

## Complexometric method for the determination of mercury using sodium metabisulphite as selective masking reagent

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A selective complexometric method is described for the determination of mercury(II) using sodium metabisulphite as a masking reagent. An excess of EDTA is added to mercury(II) solution containing associated diverse metal ions and the surplus EDTA is back titrated at pH 5-6 (hexamine buffer) with standard zinc sulphate solution using xylenol orange as indicator. An aqueous solution of sodium metabisulphite is then added to displace EDTA selectively from Hg-EDTA complex and the released EDTA is then titrated against the same standard zinc sulphate solution. Reproducible and accurate results are obtained in the range 4-100 mg of mercury with a relative error  $\leq 0.26\%$  and coefficient of variation  $\leq 0.40\%$ . The method is useful for the analysis of mercury in complexes and alloy samples.

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Mercury(II) is a protoplasmic poison, toxic even at sub-trace levels and causes many diseases<sup>1</sup>. Compounds of mercury are used widely as fungicides and pesticides. Mercury forms amalgams with many metals, which find various applications in diverse fields such as Ag-Hg in dental fillings, Zn-Hg as reducing agent in chemical synthesis, and Cd-Hg in Weston-cadmium cell. In most of these applications, often a simple, rapid and accurate analytical method for determining the mercury content in the samples is essential. Mercury(II) is usually determined in the presence of associated metal ions by the selective decomposition of Hg-EDTA complex with masking agents. When thiosemicarbazide<sup>2</sup> and thiourea<sup>3</sup> are used as masking agents, many metal ions show interference. The method using N-allylthiourea<sup>4</sup> as masking agent requires heating to decompose the Hg-EDTA complex and also precipitation of HgS occurs. 4-Amino-5-mercapto, 3-propyl-1,2,4-triazole<sup>5</sup>, thiocyanate<sup>6</sup>, 2-imidazolidine-thione<sup>7</sup>, hexahydro pyrimidine-2-thione<sup>8</sup> and acetylacetone<sup>9</sup> are also used as masking reagents for

mercury(II). Some of the reagents<sup>5,7,8</sup> require tedious and time-consuming preparation methods. 3-Mercapto propane-1,2-diol<sup>10</sup>, thioglycolic acid<sup>11</sup> and 2-mercapto propionyl glycine<sup>12</sup>, have been reported earlier as selective masking reagents for mercury.

This paper describes the application of sodium metabisulphite ( $\text{Na}_2\text{S}_2\text{O}_5$ ) as a selective masking reagent for the complexometric determination of mercury(II). Copper(II) does not interfere and the decomposition of Hg-EDTA complex takes place instantaneously at room temperature.

### Experimental Procedure

#### Materials

Analytical grade chemicals were used. A stock solution containing 3.86 mg/mL of mercury(II) was prepared by dissolving 6.83 g of mercury(II) nitrate (Merck) in one litre distilled water and standardised gravimetrically by ethylenediamine method<sup>13</sup>. EDTA solution (0.04 M) was prepared by dissolving 14.89 g of disodium salt of EDTA (Merck) in distilled water and diluting to one litre. Zinc sulphate solution (0.02 M) was standardised by oxinate method<sup>13</sup>. Sodium

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metabisulphite (Merck) was used as 2% solution in distilled water. Xylenol orange indicator (0.5%) was prepared in distilled water.

#### Determination of mercury

To a solution containing 4-100 mg of mercury(II) and varying amounts of foreign ions, 1-25 mL of 0.04 M EDTA was added and the mixture was diluted to about 100 mL with distilled water. The pH of the solution was adjusted to 5-6 by adding solid hexamine. The surplus EDTA was backtitrated against standard zinc sulphate solution to a sharp colour change of xylenol orange from yellow to red. To this, an excess of 2% sodium metabisulphite solution (1 mL for each 4 mg of Hg) was added and the contents were mixed well. The liberated EDTA was then titrated against the same standard zinc sulphate solution as before. The second titre value is equivalent to the mercury content in the aliquot.

#### Analysis of alloy samples

A known weight (0.2-0.3 g) of alloy sample was dissolved in minimum amount of concentrated nitric acid by slow heating. Tin present, if any, precipitated as metastannic acid and was filtered off. The solution or filtrate was diluted with distilled water and made up to 100 mL in a standard flask. Aliquots of 10 mL were used for the determination of mercury by the procedure described.

#### Analysis of mercury complexes

Mercury(II) complexes with thiourea, thiocarbohydrazide, 1,2,4-triazole-3(5)-thiol, thionalide, 4-amino-5-mercapto-3-methyl-1,2,4-triazole were prepared and purified as in the reported-procedures<sup>14-17</sup>. A known weight of the complex (0.1-0.2 g) was carefully decomposed with aqua-regia by evaporation to near dryness. The residue was cooled, dissolved in distilled water and made up to 100 mL in a standard flask. Aliquots of 10 mL were used for titration by the recommended procedure.

#### Results and Discussion

Sodium metabisulphite selectively decomposes Hg-EDTA complex and release EDTA quantitatively. The mercury(II) then forms a stable soluble complex with the reagent. Mercury(II) being a soft metal ion, prefers to bond strongly with sulphur containing ligands<sup>18,19</sup>. It is, therefore, reasonable to expect that Hg-reagent complex formed is apparently more stable than Hg-EDTA complex. The instantaneous release of EDTA from Hg-EDTA complex at room temperature itself supports this view. Further, no precipitates are formed

during titrations under the experimental conditions. This helps in the detection of sharp end-point.

