Hydrazine Carbothioamide 2-[(4-Hydroxy-3-methoxyphenyl)methylene] as a Selective Reagent for Mercury(II)

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Hydrazine carbothioamide 2-[(4-hydroxy-3-methoxyphenyl)methylene] is proposed as a selective reagent for the rapid spectrophotometric determination of mercury(II). The reagent instantaneously forms an orange yellow coloured 1:2 complex in alkaline medium at room temperature. The complex exhibits an absorption maximum at 402 nm with a molar absorptivity of $1.37 \times 10^4$ litre mol$^{-1}$ cm$^{-1}$. Beer's law is valid over the concentration range of 0.1-9.5 ppm of Hg(II).

Mercury is an health hazard in places where the mercury/electrolytic cells operate. The volumetric and gravimetric methods are rather time consuming and seldom applicable to microgram quantities\(^1\). A limited number of reagents available for the spectrophotometric determination of mercury suffer from one disadvantage or the other. Hydrazine carbothioamide 2-[(4-hydroxy-3-methoxyphenyl)methylene] (HCHMM) was prepared by Guha-Sircar et al.\(^2\) who used it as a reagent for the detection of few metal ions. In this note we report the usefulness of HCHMM, as a sensitive and selective reagent for the rapid spectrophotometric determination of mercury(II).

The stock solution of mercury(II) was prepared by dissolving mercury(II) chloride (~1 g, AR) in 0.1 M hydrochloric acid (1 litre) and the solution was standardized by the potassium iodate method\(^4\). HCHMM was prepared by the reaction of hydrazine carbothioamide with vanillin and was purified by the recommended method\(^5\). A 0.3% solution of HCHMM was prepared in 85% ethanolic concentration (v/v).

Solutions of diverse ions of suitable concentrations were prepared using analytical grade reagents.

A Beckman spectrophotometer, model DB with matched 1 cm silica cells was used for absorbance measurements.

**Procedure**

To an aliquot of the stock solution containing 5-237.5 \(\mu\)g of mercury(II), was added ethanol (6 ml), HCHMM (3 ml, 0.3%), and sodium hydroxide (1 M, 3.5 ml) and the resulting solution was diluted to 25 ml with doubly distilled water. It was mixed well and the absorbance measured at 402 nm against a reagent blank prepared in the same manner. The amount of mercury was then deduced from the standard calibration graph.

HCHMM instantaneously forms an orange yellow complex with mercury(II) in acid medium (HCl, H$_2$SO$_4$, CH$_3$COOH or H$_3$PO$_4$) as well as in alkaline medium at room temperature (27°C). However, the complex is stable in acid medium for less than 2 min; while it is stable for 1 hr in alkaline medium, hence the alkaline medium was chosen. The complex gives maximum absorbance in the NaOH concentration range of 0.08 to 0.24 M. Hence, all studies were confined to 0.14 M sodium hydroxide. The effective ethanolic concentration is 28-72% (v/v). Below this alcoholic range turbidity is obtained while above this range maximum absorbance is not attained. Hg(II)-HCHMM system absorb maximally in the region 400-404 nm; at this wavelength the absorption due to the reagent and Hg(II) solution is negligible. A twenty-one-fold molar excess of the reagent over mercury (II) is required in order to obtain maximum absorbance. The absorbance readings are constant in the temperature range 5-40°C. Above 40°C the absorbance gradually decreases. The order of the addition of reagents was not critical.

The Hg(II)-HCHMM complex obeys Beer's law over the concentration range of 0.2-9.5 ppm of mercury. The optimum concentration range evaluated by Ringbom's method is 0.5-9.3 ppm. The molar absorptivity is $1.37 \times 10^4$ litre mol$^{-1}$ cm$^{-1}$ and Sandell's sensitivity is 14.6 ng cm$^{-2}$. The standard deviation calculated from 10 determinations in solutions containing 4 ppm of mercury(II) each is 0.006 ppm. Errors are in general about ±2%.

Job's method of continuous variation\(^6\) and mol ratio\(^7\) method indicate the formation of 1:2 complex (metal-ligand) having a log $K$ value of 6.7 at 27°C. Ion exchange experiments indicate that the complex is cationic in nature.

The following amounts (\(\mu\)g/ml) of foreign ions were found to give less than 2% error in the determination of 4 \(\mu\)g of mercury(II) per ml. Sb(III) 60, Cu(II) 1.8, Ag(I) 15, Ru(II) 16, Os(VIII) 15, Ir(III) 10, Pb(II) 120, Bi(III) 12, Bi(III) 36**, Fe(III) 40, Fe(II) 71†, Ni(II) 1.5, Ni(II) 2.5*, Zn(II) 118, Zn(II) 140*, Rh(III) 12, Pt(IV) 14, Pt(IV) 20‡, Pd(II) 1.4, Pd(II) 1.6**, Co(II) 10.4, Au(III) 14, Au(III) 20**, Ti(IV) 1, Cr(VI) 20, Mn(II) 2, W(VI) 1449, Cd(II) 45, Cd(II) 140**, Se(II) 118, As(III) 146,
fluoride 10800, chloride 67000, bromide 96000, iodide 5600, nitrate 9600, sulphate 9600, phosphate 860, acetate 5600, citrate 7600, and EDTA 440. Many cations and anions do not interfere. Interference from platinum metals and other cations could be reduced by using citrate*, phosphate** and EDTA† as masking agents.

The method was extended to the determination of mercury in synthetic mixtures corresponding to minerals, alloys and chlorite cell liquors. The results obtained were quite satisfactory.

References