*Asian Journal of Chemistry* Vol. 8, No. 2 (1996), 232–234

# Potentiometric Determination of Isonicotinic Acid Hydrazide with Manganese(IV)

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The results of the potentiometric determination of isonicotinic acid hydrazide (INH) with manganese(IV) in sulphuric acid medium are reported. The potential break at the equivalence point is about 150 mv per drop (0.05 mL) of 0.025 M isonicotinic acid hydrazide. The acidity range for the reaction is 2–4 M. Four moles of manganese(IV) are reduced for every 2 moles of INH.

## INTRODUCTION

Isonicotinic acid hydrazide (INH) is an extremely valuable antitubercular agent in chemotherapy. It is commercialised under the variety of trade names nydrazide, continzin, pyricidin, isonex and isokin. The tuberculostatic activity is attributed to the formation of chelates with transition metal ions Cu(II), Ni(II) and Zn(II) that are found in biological fluids. In view of its extensive importance as a drug, its determination is of considerable importance. The chemistry of manganese(IV) sulphate seems to be limited for potentiometric titrations. However, it is acquiring importance as an oxidising agent even for potentiometric determinations in view of its high redox potential.

A perusal of the literature indicated that a number of oxidants have been recommended for either a direct titration or an indirect determination of isonicotinic acid hydrazide. Potassium bromate was used in conjunction with bromide for the indirect back titration of iodometric technique[2–9] or for direct titrimetric method using indicators like indigocarmine[6], naphthoflavone[8], methyl red[11], methyl orange[9–11] and *p*-ethoxycheysoidins[10]. There seems to be a variation in different reports with regard to the optimum concentration of the acid for the complete oxidation of isonicotinic acid hydrazide. Merz and Shirm[12] recommended direct titrimetric procedure for the estimation of isonicotinic acid hydrazide with Mn(VII) in cold, 10–20% sulphuric acid medium but the end point colour stability was quoted to be 10 seconds only. Vulterin and Zyka[13] titrated isonicotinic acid hydrazide to a potentiometric 10–25% potassium hydroxide. Muralikrishna *et al.*[14, 15] developed conditions for an indirect and direct determination of isonicotinic acid hydrazide with manganese(IV) using ferroin as an indicator. Isonicotinic acid hydrazide has not been determined potentiometrically with manganese(IV).

Hence, the authors has taken up the study of the potentiometric determination

of isonicotinic acid hydrazide with manganese(IV) and developed conditions for its determination.

## EXPERIMENT

A 0.05 M manganese(IV) sulphate was prepared and standardised[1]. A 0.025 M INH was prepared and its purity was checked by the reported procedures[16, 17]. Sulphuric acid of analytical reagent grade in used in this investigation. An Elico digital pH meter (Model Li 122) is combination with platinum and calomel electrode was used in the potentiometric titration.

## RESULTS AND DISCUSSION

A preliminary study of the reaction between manganese(IV) sulphate and INH has indicated it to be very rapid as evidenced by the brisk evolution of the nitrogen gas and rapid decolorisation of the gray colour of the Mn(IV) ion over a wide range of sulphuric acid studied (1.5 M to 5 M). The author has taken up a detailed study of the reaction to ascertain the optimum concentration of the sulphuric acid needed for a rapid and accurate potentiometric titration for the determination of INH with manganese(IV). The experiment indicated that the potentials were readily stabilized when manganese(IV) is taken as a titrant. Hence, subsequent studies were carried out taking INH as titrant.

5 mL of 0.05 M manganese(IV) solution taken in a 100 mL beaker are treated with varying volumes of sulphuric acid to give an overall concentration of 1.5 M to 5 M on dilution to 35 mL. The total volume of the mixture is made up to 50 mL with distilled water and titrated potentiometrically with 0.025 M isonicotinic acid hydrazide solution. When the sulphuric acid concentration at the equivalence point is kept at 1.5 to 4 M, the potentials obtained by the platinum electrode dipping into the titration mixture are found to be stable within about 1 or 2 min after addition of each portion of the titrant. Just before the equivalence point about 1–2 min waiting is found necessary for recording the potential data. Moreover, the titration in 0.5–1.5 M sulphuric acid leads to the result that could not conform to any stiochiometric oxidation path of INH.

However, when the sulphuric acid concentration at the equivalence point lies between 2 M–4 M, the potential attainment is quite rapid up to the equivalence point. Still, it is found necessary to wait for about 1 or 2 min for a stable potential reading to be recorded at the equivalence point. Under these conditions, the potential break at the equivalence point is about 150 mv per drop (0.05 mL) or 0.025 M isonicotinic acid hydrazide. It is found that 4 moles of manganese(IV) are reduced for every 2 moles of INH.

According to the equation it can be seen clearly :

$$4Mn^{4+} + 2C_5H_4NCONHNH_2 + H_2O \rightarrow 4Mn^{2+} + 2C_5H_4NCOOH + 2N_2 + 6H^+.$$

### Recommended Procedure

A fixed aliquot of standard manganese(IV) sulphate solution is taken into a 100 mL beaker and made up to 35 mL with (1 : 1) sulphuric acid and redistilled

water such that the concentration of sulphuric acid at the equivalence point lies between 2 M–4 M. The solution is then titrated with the test sample of isonicotinic acid hydrazide solution waiting for about 1 to 2 min at the equivalence point for attainment of stable potential, stirring the mixture with an electromagnetic stirrer throughout the titration. The test sample to be analysed is dissolved and made up to mark in an appropriate volumetric flask to give a solution corresponding to 0.023 M–0.026 M. The total amount of INH in 100 mL is calculated from the volume of INH consumed for known amount of manganese(IV) solution. Some representative results are recorded in Table-1. The stoichiometric studies of the reaction show that four moles of manganese(IV) are reduced for every two moles of INH.

TABLE-1
POTENTIOMETRIC DETERMINATION OF ISONICOTINIC ACID HYDRAZIDE (INH) WITH MANGANESE(IV)

| S.N. | INH (m moles) | | % relative error |
|---|---|---|---|
| | Taken | Found | |
| 1 | 0.0589 | 0.0595 | +0.85 |
| 2 | 0.1029 | 0.1039 | +0.97 |
| 3 | 0.1175 | 0.1182 | +0.60 |
| 4 | 0.1469 | 0.1479 | +0.68 |
| 5 | 0.2352 | 0.2375 | +0.98 |
| 6 | 0.2940 | 0.2968 | +0.95 |

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(*Received*: 25 July 1995; *Accepted*: 24 October 1995) AJC-1029