#### Effect of excess reagent

The addition of sodium metabisulphite in the molar ratio of 1:5 (Metal:Reagent) was found to be sufficient for the instantaneous and quantitative release of EDTA from Hg-EDTA complex. However, no adverse effects were noticed on adding large excess of the reagent.

#### Reliability of the method

To assess the accuracy and precision of the proposed method, determinations of mercury at different concentration levels were carried out as per the recommended procedure. It is evident from the results (Table 1) that the observed relative error of the method is less than 0.26% and the coefficient of variation not more than 0.40%. Thus the method is accurate besides being precise.

#### Effect of foreign ions

The effect of the presence of various foreign ions on the quantitative determination of mercury were studied with aliquots containing 19.30 mg of mercury(II). Of the various cations and anions tested individually in the determination of mercury(II), no interference was observed in the presence of 200 mg of Zn(II), Pb(II), acetate, borate, citrate, fluoride, nitrate, oxalate, sulphate; 150 mg of chloride; 100 mg of

Table 1—Determination of mercury in mercury(II) nitrate solution

Mercury, mg		Coefficient of variation (%)	Relative error (%)
Taken	Found*		
3.86	3.87	0.40	+0.26
7.72	7.71	0.28	-0.13
11.58	11.61	0.37	+0.26
19.30	19.28	0.26	-0.10
38.60	38.50	0.11	-0.26
57.90	58.00	0.07	+0.17
77.20	77.26	0.11	+0.08
100.36	100.52	0.11	+0.16

\* Average of six determinations

Cu(II), Cd(II), Ni(II), Co(II), Bi(III); 40 mg of Ag(I), Al(III), Fe(III), Mo(VI), Ti(IV); 20 mg of Mn(II); 15 mg of Ru(III), Rh(III), Pt(IV), Ir(III), Au(III), As(V). The metal ions such as Tl(III), Pd(II) and Sn(IV) show severe interference. This is due to the simultaneous release of EDTA from their respective EDTA complexes by the reagent. However, the interference of Tl(III) (up to 40 mg), Pd(II) (20 mg) and Sn(IV) (40 mg) can be eliminated by premasking these ions with hydrazine sulphate, L-histidine and sodium fluoride respectively.

#### Analytical applications

The present method was applied to the determination of mercury in alloy samples. The results (Table 2) are in reasonably good agreement with those obtained gravimetrically by periodate method<sup>13</sup>. The method developed was also applied to the determination of mercury in its complexes (Table 3). From the experimental results, it can be concluded that the method can be conveniently employed for the rapid analysis of such samples with a fair degree of accuracy.

Table 2—Determination of mercury in alloy samples

Alloy sample	Mercury* present (%)	Mercury** found (%)	Relative error (%)
Dental amalgam (Hg-Ag-Sn-Cu)	41.80	41.68	-0.29
Hg-Zn alloy	25.08	25.14	+0.24
Hg-Cu alloy	50.16	50.04	-0.24

\* Estimated gravimetrically by periodate method.  
\*\* Average of three determinations.

Table 3—Determination of mercury in complexes

Complex	Mercury present (%)	Mercury* found (%)	Relative error (%)
Hg(CH <sub>3</sub> N <sub>2</sub> S)Cl <sub>2</sub> ·½H <sub>2</sub> O <sup>a</sup>	56.18	56.08	-0.18
Hg(CH <sub>3</sub> N <sub>2</sub> S)Cl <sub>2</sub> <sup>b</sup>	47.28	47.18	-0.21
Hg(CH <sub>3</sub> N <sub>2</sub> S)Cl <sub>2</sub> <sup>c</sup>	41.46	41.56	+0.24
Hg(C <sub>6</sub> H <sub>5</sub> N <sub>2</sub> S) <sub>2</sub> <sup>d</sup>	49.55	49.42	-0.26
Hg(C <sub>6</sub> H <sub>5</sub> ONS) <sub>2</sub> <sup>e</sup>	31.70	31.62	-0.25
Hg(C <sub>6</sub> H <sub>5</sub> N <sub>2</sub> S) <sub>2</sub> <sup>f</sup>	43.71	43.60	-0.25
[Cu(en) <sub>2</sub> ][HgI <sub>4</sub> ]	22.49	22.54	+0.22
Hg[Zn(CNS) <sub>2</sub> ]	40.26	40.34	+0.20

\* Average of three determinations.

Mercury complex with thiourea<sup>ab</sup>, thiocarbonylhydrazide<sup>c</sup>, 1,2,4-triazole-3(5)-thiol<sup>d</sup>, thionalide<sup>e</sup>, 4-amino-5-mercapto-3-methyl-1,2,4-triazole<sup>f</sup>.

#### Conclusions

To conclude, the proposed method is simple and rapid besides being accurate. It does not require any heating for the quantitative release of EDTA from the Hg-EDTA complex. Sodium metabisulphite is readily available, cheap and water soluble reagent, so that it can be used conveniently. The reagent forms no precipitate either with mercury(II) or the titrant under the experimental conditions. This facilitates the detection of a sharp end-point. The method is fairly selective, so it can be used successfully for the rapid analysis of mercury in its complexes and alloy samples.

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