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Indirect Complexometric Determination of Mercury Using Potassium Iodide as Selective Masking Agent

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This paper describes a indirect complexometric method for the determination of mercury in the presence of co-ions, based on the selective masking ability of potassium iodide. To the mixture of mercury (II) and other metal ion solution, EDTA solution was added in excess of the metal ions present. The pH of the solution was adjusted to 5.0-6.0 using solid hexamine (10 ± 2 g) and surplus EDTA was titrated with zinc sulfate solution using xylenol orange indicator. An excess of solid potassium iodide was then added to decompose the Hg-EDTA complex and the released EDTA was titrated with standard zinc sulfate solution. Accurate results were obtained for 4.5-80 mg (2.24×10^{-5} M - 3.99×10^{-4} M) of mercury with relative errors ≤ 0.4 %, standard deviations ≤ 0.07 mg. Sn(IV) and Au(III) interferes but can be masked using sodium fluoride. The method can be applied in the analysis of mercury in its alloys and complexes.

Key words: complexometry, EDTA, mercury determination, potassium iodide, masking agent.

Introduction

Mercury forms useful amalgams with alkali metals, transition metals and heavy non-transition metals such as Sn, Pb, Bi or Ba. Because of the extensive application and toxic nature of mercury amalgams and compounds, a selective analytical method for the determination of mercury became very important and hence, masking agents such as thiosemicarbazide,[1] cysteine[2] thiourea[3] and N-allylthiourea[4] (pH $\geq$ 9) were used for the selective determination of mercury. All of the above reagents quantitatively liberate EDTA from Hg-EDTA complex. Interference by copper is considerable using the above reagents. 4-amino-5-mercapto-3n-propyl-1,2,4-triazole,[5] 2-imidazolidenethione[6] thiocyanate,[7] hexahydropyrimidine- 2-thione,[8] 2-mercaptoethanol[9] sodium sulfite[10] acetylacetone[11] nitrite[12] and thiosulfate[13] are also used as masking reagents for the determination of mercury. There was interference due to T1(III) and Pd(II) for the above reagents except for acetylacetone[11] as a masking agent. Determination of mercury above 56 mg (2.79×10^{-4} M) is not accurate with acetylacetone as a masking agent due to the lack of sensitivity of the reagent. Interference due to Cl^- and Br^- was also not reported.

In this study potassium iodide was used as a masking agent for the indirect determination of mercury.

Reagents and Solutions

All reagents used were of analytical grade. Mercuric nitrate solution, 0.01 mol 1^{-1}, was prepared and standardized by the ethylenediamine method.[14] Zinc sulfate solution,0.02 mol 1^{-1}, was prepared in distilled water. EDTA solution, appox. 0.04 mol 1^{-1}, was prepared by dissolving disodium salt of EDTA in distilled water. 1% (W/W) xylenol orange indicator was made using ground potassium nitrate crystals. Potassium iodide crystals and hexamine were used unaltered.

Procedure

To an aliquot of acidic solution containing 4.5-80 mg (2.24×10^{-5} M - 3.99×10^{-4} M) of mercury (II), 5-30 ml of approx. 0.04 mol 1^{-1} EDTA solution was added and diluted to about 100 ml. About 0.03 g of xylenol orange indicator was added and the pH of the solution was adjusted to 5.0-6.0 using hexamine (10 $\pm$ 2 g). The surplus EDTA was titrated with 0.02 M zinc sulfate solution. To this solution solid potassium iodide crystals were added until there was no precipitate of HgI_2. The liberated EDTA was then titrated with 0.02 M zinc sulfate solution. This second titre value corresponds to the mercury (II) present.

$$1 \text{ ml of } 0.02 \text{ M } ZnSO_4 = 4.0118 \text{ mg of Hg.}$$

Results and Discussion

The absolute formation constant ($\log \beta$) of the Hg-EDTA complex has been reported to be 21.9[15], yielding a log conditional stability constant of 15.3 at pH 5.0. Mercury (II) forms a stable soluble complex with I^- as $[HgI_4]^{2-}(\log \beta = 29.8)$[16]. Potassium iodide is a good masking agent for mercury (II) in direct EDTA titrations.[17] At pH 10, potassium iodide is used as an indirect masking agent in the determination of mercury,[18] but several cations such as Zn (II), Ni (II), Co (II), Mg (II), Ca (II) interfere considerably. At pH 5.0-6.0 potassium iodide in excess (molar ratio 1:10::Hg:KI) is able to displace EDTA quantitatively from Hg-EDTA complex. It was found that 80-100 mg (4.8×10^{-4} M - 6×10^{-4} M) of potassium iodide caused the immediate release of the EDTA bound to 12 mg (5.98×10^{-5} M) of mercury, giving a clear solution. Lower quantities of potassium iodide resulted in a turbid solution of HgI_2. An excess of the reagent had no adverse effect on the determination of mercury present in mercuric nitrate solution.

