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N-Benzenesulphonyl *β*-Alanine as a Masking Agent for Hg(II)

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N-Benzenesulphonyl glycine and *N*-benzenesulphonyl α-alanine form water soluble complexes with Hg(II), Cu(II), and Ag(I). But *N*-benzenesulphonyl *β*-alanine ($R_b{}^\beta H_2$) gives only stable complex ion $Hg(R_b{}^\beta)_2{}^{2-}$, showing that $R_b{}^\beta H_2$ is a highly selective masking agent for Hg(II). Utilising this masking property, methods for detection and determination of Hg(II) have been developed. $R_b{}^\beta H_2$ reacts with Hg(II) at pH≈8, yielding the ion $Hg(R_b{}^\beta)_2{}^{2-}$ and on subsequent treatment with KI, two equivalents of alkali are liberated. On titrating the alkali liberated with a standard acid, the amount of Hg(II) may be calculated. Interferences due to diverse ions have been studied; Br^- and I^- interfere. The spot test of Hg(II) based on the same principle has been developed and it appears to be specific under specified condition. The limit of identification is 0.5 μg with a dilution limit of 1:100000.

A rapid and accurate method for determination of Hg(II) has been described using *N*-benzenesulphonyl glycine (R_bH_2).[1] *N*-Benzenesulphonyl glycine forms water soluble complexes[2] $K_2Hg(R_b)_2$, $Na_2Cu(R_b)_2$, and $KAg(R_b)$ which are stable at pH≈8 or higher. The comparable results are also obtained with the ligand *N*-benzenesulphonyl α-alanine ($R_b{}^\alpha H_2$);[3] the Ag(I) compound could not be isolated in the pure state. But *N*-benzenesulphonyl *β*-alanine ($R_b{}^\beta H_2$) gives at higher pH only stable complex[3] $K_2Hg(R_b{}^\beta)_2$ showing that $R_b{}^\beta H_2$ is highly selective masking agent for Hg(II). Utilising this masking property of $R_b{}^\beta H_2$, detection as well as determination of Hg(II) is possible in presence of various commonly associated cations and anions such as Ag(I), Cu(II), Be(II), Mg(II), Zn(II), Cd(II), Pb(II), Al(III), Fe(III), Cr(III), Bi(III), Zr(IV), Th(IV), U(VI), chloride, sulphate, acetate, phosphate, molybdate, and vanadate.

The compound $R_b{}^\beta H_2$ is a monobasic acid but the dissociation of the hydrogen attached to the nitrogen increases so much on complex formation that it becomes possible to titrate with an alkali in the case of $H_2Hg(R_b{}^\beta)_2$, affording complex salts. Thus when Hg(II) solution is titrated with a standard alkali solution in presence of $R_b{}^\beta H^-$ ($R_b{}^\beta H_2$ made neutral to phenolphthalein with KOH), then there occurs the following reaction:

$$Hg^{2+} + 2R_b{}^\beta H^- + 2OH^- = Hg(R_b{}^\beta)_2{}^{2-} + 2H_2O$$

In presence of other metal ions stated above, during this titration Hg(II) gives water soluble $Hg(R_b{}^\beta)_2{}^{2-}$ anion and the other metal cations are precipitated mostly as their hydrous oxides. On adding excess of KI to the neutralised solution, $Hg(R_b{}^\beta)_2{}^{2-}$ reacts according to the following equation:

$$Hg(R_b{}^\beta)_2{}^{2-} + 4I^- + 2H_2O = HgI_4{}^{2-} + 2R_b{}^\beta H^- + 2OH^-$$

The moles of alkali liberated are equivalent to twice those of Hg(II) present. Therefore

$$1\ ml \text{ of } (N)\ H_2SO_4 \equiv 100.3 \text{ mg of mercury}$$

Based on the same principle a virtually specific spot test has been developed for Hg(II).

Experimental

Reagents and Solutions. All solutions were prepared with carbon dioxide free water and the reagents used were of A. R. quality except in a few cases where they were properly purified. The reagent $R_b{}^\beta H_2$ was prepared and purified in the laboratory following the method stated in the literature.[4]

A standard alkali solution was prepared by dissolving pure KOH in water and standardised against $KH(IO_3)_2$ using phenolphthalein as indicator.

A standard dilute sulphuric acid solution was prepared by standardising against above alkali using phenolphthalein as indicator.

For preparing stock solution of $R_b{}^\beta H_2$, it was suspended in water and titrated with KOH solution to phenolphthalein end point and diluted so that the strength was about 3.5%.

Stock mercuric nitrate solution was prepared by dissolving pure HgO in nitric acid, free from nitrous fumes. This solution was standardised gravimetrically[5] as HgS and volumetrically with *N*-benzenesulphonyl glycine[1] along with free as-

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[1] N. N. Ghosh and M. N. Majumdar, *J. Indian Chem. Soc.*, **41**, 286 (1964).

[2] N. N. Ghosh and M. N. Majumdar, *ibid.*, **40**, 945 (1963).

[3] N. N. Ghosh and A. Bhattacharyya, *ibid.*, **46**, 1040 (1969).

[4] H. V. Pechmann, *Ann. Chem.*, **264**, 289 (1891).

