STUDIES ON THE METAL COMPLEXES OF HYDROXAMIC ACIDS. PART I. SPECTROPHOTOMETRIC DETERMINATION OF MANGANESE WITH NICOTINO- AND *iso*NICOTINOHYDROXAMIC ACIDS

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Nicotino- and *iso*nicotinohydroxamic acids are proposed as reagents for the spectrophotometric determination of manganese, by making use of the red-violet colour formed by the interaction of the metal with the reagents in ammoniacal medium (at or above p_H 9). The colour intensity is measured at 480-490 mμ for nicotino- and at 470-480 mμ for *iso*nicotinohydroxamic acid. Beer's law is obeyed and the Sandell sensitivities are 0.014 γ for nicotino- and 0.013 γ for *iso*nicotinohydroxamic acid. Job's method indicates 1 : 3 complex between the metal and the reagents. In the coloured products, manganese is believed to be in tervalent state. Copper, nickel, cobalt, silver and iron interfere seriously in the estimation of manganese. However, the first four interfering metals can be masked by sodium cyanide.

Picolinohydroxamic acid, curiously enough, exhibits only a faint red-violet colour under the same conditions, but fades rapidly.

Hydroxamic acids, having the group $-\overset{\displaystyle O}{\overset{\displaystyle \|}{C}}\text{-NHOH}$ or $-\overset{\displaystyle OH}{\overset{\displaystyle |}{C}}=\text{NOH}$, form, in general, strongly coloured complexes with iron, vanadium, uranium and molybdenum. Recently, a few hydroxamic acids have been studied as colorimetric reagents for these metals. Benzohydroxamic acid has been used for the detection and colorimetric estimation of vanadium in 50% alcohol (Dasgupta and Singh, *J. Sci. Ind. Res.*, 1952, **11B**, 268) and also by extraction of the aqueous colour with hexanol (Wise and Brandt, *Anal. Chem.*, 1955, **27**, 1392). Salicylohydroxamic acid has been studied as a colorimetric reagent for vanadium, molybdenum and uranium (Bhaduri and Rây, *Science & Culture*, 1952, **18**, 97), and afterwards also for titanium (Xavier, Chakraburtty and Rây, *ibid.*, 1954, **20**, 146). Oxalohydroxamic acid has been used for indirect colorimetric estimation of zirconium and calcium (Dhar and Das Gupta, *J. Sci. Ind. Res.*, 1952, **11B**, 500, 520). Although a few hydroxamic acids have been studied, these studies are far from exhaustive. With a view to finding out more sensitive and effective reagents for the colorimetric estimation of metals, a systematic study on the coloured complexes of different metals with pyridine-hydroxamic acids was undertaken.

Nicotino- and *iso*nicotinohydroxamic acids have been found to develop intense red-violet colour with traces of manganese in ammoniacal medium, which is highly sensitive and useful for the estimation of the metal. On the other hand, with picolinohydroxamic acid, a faint red-violet colour appears only on prolonged agitation and this colour is very much unstable and fades away with precipitation of manganic hydroxide. An account of the spectrophotometric determination of manganese with nicotino- and *iso*nicotinohydroxamic acids is reported in the present

communication. Das Gupta and Singh (*loc. cit.*) have studied the reaction between manganese and benzohydroxamic acid in a qualitative manner.

When nicotino- and *isonicotinohydroxamic* acids are added to an extremely small amount of manganese and the medium is made ammoniacal, there develops an intense red-violet colour. In place of ammonia, caustic soda, methylamine, ethylamine or ethanolamine may be used, but ethylenediamine appears to have a masking effect on manganese. However, ammonia was preferred, because, in its presence, the coloured product was found to be the most stable and also because of its forming soluble complexes with many inorganic cations. The coloured products do not attain their maximum intensity immediately except in presence of excess reagents and at a p_H of or above 9. The maximum absorption regions of the colour are at 480-490 mμ for nicotino- and 470-480 mμ for *isonicotinohydroxamic* acids, where the reagent solutions have no absorption. For complete colour formation the minimum quantity of the reagent necessary amounts to at least fifteen times the molar proportion of manganese, a very large excess having no adverse effect on the optical density. The coloured products obey Beer's law very closely over the range 0.25 to 10 p.p.m. of manganese. According to Sandell's definition ("Colorimetric Determination of Traces of Metals", 2nd ed., p. 50, Interscience Publishers, Inc., 1950), the sensitivities of the reagents for manganese are 0.014γ per cm^2 for nicotino- and 0.013 γ for *iso*-nicotinohydroxamic acids. The colours are stable at room temperature (20°-30°) and the optical densities remain unchanged at least for a day.

