HCl, transferred to a 25 ml volumetric flask, made up to the mark and measured spectrophotometrically at 705 nm against a reagent blank prepared in a likewise manner.

The reagent has a negligible absorption at 705 nm. In the absence of interfering ions, a $1 \times 10^{-3}M$ reagent solution is adequate for complete colour development with Fe(II). In the presence of high concentration of foreign ions, a saturated reagent solution should be used.

The green complex obeys Beer's law in the range 0·2-5·6 µg/ml of Fe(II), the molar absorptivity and Sandell sensitivity[9] at λ_{max} (705 nm) being $1·8 \times 10^4$ litre mole⁻¹ cm⁻¹ and 0·003 µg of Fe(II) cm⁻² respectively. The colour is stable indefinitely at pH 4·5-6 but once it is made highly acidic, it begins to fade slowly. The absorbance measurements should, therefore, be made within 30 min of the acidification of the sample-NHQS system.

The ions commonly associated with Fe(II) in natural or synthetic mixtures, viz. Al(III), Cu(II), Ni(II), Zn(II), Mn(II), Hg(II), Cd(II), Mg(II), Be(II), Cr(VI), UO_2(II), Ca(II), Na(I), K(I), are tolerated in ratios 1:100: : Fe(II): foreign ion. Presence of SO_4^{2-}, NO_3^-, CH_3COO^-, Cl⁻, Br⁻, I⁻ has no effect on the determination. Complexing ions citrate, tartarate, ascorbate and thiosulphate are tolerated in ratios 1:1000. Gold(III), V(IV), Ce(III), Th(IV), La(III) and Ti(IV) are tolerated if present in concentrations 25 times to that of Fe(II) while Pt(IV), Ru(III), Os(III), Pd(II), Ag(I) and Co(II) can be present in a concentration comparable to that of Fe(II). Attempts to mask Co(II) with citrate, tartarate, thiosulphate and nitrite were unsuccessful.

Determination of Fe(II) in tap water — Tap water (2 litres) was concentrated to 5 ml by boiling. After cooling, it was brought to pH $\simeq 4$ with HCl and 2 ml of 1% hydroquinone solution was added to it to reduce Fe(III) to Fe(II). From this solution, Fe(II) was determined as described before. Quadruplicate measurements yielded a value $0·84 \pm 0·02$ ppm.

Composition of the complex — Aly *et al.*[8] had proposed that in Fe-NHQS system Fe(II) is chelated to the oxygens of nitroso and hydroxyl groups of the ligand. The unpublished kinetic and potentiometric studies of the present workers endorse this view and confirm that in the green complex, Fe and NHQS are combined in a ratio 1:3.

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Hexacyanoferrate(III) as a Primary Standard for the Determination of Sb(III) in Bicarbonate Medium

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Arsenic(III) and antimony(III) in bicarbonate medium can be determined using hexacyanoferrate (III). The method involves liberation of iodine from potassium iodide by ferricyanide in the presence of zinc sulphate and titration of this iodine with As(III) or Sb(III).

SEVERAL methods, such as gravimetric[1], amperometric[2], potentiometric[3], spectrophotometric[4] and titrimetric, are available for the determination of As(III) and Sb(III). Amongst the various titrimetrics methods[5-14] indirect cerimetric method[12] in acid medium and chloramine-T method[6] in alkaline medium, appear to be most suitable. In the iodine method[10], which is simple and is applicable in bicarbonate medium, iodine is not a primary standard. Other methods of determination are either not direct or not easy to manipulate. Recently silver(III)[15], copper(III)[16] and N-bromosuccinimide[17] have also been reported to react with As(III). It has been found by Deshmukh and Sant[18] that hexacyanoferrate(III) can be employed for the determination of As(III) in bicarbonate medium. In the present note an improvement over this method has been suggested. It is found that KI can be added directly in the bicarbonate medium and that there is no necessity of adding HCl. The determination of Sb(III) is also described.

Potassium hexacyanoferrate(III), zinc sulphate, sodium bicarbonate and potassium iodide were of BDH (AnalaR) quality. Sodium metaarsenite (Riedel) was employed as source of As(III) and potassium antimonyl tartrate (May & Baker) for Sb(III). Solutions were prepared by direct weighing in redistilled water (second distillation from permanganate). Aqueous solutions of As_2O_3 obtained by boiling it with water and acid solutions of Sb_2O_3 obtained by boiling it with 30% perchloric acid, could also be used. Alkaline solutions of As(III) after neutralizing it with HCl could also be used. These solutions were standardized iodometrically[10].

