Potentiometric Titration of Iron(III) with Hydrazine Sulphate at Room Temperature

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Conditions have now been developed for a direct potentiometric titration of iron(III) with hydrazine sulphate at room temperature. Osmium tetroxide markedly catalyses the reaction in medium of 2.0—3.0 pH. Under the conditions prescribed four moles of iron(III) are reduced per every mole of hydrazine oxidised. Application of the new method to the assay of iron(III) in an alloy is also considered.

Hydrazine sulphate, $N_2H_4 \cdot H_2SO_4$ is now readily available at the purity required of a primary standard. It is non-hygroscopic and has a long shelf life. Aqueous hydrazine sulphate solutions are reported to be stable even for a long period of two months.[1] In view of these considerations it has been proposed as a primary standard in acid-base titrimetry[2] and in redox titrimetry.[3] The use of the hydrazine sulphate as a reducing agent has been reviewed by Berka, Vulterin, and Zyka.[4] A survey of the literature shows that the reagent has not been used till now for the detremination of iron(III). Many years ago Kirk and Browne[5] propounded an interesting hypothesis that one electron oxidising agents react with hydrazine to give nitrogen and ammonia according to the equation:

$$N_2H_4 - e \longrightarrow \frac{1}{2}N_2 + NH_3 \qquad (1)$$

and with two electron oxidising agents giving only nitrogen according to the overall equation

$$N_2H_4 - 4e \longrightarrow N_2 + 4H^+ \qquad (2)$$

The stoichiometry of four equivalents of oxidising agent per mole of hydrazine required by Eq. (2) is found to be followed by reactions of hydrazine with iodine, bromine, iodine monochloride and thallic chloride. With one electron oxidising agents like iron(III), manganese(III), and cerium(IV) the number of equivalents of oxidising agent per mole of hydrazine was never found to be one as required by Eq. (1) but was found to be lying between 1 and 2. For the reaction with cerium(IV) in sulphuric acid medium Benrath and Ruland,[6] and Gopala Rao, Subramanyam, and Krishna Rao[7] obtained values of 1.221 and 1.224 respectively for the value of the equivalents of cerium-(IV) reacted with one mole of hydrazine at 80—90°C. The latter workers showed that a direct titration of hydrazine in 1N sulphuric acid medium can be made at 50° with a potentiometric end-point in the presence of manganous sulphate as a catalyst. It was observed that manganese(II) not only affected a considerable acceleration of the reaction but also brought down the stoichiometry of the reaction from 1.224 to 1.016. The value of 1.016 is closer to 1.0 as required by the hypothesis of Kirk and Browne and this improvement in stoichiometry could be understood in terms of the hypothesis because manganese(II) acts as a catalyst through a one-electron mechanism by its oscillation between the +2 and the +3 oxidation states. A more striking change in the stoichiometry was observed by Gopala Rao and Krishna Rao[8] in their titration of hydrazine hydrochloride in hydrochloric acid medium with cerium(IV) nitrate at room temperature in the presence of potassium bromide as a mediator. In this case there is a swing in the stoichiometry of the reaction in the other direction, changing from 1.224 to 4.0. The reaction of hydrazine with cerium(IV) in the presence of potassium bromide undoubtedly occurs through bromine as per Eq. (2) above. Having thus achieved the change of type in the case of hydrazine-cerium(IV) reaction from a mixed type to an accurately stoichiometric 2-electron type with the use of bromide as a mediator or from a mixed type to a very nearly 1-electron type with the use of manganese(II) as a catalyst, we undertook an investigation to see if the iron(III)-hydrazine reaction can also be made to conform to an accurate integral stoichiometry of any one type. Studying the reaction of iron(III) with hydrazine in sulphuric acid medium at 80—90° under varying conditions of acidity and ratio of the reactants but always keeping iron(III) in excess, Cuy[9] found that the stoichiometry varied in the limits 1.32—1.92. A few representative results are listed in Table 1.