[5] A. I. Vogel, "A Text Book of Quantitative Inorganic Analysis," Longmans, Green and Co., Ltd., London (1968), p. 487.

TABLE 1. DETERMINATION OF Hg(II)

Hg(II) soln. taken in m*l*	Hg present in mg	Alkali reqd. in m*l* (0.04139N KOH soln.)	Acid reqd. in m*l* (0.04458N H_2SO_4)	Concentration of free acid found	Hg found in mg	Error %
4	35.58	13.85	7.95	0.05469N	35.55	−0.10
5	44.48	17.30	9.95	0.05448N	44.49	+0.02
6	53.38	20.75	11.95	0.05440N	53.44	+0.11
8	71.17	27.70	15.90	0.05469N	71.11	−0.09
10	88.96	34.60	19.95	0.05424N	89.21	+0.28

sociated acid. Concentrations of Hg(II) and free acid were found to be 0.04435M and 0.05450N, respectively.

Spot Test for Hg(II). *Procedure*: The solution of Hg(II) nitrate containing some other ions was treated with excess of $R_b{}^{\beta}H^-$ and slight excess of alkali using phenolphthalein (one drop of 1% ethanolic solution) till it became pink in colour. It was boiled for one minute, whereby other metals completely precipitated as oxide, just decolourised with dil H_2SO_4 solution and centrifuged. To one drop of the colourless test solution on a spot plate, one drop of 1% KI solution was added. A pink colour appeared due to liberation of alkali, confirming the presence of Hg(II). The limit of identification was found to be 0.5 μg of Hg(II) with a dilution limit of 1 : 100000.

Interferences: The spot test described above was highly selective and appeared to be specific under specificed conditions. Interferences were not found with Ag(I), Cu(II), Be(II), Mg(II), Zn(II), Cd(II), Pb(II), Al(III), Cr(III), Bi(III), Ti(IV), Th(IV), Zr(IV), U(VI), phosphate, molybdate, and vanadate. Chloride in small concentration did not interfere. Bromide and iodide interfered. However by adding excess of $AgNO_3$, the interference due to chloride, bromide, and iodide for identification of Hg(II) may be eliminated. But there was a decrease in sensitivity particularly in presence of iodide.

Volumetric Determination of Hg(II). *Procedure*: A known volume of the standard Hg(II) solution was taken in a flask, treated with excess [about 3 to 4 times the amount of Hg(II) present] of the prepared reagent ($KR_b{}^{\beta}H$). The volume at this stage was kept about 50 m*l*. After adding two drops of 1% ethanolic solution of phenolphthalein, it was titrated with a standard alkali solution till a pink colour appeared. The amount of alkali consumed was equivalent to the sum of the free acid and twice the moles of Hg(II) present. To this solution excess of KI ($\approx$2 g) was added, when colour of the solution changed to deep pink due to liberation of alkali. This was titrated with a standard acid solution. The amounts of Hg(II) and free acid, taken and found by estimation, are shown in Table 1.

For determination of Hg(II) when associated with other metal ions the method was modified as follows: the solution was titrated with an alkali solution till a pink colour appeared and a slight excess was added. The volume at this stage was 50—60 m*l*. This mercury solution with the precipitated oxides of other metals was boiled for 2 min. The excess of alkali was then just neutralised, cooled and the volume was made upto 100 m*l*. The precipitates were then allowed to settle for about 1 hr. Fifty milliliters of the clear supernatant liquid was pipetted out and Hg(II) was estimated. The determination of Hg(II) at this stage was made to confirm that the extraction of Hg(II) as water soluble complex ion $Hg(R_b{}^{\beta})_2{}^{2-}$ was quantitative or not. In typical cases titrations, 5 m*l* of standard Hg(II) nitrate solution [containing 44.48 mg of Hg(II)] was taken along with other metal salt solutions. Foreign ions with the amounts in the parentheses that were tolerated are stated in Table 2.

TABLE 2. EFFECT OF FOREIGN IONS

Cations	Ag^+(37.6 mg), Cu^{2+}(35.52 mg), Pb^{2+}(64.0 mg)
	Be^{2+}(5.0 mg), Mg^{2+}(12.1 mg), Cd^{2+}(54.4 mg), Zn^{2+}(24.0 mg)
	Al^{3+}(7.2 mg), Fe^{3+}(10.4 mg), Cr^{3+}(10.5 mg), Bi^{3+}(64.0 mg)
	Zr^{4+}(10.6 mg), Th^{4+}(21.8 mg), $UO_2{}^{2+}$(45.6 mg)
Anions	Cl^-(25 mg), Cl^- with excess of $AgNO_3$(37.5 mg), $SO_4{}^{2-}$(560 mg)
	CH_3COO^-(780.0 mg), $HPO_4{}^{2-}$(43.04 mg), $MoO_4{}^{2-}$(41.5 mg), $VO_3{}^-$(46.2 mg)

Interferences: All cations which were precipitated as hydrous oxides gave low results when present in large amounts due to adsorption. Anions-acetate, sulphate, chloride in small concentration, phosphate, molybdate, and vanadate did not interfere, but chloride in large concentration, bromide and iodide interfered. However by adding excess of $AgNO_3$ to the original solution, the interferences due to chloride could be eliminated.

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