The following observations about the colour appear to be pertinent. The colour is not developed at all in presence of a strong reducing agent, e.g. hydroxylamine or hydrazine. On the other hand, in presence of a trace of hydrogen peroxide, the colour appears immediately, although excess hydrogen peroxide destroys the colour, due probably to the oxidation of the hydroxamic acids. Besides, the colour resembles that of manganic^{III} complexes. Hartmann and Schlafer (*Angew. Chem.*, 1954, **66**, 768) report 475 mμ as the absorption maximum for the Cs-Mn^{III} alum colour. Scheffer and Hammaker (*J. Amer. Chem. Soc.*, 1950, **72**, 2575) report 460 mμ as the absorption maximum of $[MnF_6]^{3-}$ ion. Cartledge and Ericks (*ibid.*, 1936, **58**, 2065) report 520 mμ as the absorption maximum of trioxalato-manganic^{III} ion and 450 mμ as that of diaquo-dioxalato-manganic^{III} ion. All these facts, taken together, strongly support the idea that the coloured complexes in the present case contain presumably tervalent manganese, formed through aerial oxidation of Mn^{II}. The colour is not formed in an atmosphere of carbon dioxide.

Ions like SO_4^{2-}, NO_3^-, Cl^-, SCN^-, CO_3^{2-} $S_2O_3^{2-}$, I^-, Cd^{2+} Zn^{2+}, Al^{3+} MoO_4^{2-}, WO_4^{2-} etc do not interfere even when present in large amounts. In presence of appreciable amounts of BO_3^{3-}, PO_4^{3-}, tartrate and oxalate, the colour develops slowly and should be measured after 30 minutes. CN^- up to 200γ does not interfere. In presence of vanadium, titanium and uranium, the colour is measured at 540-560 mμ. Interfering effects due to copper, nickel, cobalt and silver can be eliminated by the addition of a little sodium cyanide. Mercury can be masked by an excess of KI. However iron interferes at all concentrations and should be removed before the determination.

EXPERIMENTAL

A Unicam SP 600 spectrophotometer was used for measuring the optical density of the solutions using Corex glass cells of 1 cm thickness. Measurements of p_H were made with the help of a Cambridge p_H-meter.

A 2% solution of G.R. manganous sulphate was prepared to which a few drops of G.R. H_2SO_4 were added. The manganese content of this solution was determined gravimetrically as pyrophosphate. From this solution, by stepwise dilution, a solution containing 0.05 mg. of Mn was prepared. This solution was used for the spectrophotometric determination of manganese.

Preparation of the Reagents.—Nicotino- and *isonicotinohydroxamic* acid hydrochlorides were prepared according to the method outlined by Gardner *et al.* (*J. Amer. Chem. Soc.*, 1951, **73**, 5455). Nicotinic acid and *isonicotinic* acid (35 g. each) were converted into ethyl esters by following the methods of Laforge (*ibid.*, 1928, **50**, 2479) and of Supriewski and Serafinowna (*Arch. Chem. Farm.*, 1936, **3**, 109). Sodium (12 g.) was dissolved in about 400 c.c. absolute ethyl alcohol (twice distilled over lime and then over sodium). To perfectly dry and finely powdered hydroxylamine hydrochloride (35 g.), taken in a three-necked flask fitted with an efficient mechanical stirrer, was added about 100 c.c. of absolute alcohol and the mixture stirred. The sodium ethoxide solution was now added in small amounts at a time, while stirring was continued for about 1½ hours and was filtered. The filtrate was taken in a flask, treated with the ester (30 g.) and allowed to stand at 20-25° for about 12-16 hours, under constant stirring. This was afterwards evaporated to dryness on the waterbath under reduced pressure and the residue was extracted with boiling ethyl alcohol (500 c.c.) and filtered. Dry HCl gas was passed in the cold, when crystals of the crude hydroxamic acid hydrochloride separated. These were filtered, dissolved in minimum amount of hot water (about 20 c.c.) and then filtered again. To the filtrate was added about 200 c.c. alcohol and the mixture cooled when crystals of the pure hydrochloride separated. These were filtered, washed with alcohol and finally dried in air as shining, almost colorless crystals (m. p. of nicotinohydroxamic hydrochloride 185-86° and that of isonicotinohydroxamic hydrochloride, 206-207°) ; yield 16-20 g.