It would thus appear that iron(III) functions both as a one-electron type and a two-electron type oxidising

Table 1. Stoichiometry of the iron (III) hydrazine reaction

Acidity	Initial Fe(III) / N_2H_4	Stoichiometry no. of moles of iron(III) consumed per mole of N_2H_4
2N	66	1.32
2.6N	200	1.45
0.12N	66	1.74
0.11N	200	1.92

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5) Kirk and Browne, *J. Amer. Chem. Soc.*, **50**, 337 (1928).
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agent for hydrazine, with regard to the type classification of Kirk and Browne. This classification has been adopted by many kineticists[10-12] in their studies of the hydrazine-iron(III) reaction. A close look at the results of Cuy shows that the two-electron type of oxidation increasingly manifests itself with decreasing acidity and with increasing proportion of iron(III). This may be understood in terms of hydrolysis of iron(III) and its dimerisation. Remy[13] states that the exchange of OH^- group for ClO_4^- in aqueous iron(III) perchlorate solution is associated with a simultaneous condensation process of the type

$$2Fe(ClO_4)_3 + H_2O \rightleftharpoons [(ClO_4)_2Fe\text{-}O\text{-}Fe(ClO_4)_2] + 2HClO_4$$

Millburn and Vosburgh,[14] from a spectrophotometric study of 0.01—0.001M iron(III) perchlorate solutions, suggested the dimerisation of the first hydrolysis product by the following scheme.

$$Fe^{3+} + H_2O \longrightarrow [Fe(OH)]^{2+} + H^+$$
$$2Fe(OH)^{2+} \longrightarrow [Fe(OH)_2Fe]^{4+}$$

Whatever may be the formula of the dimeric species, it will be noted that the dimeric species functions as a two-electron oxidiser. Even at the low acidity of 0.11N sulphuric acid, there is still a good deal of one electron type of oxidation of hydrazine because the maximum stoichiometry obtained was only 1.92 and not 4. Moreover the rate of oxidation of hydrazine by iron(III) in this acidity range is not fast enough at room temperature or even at 80 or 90° to facilitate a direct titration. We have now made the interesting observation that the use of osmium tetroxide in trace amounts profoundly accelerates the reaction besides regulating the reaction type to accurately conform to a stoichiometry of 4.0. The details of a potentiometric titration of iron(III) with hydrazine sulphate are presented below. A visual titration was not found possible using the redox indicators, methylene blue, thionine, and variamine blue.

Experimental

Reagents. *Hydrazine Sulphate Solution*: A 0.1M stock solution was prepared from AR, BDH hydrazine sulphate, $N_2H_4\text{-}H_2SO_4$, which was dried at 150°C for one hour. The weight purity agreed within ±0.2% with the purity determined by the bromate method of Kurtenacker and Wagner[15] as modified by Kolthoff.[16] This stock solution was suitably diluted with distilled water when required.

Iron(III) Solution: A 0.1M solution is prepared from AR, BDH ferric ammonium sulphate in 0.2N sulphuric acid. The solution was standardised by photochemical reduction with oxalic acid and subsequent titration with sodium vanadate following the method of Gopala Rao and Madhusudana Rao,[17] and also by the standard procedure of reduction in the Jone's reductor and titration of the reduced solution with standard dichromate solution.

Osmium Tetroxide Solution: A 0.2% solution of osmium tetroxide was prepared in 0.1N sulphuric acid from a sample supplied by M/s. Johnson Mathey, England.

All other chemicals employed in this investigation are of analytical reagent grade. The pH of the titration mixtures was adjusted with a 10% solution of sodium bicarbonate with the aid of strips of indicator-paper supplied by M/s. British Drug House (India) Ltd.

Apparatus. The potentiometric titration assembly employed in this investigation comprises of a Junior potentiometer, a Taut suspension galvonometer (both supplied by M/s. W. G. Pye & Co., England), a bright platinum rod as indicator electrode, and a saturated calomel electrode as a reference electrode. Contact between test potential and the reference electrode has been established by means of a porous plate-end salt bridge filled with a saturated solution of potassium sulphate. The titration vessel consists of a 150 m*l* Pyrex beaker fitted with a five-holed rubber stopper. The holes accomodate respectively a salt bridge, an indicator electrode, the nozzle of a microburette, and the inlet and outlet tubes for nitrogen.

