse away. This reaction is somewhat unspecific.

Carrier (or) Collector

This is the material which when added to the solution at fairly high concentration is subsequently precipitated and with which the trace components are precipitated.

Dithizone- A reagent for estimation of mercury (2)

Diphenyl thiocarbazone (Dithizone) behaves in solution as a tautomeric mixture:



$$\underset{\textstyle N=NC_6H_5}{\text{HS-C}} = N\text{-}NHC_6H_5 \longleftrightarrow S = \underset{\textstyle N=NC_6H_5}{\text{C}}\text{-}NH\text{-}NHC_6H_5$$

It functions as a monoprotic acid ($pK_a = 4.7$) until a pH of about 12. The acid proton is that of the thiol group. Primary metal dithizonates are formed according to the reaction

$$M^{n+} + nH_2Dz \longleftrightarrow M(HDz)_n + nH^+$$

Some metals notably mercury, copper, silver, gold, bismuth and palladium form a secondary complex at a higher pH range or with a deficiency of the reagent.

$$2M(HDz)_n \longleftrightarrow M_2Dz_n + nH_2Dz$$

In general the primary dithizonates are of greater analytical utility than secondary dithizonates, which are less stable and less soluble in organic solvents.

Dithizone is a violet-black solid, which is insoluble in water, soluble in dilute ammonia solution, and also soluble in chloroform and in carbon tetrachloride to yield green solution. It is an excellent reagent for determination of small quantities of many metals and can be made selective for certain metals by resorting to one of the following procedures:

a. Adjusting the pH of the solution to be extracted. Thus from dilute acid solution (0.1-0.5 N) silver, mercury, copper and palladium can be separated from other metals; bismuth can be extracted from a weakly acidic medium; lead and zinc from a faintly alkaline or neutral medium; cadmium from a strongly basic solution containing citrate or tartrate.

b. Adding a complex-forming agent or masking agent, e.g., cyanide, thiocyanate, thiosulphate, or EDTA.

INSTRUMENTATION

A Spectronic-20 D UV Visible spectrophotometer (Milton Roy and Company, UK) was used for measuring the absorbance of the mercury-dithizone complex. The solution was taken in a 10 mm glass cuvette.

REAGENTS

All the reagents used were of analytical grade.

Preparation of required solutions

a. A stock solution of Hg (II)(1000 µg/ml) was prepared by weighing 0.1354 gm, and diluting it in 100 ml of water. From this the working solution of 100 µg/ml was prepared by taking 10 ml of the stock solution and making it up to 100 ml in a standard flask with water.

b. Dithizone solution is prepared in carbon tetrachloride by taking 0.005 gm in 100 ml.

c. 0.585 gm of Sodium chloride was dissolved in 100 ml of water to prepare a 0.1N solution.

d. 5 gm of Aluminium Sulphate was dissolved in minimum amount of water and Ammonium Hydroxide to prepare the required Aluminium Hydroxide slurry.

Calibration graph

The λ_{max} of Hg(II) complex with dithizone was obtained by scanning a wide range of wavelengths. The λ_{max} was found to be 490 nm. A calibration graph was prepared in the range 0.4 -1 ml of 100 µg/ml of Hg (II). The Hg (II) solution was mixed with 5 ml of 1N H_2SO_4 and diluted to 10 ml. The resulting solution was extracted with dithizone in carbon tetrachloride (10 ml). A blank was performed in the absence of Hg (II) and the blank corrected absorbance was measured. (Table 1).

Proposed Method for the removal of mercury(II)

4 ml of 10 µg/ml Hg (II) was added to 5ml of 1N Sodium chloride and 10 ml of Aluminium hydroxide slurry. The resulting solution was digested on a water bath for 2 minutes, allowed to cool and filtered using a G3 sintered crucible. The filtrate was discarded and the precipitate was dissolved in minimum amount of sulfuric acid and extracted with 10 ml of dithizone in carbon tetrachloride. The absorbance of the extract was measured and the concentrations of Hg (II) were established with respect to calibration graphs. (Table 2)

Effect of sample volume

The effect of change in the sample volume from 10 to 25 ml on the collection of mercury (II) was studied. Using 4 ml of 10 µg/ml of mercury (II) and 10 ml of the slurry, the separation and determination was carried out as described earlier. It was found that the recovery of mercury (II) is quantitative until a sample volume of 25 ml and a further increase in the sample volume caused a gradual decrease in its recovery. (Table 3)

Analysis of Hg(II) in synthetic mixture

A synthetic mixture was prepared with varying amounts of mercury (II), copper (II), cadmium (II) and cobalt (II). 5ml of 0.1N Sodium chloride and 10 ml of aluminium hydroxide slurry were added to the synthetic mixture and filtered using a sintered crucible. The filtrate was dissolved in minimum amount of sulphuric acid and the filtrate was extracted with 10ml of freshly prepared dithizone (in carbon tetrachloride). The absorbance was recorded. The same process was repeated for varying amounts of mercury (II).The results were found to be satisfactory. The effect of interfering ions was found to be minimum (Table 4).

TABLE 1. Calibration results

S. No	Concentration of Hg (II) (in µg/10 ml aqueous volume)	Absorbance
1	40	0.786
2	60	0.815
3	80	0.830
4	100	0.835

TABLE 2. results from the method developed

S. No	Amount of Hg (II) (in µg)	Amount of Hg (II) recovered (in µg)
1	40	39.64
2	60	59.85
3	80	79.81
4	100	99.64

TABLE 3. Effect of sample volume

S. No	Sample volume (in ml)	Amount of Hg (II) recovered (in µg)
1	10	39.28
2	15	39.05
3	20	38.75
4	25	38.60
5	50	29.15

TABLE 4. Analysis of Hg(II) in synthetic mixture

S. No	Composition of mixture (in ml)	Amount of Hg (II) found (in µg)
1	Cu^{2+}(500)+Hg^{2+}(40)	39
2	Cd^{2+}(1000)+Co^{2+}(1000) +Cu^{2+}(1000)+Hg^{2+}(60)	57
3	Cd^{2+}(1000)+Co^{2+}(1000) +Cu^{2+}(1000)+Hg^{2+}(80)	78
4	Cd^{2+}(1000)+Co^{2+}(1000) +Cu^{2+}(1000)+Hg^{2+}(100)	96

CONCLUSIONS

Thus a simple and rapid method has been developed for the effective removal of mercury by using alumiumum hydroxide as the collector. The extraction of mercury by dithizone (in carbon tetrachloride as diluent) was found to be effective.

This method has been found to be effective for concentrations of mercury (II) varying from 40-100 mg in 25 ml of aqueous volume. The recovery decreased when the sample volume was increased to 50 ml, and the method can be used for the collection of Hg (II) of concentrations down to 1.6 µg/ml.. The effect of varying the sample volume and interfering ions were studied and the results were found to be satisfactory.

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