Precision and Accuracy

To find out the accuracy and precision of the method, several determinations of mercury at different concentration levels were carried out using potassium iodide. The results obtained are shown in Table 1 with relative errors $\leq$ 0.4 % and standard deviations $\leq$ 0.07 mg. On comparing calculated t values for the determination of mercury between the range 4.5-80 mg (2.5-45 ml of $8.88 \times 10^{-3} Ml^{-1}$) with the tabulated value (t = 2.776), for degree of freedom four at a 5% level of significance, in most cases there was no significant difference between the values given by the standard method[14] and the method proposed.

Table 1. Determination of mercury in mercuric nitrate solution (n=5) using potassium iodide

Mercury present (mg)	Mercury found (mg)	Standard deviation (mg)	Student's t value	Relative error (%)
4.45	4.45	0.02	0.000	0.00
8.90	8.93	0.04	1.677	+0.34
17.81	17.86	0.04	2.795	+0.28
26.71	26.72	0.04	0.559	+0.04
35.62	35.62	0.07	0.000	0.00
44.52	44.47	0.04	2.795	-0.11
66.78	66.75	0.03	2.236	-0.05
80.14	80.21	0.07	2.236	+0.09

t = 2.776 for 5% level of significance.

Effect of Foreign Ions

The effect of different cations and anions on the quantative determination of mercury (II) was studied with aliquots containing 17.81 mg (8.88 $\times$ 10^{-5} M) of mercury(II). 100 mg; of Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Mg(II), Pb(II), or Ba(II); 50 mg of Ce(III), La(III) or Sm(III), 25 mg of Pd(II), Al(III), Tl(III), In(III), Cr(III), Fe(III), Y(III), Bi(III), V(IV), Ti(IV), Zr(IV), Pt(IV) or U(VI); 60 mg of F^-, Cl^-, Br^-, NO_3^-, CH_3COO^- or $C_2O_4^{2-}$ showed no intereference with relative errors $\leq$ 0.3 %. Hydrolysis of Sn(IV) and reduction of Au(III) by EDTA can be avoided by using fluoride (10% NaF 5-10 ml) for 10 mg of Au(III) and 20 mg of Sn(IV). It is worthy of note that there was no interference from Cu(II), Tl(III), Pd(II) and Cl^-. An excess of potassium iodide was able to release quantitatively the bonded EDTA only from the relatively weak Hg-EDTA complex in experimental conditions.

Applications

Analysis of Mercury in Artificial Mixtures

Mercury forms solid alloys with zinc and tin containing 42% and 15% mercury respectively. It also forms amalgams with Mg and Cu as MgHg and CuHg. Known amounts of pure Zn, Sn, Mg or Cu metal with pure Hg were taken and dissolved in a minimum amount of aqua regia and the oxides of nitrogen were expelled using concentrated H_2SO_4 until evolution of the brown fumes closed. The residue was extracted with distilled water and made up to 250 ml in a standard flask. Aliquots of 10 ml were used for titration using the recommended procedure. The results are shown in Table 2.

Analysis of Mercury Complex

Mercury complex of ethylene thiourea is prepared using the reported procedure[19] and a known amount of the complex was decomposed using 2N HNO_3 and few drops of concentrated HCl and heated until nearly dry. The residue was dissolved in water and made up to 100 ml in a standard flask. Aliquots of 10 ml were used for the determination of mercury using the method proposed. Good degrees of recovery and relative standard deviations were obtained (Table 3).

Table 2. Determination of mercury(II) in artificial mixtures of metals corresponding to alloy composition (n=3)

Mixture	Composition (%)	Hg found (%)	R.S.D. (%)
Hg + Zn	42 + 58	41.8	0.1
Hg + Mg	50 + 50	49.8	0.2
Hg + Cu	50 + 50	50.2	0.1
Hg + Sn*	15 + 85	14.9	0.2

Fluoride used to mask Sn(IV)

R.S.D.: Relative Standard Deviation

Table 3. Analysis of Mercury Complex (n=3)

Complex	Hg present (%)	Hg found (%)	R.S.D. (%)
$Hg(C_3H_6N_2S)_2Cl_2^*$	42.18	42.06	0.12

Mercury complex of imidazolidine-2-thione

R.S.D.: Relative Standard Deviation

Conclusions

The masking agent potassium iodide is readily available and the addition of excess reagent liberates EDTA quantitatively from Hg-EDTA complex. The method is simple and accurate as it does not require heating before the second titration in addition to standardizations of EDTA.

This method extends the working range up to about 80 mg (3.99×10^{-4} M) of mercury compared with 56 mg (2.79×10^{-4} M) of mercury for acetylacetone reagent.

There is no interference from 100 mg of Cu(II), 25 mg of Tl(III) and Pd(II) for about 18 mg of mercury(II). Interference from Sn(IV) and Au(III) can be eliminated by using fluoride ions as a secondary masking agent. The lack of effect of foreign ions on the accuracy and precision indicates that the method may be suitable for the determination of mercury in its alloys and complexes.

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