Our preliminary experiments have shown (i) that the reduction of iron(III) with hydrazine sulphate in an acid solution is extremely slow at room temperature (ii) the speed of reduction increases with decreasing acidity of the medium (iii) even in a medium of pH 2.0—3.0 the reaction is too slow for a potentiometric titration to be carried out at room temperature. (iv) At higher temperatures the iron-(III) solution undergoes rapid hydrolysis in this pH range and precipitates as the hydroxide. However we made the interesting observation that when traces of osmium tetroxide are added to the reaction mixture, the reaction is markedly accelerated at room temperature in this pH range and this catalysed reaction can be utilised for a direct potentiometric titration of iron(III) with hydrazine sulphate.

Effect of Varying the pH *of the Medium.* The influence of pH on the shape of the *E-V* curve is shown in Fig. 1. When the pH of the iron(III) solution is 1.0 the potentials attain stable values in about two min in the early stages of the titration, but a wait of 10—12 min is required near the equivalence point. Moreover, at this pH, the potential break at the equivalence point was not quite satisfactory being about 15 mV for 0.04 m*l* of the titrant. At pH 2.5—3.0, the potentials attain stable values within one minute in the early stages of the titration, in about 2—3 min near the equivalence point and in about 5 min at the equivalence point. The potential break at the equivalence is about 60—70 mV per 0.04 m*l* of 0.025M hydrazine sulphate. In titrations with a 0.1M solution of hydrazine sulphate, the break in potential at the equivalence point is about 90 mV per 0.04 m*l* of the titrant.

Effect of Oxygen of the Air. Titrations conducted in presence of atmospheric oxygen gave results which agree with those conducted in an inert atmosphere. This shows that nitrogen evolved in the reaction is sufficient to act as a blanket against the interference of the oxygen of the air.

Stoichiometry. Under the conditions prescribed, it has been found that four moles of iron(III) are reduced per mole of hydrazine oxidised, in accordance with the equation

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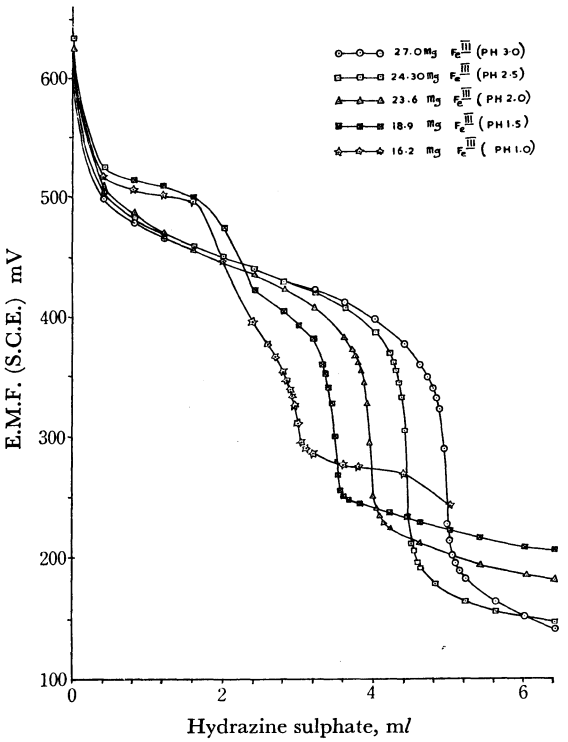

Fig. 1. Effect of pH on the potential break at the equivalence point in the titration of iron(III) with 0.025M hydrazine sulphate.

$$N_2H_5^+ + 4Fe^{3+} \longrightarrow N_2 + 4Fe^{2+} + 5H^+.$$

Effect of Varying Osmium Tetroxide Concentration. Our experiments with varying amounts of osmium tetroxide have shown that a minimum of 0.2 ml of a 0.2% solution of the catalyst is needed for a satisfactory potentiometric titration while quantities beyond 0.5 ml result in slightly higher titers.