A freshly prepared 1% reagent solution was used. Solutions of diverse ions were prepared from suitable salts.

Optimum Wave-length for Measurement of the Optical Density of the Colour.—The absorption spectra of the coloured products (Mn content 8 γ per c.c.) in presence of a large excess of the reagents and at a p_H 9 are represented in Fig. 1, together with those of the same amount of the reagent (against water) at the same p_H. It follows from the figure that optimum wave-length for measurement of the optical density is 480-490 mμ for nicotino- and 470-480 mμ for *isonicotinohydroxamic* acid. At these wave-lengths the reagents have got very little absorption. All subsequent measurements were therefore carried out at these wave-lengths against a reagent blank, having the same amount of the reagent as in the coloured product and the same p_H.

FIG. 1

Absorption spectra of coloured products.
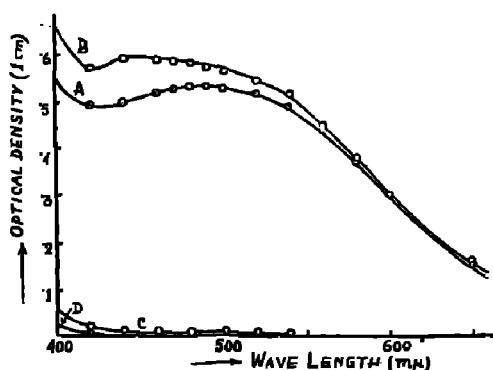
A.   Mn-nicotinohydroxamic acid : p_H 9 ; 8 γ Mn/c.c.

B.   Mn-*iso*nicotinohydroxamic acid : p_H 9 ; 8 γ Mn/c.c.

C.   *iso*Nicotinohydroxamic acid p_H 9 ; 0.2% solution.

D.   Nicotinohydroxamic acid : p_H 9 ; 0.2% solution.

Effect of p_H on the Colour Intensity.—With excess of the reagent, optical density was found to increase with increasing p_H up to 9, but thereafter there was no further rise even when a large excess of ammonia was used to make the medium strongly ammoniacal.

Effect of Reagent Concentration on the Colour Intensity.—Variation of the reagent concentration, maintaining the p_H at 9, shows that for maximum colour formation, an amount of the reagent at least fifteen times the molar proportion of manganese is necessary and that a reagent concentration as high as 150 times has no effect on the colour intensity. Generally, for a total of 0.2 mg. Mn, 5 c.c. of 1% reagent solution was used for all the estimations.

Effect of Time on the Colour Intensity.—When the p_H and the reagent concentrations are optimum, the colour takes less than 5 minutes to attain its maximum intensity, otherwise the colour develops slowly.

Adherence to Beer's Law.—The coloured product very closely obeys Beer's law over the entire range of investigation, *i.e.*, from 0.25 γ to 10 γ of manganese. However for maximum precision, practical range of measurement should be from 1.5 to 10 γ as the optical density then lies within 0.1 to 0.68.

Stability of Colour.—The colour is perfectly stable at room temperature. A solution having 8γ manganese and excess reagent in presence of excess ammonia gave the same optical density even after a day. The colour intensity remained unchanged within 20-30° over which the readings were taken.