Procedure — Hexacyanoferrate(III) solution (2-10 ml) of suitable concentration, saturated solution of sodium bicarbonate (5 ml) and potassium iodide (2 g) were taken in an Erlenmeyer flask and the volume made up to 25 ml. $0·2M$ $ZnSO_4$ solution (5 ml) was added with shaking. The liberated iodine was titrated against the unknown As(III) or Sb(III)

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**TABLE 1 — DETERMINATION OF Sb(III) BY $K_3Fe(CN)_6$ IN BICARBONATE MEDIUM**

[Saturated $NaHCO_3$, 5 ml; $0.2M$ $ZnSO_4$, 5 ml; total volume, 25 ml]

| $[K_3Fe(CN)_6]$ used $M \times 10^3$	Sb(III) (mg) Taken	Found	Error (%)
20	72·9	72·9	—
16	58·5	58·3	−0·3
2	3·9	43·6	−0·7
10	36·7	36·8	+0·3
8	29·0	29·1	+0·35
4	14·6	14·55	−0·3
2	7·29	7·29	—
1·6	5·86	5·88	+0·3
1·2	4·36	4·37	+0·2
1·0	3·64	3·65	+0·3
0·8	2·925	2·92	−0·6
0·4	1·46	1·455	−0·3
0·2*	0·729	0·729	—

*10 ml of $ZnSO_4$ instead of 5 ml were used.

solution from the burette using starch as an indicator. The results in most cases were within $\pm 0.5\%$. The results with Sb(III) are recorded in Table 1.

In strongly acidic solution[19] reaction (1) proceeds in the forward right direction whereas the course is reversed in neutral solutions.

$$2Fe(CN)_6^{3-} + 2I^- \rightleftharpoons 2Fe(CN)_6^{4-} + I_2 \qquad ...(1)$$
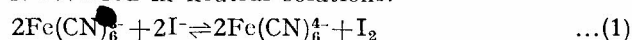
In bicarbonate medium, the reaction can be made to go in the forward direction by employing zinc sulphate[20]. The formation of the precipitate of zinc ferrocyanide shifts the equilibrium towards the right. The use of bicarbonate medium to shift the equilibrium(2) to the right is well known.

$$As(III) \text{ or } Sb(III) + I_2 + H_2O \rightarrow As(V) \text{ or } Sb(V) + 2I^- + 2H^+ \qquad ...(2)$$
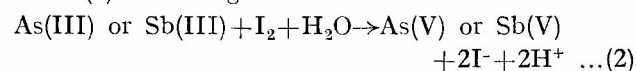
The method is thus a combination of iodometry and iodimetry.

When using hexacyanoferrate(III) in concentration range $0.0001M$-$0.002M$, 10 ml of $0.2M$ $ZnSO_4$ must be added to obtain correct results. It was found that larger quantities of $ZnSO_4$ are required if more than the recommended quantity of $NaHCO_3$ is used.

For Sb(III) solutions the method is not applicable for concentrations less than $0.002M$. The tolerable limit of tartarate is five times that of Sb(III) used.

The titrations cannot be performed by using hexacynoferrate(III) in the burette, and arsenite or antimony(III) along with KI, $NaHCO_3$ and $ZnSO_4$ in the flask. The reason for this is not obvious. A white precipitate of unknown composition is formed.

A determination with permanganate under identical conditions is also possible.

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Determination of Ba(II) by Precipitation as Barium Oxalate from Homogeneous Solution by Diffusion Method

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Preparation of barium oxalate from homogeneous solution by diffusion technique using ammonia has been advantageously utilized for the gravimetric estimation of Ba(II). Precipitation is slow in the presence of ammonia and is quantitative between pH 9·5 and 10·5. Good recoveries of Ba(II) are made in the presence of moderate concentrations of Mg(II), Zn(II), Al(III), Co(II), Ni(II) and Mn(II). Fe(III) and Cu(II) interfere. Anions such as acetate, Cl⁻ and NO_3^- do not interfere.

THE conventional method for the determination of Ba(II) as barium oxalate is not useful for its quantitative estimation[1,2]. However, gravimetric determination of barium as barium oxalate can be carried out satisfactorily by precipitating barium oxalate from a homogeneous solution, applying the diffusion technique. The results of such a study are reported in this note.

The results (Table 1) show that 60·95 to 304·76 mg of barium can be determined with fair accuracy. The unprecipitated barium, found in the filtrate by the tracer technique, was about 50 μg for 152·38 mg.