Recommended Procedure. The pH of an aliquot of the iron(III) solution taken in a titration vessel is carefully adjusted with the aid of strips of pH indicator paper to lie between 2.5 and 3.0 using a 10% solution of sodium bicarbonate. Then 0.2 ml of a 0.2% solution of osmium tetroxide is added, the mixture diluted to 50 ml and then titrated with a 0.025—0.1M hydrazine solution to a potentiometric endpoint using the titration assembly described above. The potential values were recorded with a wait of one minute after the addition of each drop of the titrant in the initial stages of the titration, and after a wait of 2 min near the equivalence point. During the titration a drop or two of bicarbonate solution is added from time to time to neutralise the acid formed in the reaction. The potential reading at the equivalence point is noted after a wait of 5 min. After the equivalence point the potentials again attain stable values within a minute after the addition of the titrant. Some representative results of titrations carried out according to the new procedure are recorded in Table 2.

Table 2. Recovery of iron(III) by potentiometric titration with hydrazine sulphate

Amount of iron(III), mmol	
Taken	Found
0.0634	0.0636
0.1105	0.1096
0.3120	0.3125
0.4199	0.4200
0.9287	0.9265
1.3950	1.3910
2.0410	2.0530

Titrations of dilute solutions of iron(III) with hydrazine sulfate are not possible when the over all concentration of iron(III) is below 10^{-2} mol/l. Reverse titrations of hydrazine sulphate with iron(III) are not feasible under the pH and catalyst conditions stated above. It was observed that when osmium tetroxide was added to the hydrazine sulphate solution, it was reduced to a black colloidal mass which was not reoxidised by the iron(III) solution dropped from the burette.

Interferences. Vanadium(V) and chromium(VI) interfere by simultaneously reacting with hydrazine sulphate under the experimental conditions. Molybdenum(VI) interferes at higher concentrations (when Mo(VI)/Fe(III) is 20) by formation of an insoluble white precipitate, presumably iron(III) molybdate. Molybdenum(VI) also interferes at low concentrations (1.85×10^{-2} mg/50 ml) through formation of molybdenum blue presumably by reduction of molybdenum(VI) by the iron(II) formed in the reaction. In the presence of titanium(IV) the titration of iron(III) is not possible, probably due to hydrolysis of titanium(IV) at the prescribed pH and deposition of the hydrolysed product on the platinum electrode.

Uranium(VI), vanadium(IV), copper(II), nickel(II), cobalt(II), chromium(III), and manganese(II) do not interfere. Sulphate and perchlorate also do not interfere. Chloride interferes at a final concentration greater than 35 mg/50 ml by lowering the potential break. In the presence of complexing anions like phosphate, fluoride, salicylate, and thiocyanate the titration of iron(III) is not possible.

Application of the New Procedure for the Determination of Iron(III) in Alloys

Analysis of an Alloy. An accurately weighed sample (*ca.* 1.0 g) of the alloy (soft iron nail) is treated with 25 ml of 1:1 (vol/vol) nitrogen free sulphuric acid in a 250 ml beaker covered with a watch glass and heated on a hot plate till it completely dissolves. The resulting solution which contained a few black floating particles (carbon) is filtered after dilution with water through a Whatman No. 42 filter paper into a 500 ml Pyrex beaker and treated dropwise with 0.1N solution of potassium permanganate until a very pale pink colour of $KMnO_4$ persists. The excess of permanganate is destroyed by adding one or two drops of a 10% (vol/vol) hydrogen peroxide solution. The resulting solution is gently heated to boiling on a hot plate to destroy the excess hydrogen peroxide. It is then cooled to room temperature, quantitatively transferred to a 500 ml volumetric flask and made up to the mark.

Table 3. Assay of iron(III) in an iron nail

Wt. of the sample analysed, g	Iron(III) found, g		
	Present method, g	Jone's reduction method, g	Photochemical reduction method, g
1.3058	1.3020	1.3031	1.3017
1.1810	1.1776	1.1780	1.1767
0.9894	0.9876	0.9877	0.9877

Aliquots of this solution are titrated with 0.025M hydrazine sulphate solution to a potentiometric end-point according to the recommended procedure. The results are compared with those obtained by titration with a standard solution of potassium dichromate after reduction in a Jone's reductor, and also with those obtained by the photochemical reduction method of Gopala Rao *et al.*[17] The data in Table 3 show that the results obtained by the new procedure are in excellent agreement with those obtained by the standard procedures.