Sensitivity.—The spectrophotometric sensitivity, as calculated from the Beer's law curves, is given by 0.014 γ/cm² for nicotino hydroxamic acid and 0.013 γ/cm² for *iso*nicotinohydroxamic acid (Sandell, *loc. cit.*).

Empirical Composition of the Coloured Product.—This has been determined by following Job's method of continuous variation. However, difficulties were encountered because of the precipitation of manganese in solutions containing smaller amounts of the reagents. Again, since the reagent was not in sufficient excess, the colour was rather slowly developed. Readings were therefore taken after twenty minutes of preparing the solutions. Continuous variation plots with 0.0005 M solutions (optical density against mole fraction of reagent) for both the reagents pass through a maximum at a composition of 0.75, indicating the formation of an 1:3 complex between manganese and the hydroxamic acids. As manganic salt of analytically pure grade was not available, experiments by Job's method were carried out with manganous solution (cf. Harvey and Manning, *J. Amer. Chem. Soc.*, 1952, **74**, 4744, for titanium and iron).

FIG. 2

Beer's law curves.
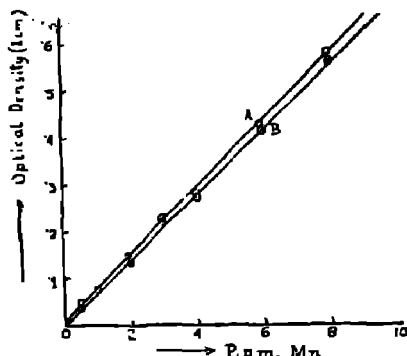
FIG. 3

Job's curve.

A. Mn-*iso*nicotinohydroxamic acid : p_H 10, 470 mμ.
B. Mn-nicotinohydroxamic acid : p_H 10, 480 mμ.
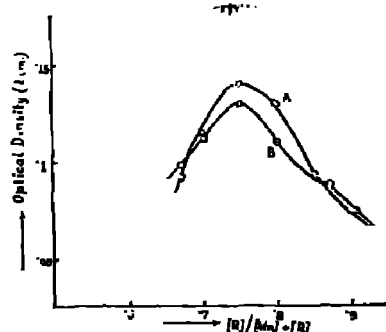
A. Mn-*iso*nicotinohydroxamic acid : p_H 9, 470 mμ.
B. Mn-nicotinohydroxamic acid : p_H 9.0, 480 mμ.

Influence of Foreign Ions on the Colour System.—The effect of various ions has been studied and the approximate tolerance limits determined. A few metallic ions seriously interfere either due to complex formation or due to their reduction. These were, however, masked by suitable complex-formers.

The tolerance limits of different ions have been determined with respect to 4 p.p.m. of Mn in a total volume of 25 c.c. An 1% reagent solution (2.4 c.c.) was used. Ions such as nitrate, sulphate, chloride, acetate, carbonate, tungstate, thiocyanate, iodide and thiosulphate do not interfere even when present in amounts exceeding 1000 p.p.m. The presence of borate, phosphate, tartrate and oxalate can be tolerated up to 1000 p.p.m. although the colour intensity should be measured after 30 minutes of preparing the solution. Cyanide and fluoride should not exceed the limit 200 p.p.m. Cadmium (1000 γ), zinc (500 γ), aluminium (250 γ) and molybdate (1000 γ) do not interfere, if excess ammonia is used to dissolve the precipitates of the metal hydroxides. Hg^{II} (500 γ) does not interfere when masked by excess KI. But Cu, Ni, Co and Ag interfere seriously even when present in small amounts. However, Cu

(200 γ), Ni (250 γ), Co (200 γ) and Ag (260 γ) can be tolerated if sodium cyanide solution (1%) is added dropwise to dissolve out the initial precipitates of the metal cyanides and the colour measured after 30 minutes. Ti (50 γ), UO_2^{2+} (80 γ) and VO^{3-} (200 γ) do not interfere when excess ammonia is used and the colour measured at 540-560 mμ. However Fe^{3+} interferes and should therefore be removed before estimating manganese.

The nature and the analytical aspects of the colour reactions of these reagents with vanadium, molybdenum and iron will form the subject matter of future communications.

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