due to ^{67}Ho Lη line can also be ruled out on the ground that no mention is made of holmium in the list of impurities, supplied by the manufacturers (M/s Johnson Matthey, London) for the spectrographically standardised praseodymium oxide sample. The $(\nu/R)^{1/2}$ value for the newly measured line is found to make a nice fit in Moseley plot for L_1O_1 transition (not reproduced here). The existence of the forbidden transition L_1O_1 in the spectrum of praseodymium has therefore been established. It may be mentioned here that the line corresponding to the transition L_1O_1 has been observed[11] in the spectra of all the elements from ^{73}Hf to ^{83}Bi and ^{90}Th. Amongst the rare earths, this transition has been reported[11] in ^{60}Nd, ^{65}Tb and ^{67}Ho to ^{71}Lu.

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TITRIMETRIC METHOD FOR THE DETERMINATION OF NICOTINOYL HYDRAZINE WITH VANADIUM(V)

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NICOTINOYL and isonicotinoyl hydrazines belong to the family of aroyl hydrazines that find extensive use in chemotherapy. The $-NH.NH_2$ group in these compounds is highly susceptible for oxidation and quite a few methods[1-11] have been reported for the titrimetric determination of isonicotinoyl hydrazine. Similar methods for the determination of nicotinoyl hydrazine are scarce. Rao and Rao[12] reported titrimetric procedures to determine isonicotinoyl hydrazine using vanadium(V) as the oxidising agent. Vulterin[13] reported the standardisation of nicotinoyl hydrazine in hydrochloric, sulphuric or phosphoric acid media to potentiometric end point using potassium bromate as an oxidant. In this communication, we report the results of our analytical studies on the determination of nicotinoyl hydrazine with vanadium(V) by titrimetric method. Both electrometric and visual indicator methods are employed for the location of the equivalence point.

Reagents: A 0.1 N solution of vanadium(V) was standardised against a standard solution of ferrous ammonium sulphate. A 0.025 M solution of nicotinoyl hydrazine was prepared by dissolving Fluka's pure sample in deionised water and standardised against a standard solution of potassium bromate[2]. A 0.1% solution of osmium tetroxide (Johnsom Matthey's London) in 0.1 N sulphuric acid was stored in an amber glass bottle. AnalaR orthophosphoric acid was used throughout this investigation. A 1% solution of diphenylamine in concentrated sulphuric acid (A.R.) and 0.2% solution of barium diphenylamine sulphonate in deionised water were employed. A Toshniwal digital pH meter (CL 44) in combination with platinum and calomel electrodes was used in the electrometric titration.

The control experiments have shown that the potentials at the platinum electrode during the electrometric titration of nicotinoyl hydrazine with vanadium(V) fluctuate and were stabilized in the presence of traces

of osmium tetroxide and hence in all experiments, the oxidimetric titration was carried out in the presence of this reagent.

Effect of varying acid concentration: Experiments showed that the variation of phosphoric acid volume from 1–16 ml (in a total volume of 50 ml of titration mixture) did not affect either the speed or accuracy of the titration while higher concentration of phosphoric acid results in a higher consumption of vanadium (V). Further, the potential break at the equivalence point was not sharp. Phosphoric acid medium of 0.3–5 M or a mixed medium of sulphuric acid (0.5–3 N) and 1 ml of 85% orthophosphoric acid was the optimum condition for good end point during the titration.

A solution of osmium tetroxide (0.2 ml of 0.1 %) in a 50 ml of the titration mixture was adequate for a satisfactory titration.

Recommended procedure: To an aliquot of (1–10 ml of 0.025 M) nicotinoyl hydrazine taken in a 100 ml beaker, 1–16 ml of 85% orthophosphoric acid (or a mixture of 3–10 ml of 1:1 sulphuric acid and 1 ml of 85% orthophosphoric acid) is added and the solution is allowed to attain room temperature. Then 0.2 ml of 0.1% osmium tetroxide is added and the resulting mixture after dilution to 50 ml is potentiometrically titrated with vanadium(V) solution.

The potential break at the equivalence point is 100–150 mv for 0.04 ml of 0.1 vanadium(V) solution. Within the range of 1–5 mmol of nicotinoyl hydrazine, the relative error is found to be 0.40 ± 0.1 %.

Determination of nicotinoyl hydrazine with visual end point: Of the several indicators tried, barium diphenylamine sulphonate, and diphenylamine are found to give satisfactory results. The preliminary studies on the oxidation of the indicator by vanadium(V) and the reduction of the oxidised product of the indicator by nicotinoyl hydrazine under the optimum acid and catalyst concentrations have shown that for a satisfactory functioning of the indicator, it is necessary to warm the reaction mixture to about 40–50°C before it is titrated with vanadium(V).

Recommended procedure: To an aliquot of (1–10 ml of 0.025 M) nicotinoyl hydrazine taken in a 100 ml beaker, 1–16 ml of phosphoric acid and 0.2 ml of 0.1% osmium tetroxide were added and the mixture after dilution to 50 ml warmed to about 40–50°C on a water bath. Two drops of the indicator solution were added to the reaction mixture and titrated with vanadium(V) solution rapidly. Appearance of a permanent bluish violet colour (barium diphenylamine sulphonate) or a permanent blue colour (diphenylamine) marks the equivalence point of the titration.

The indicator corrections for 0.1 M solutions are negligible. The results indicate that 1–5 mmol of nicotinoyl hydrazine could be satisfactorily estimated and the percentage relative error is 0.35 ± 0.15. Sucrose, starch, glucose and lactose are generally used as excipients in pharmaceutical preparations. These substances do not interfere even when present in ten-fold excess. However, oxalate and other substrates which form strong complexes with vanadium(V) interfere.

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