ABSTRACT

An analytical method has been developed for the estimation of nitric acid in acetic acid – acetic anhydride media, with a precision of 0.3%. The procedure involves the addition of a solution of potassium acetate in acetic acid to the sample. The excess is back-titrated conductometrically with a standard solution of nitric acid in acetic acid.

INTRODUCTION

A study of the formation of 1,9-diacetoxypentamethylene-2,4,6,8-tetranitramine (AcAn) from 2-acetoxymethyl-4,6,8-trinitrocyclotetramethylene tetramine (PHX), nitric acid, and acetic anhydride, the results of which are presented in a later paper, required a knowledge of the rate of nitric acid disappearance during the reaction. To this end, it was necessary to develop a method for analyzing nitric acid in an acetic acid – acetic anhydride medium, as outlined below.

EXPERIMENTAL

Potassium acetate dissolved in glacial acetic acid was added to the acetic acid – acetic anhydride reaction mixture containing the nitric acid to be analyzed. The addition was accompanied by precipitation of potassium nitrate, owing to its insolubility in the anhydride-medium. The mixture was then back titrated with a dilute acetic acid solution of nitric acid, and the titration followed conductometrically. During the course of the titration, potassium nitrate was again precipitated and a decrease in conductivity was observed.

When reaction of nitric acid with the excess alkali acetate was complete, further addition of reagent caused the conductivity to increase, unless the reagent

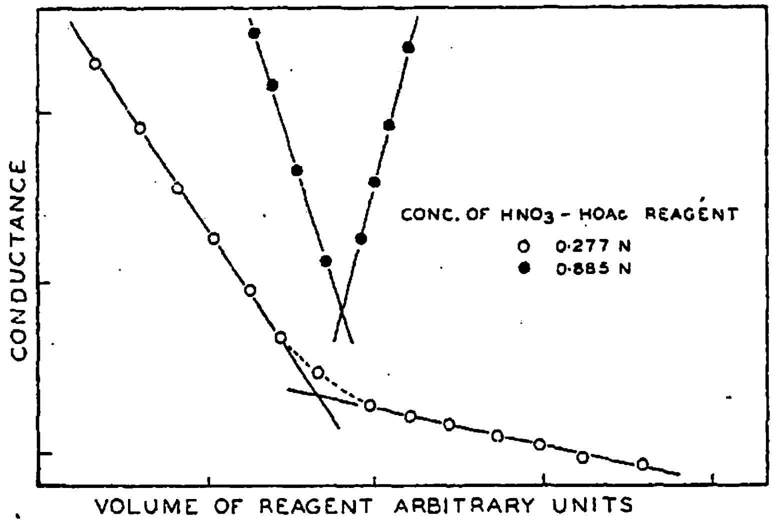

FIG. 1. Change of conductance with addition of analytical reagent.

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[2] *Holder of National Research Council Studentship. Present address: Assistant Professor, Polytechnic Institute of Brooklyn, N.Y.*

was sufficiently dilute, in which case the conductivity continued to decrease but at a smaller rate than before. An example of both types of curves is given in Fig. 1.

Using the same acetic acid solutions of potassium acetate and nitric acid, several titrations of acetic acid – acetic anhydride mixtures containing known amounts of nitric acid, permitted a linear calibration curve to be established with the aid of which solutions of unknown nitric acid content could be analyzed with a precision better than 0.3%. This calibration method was adopted in preference to direct titration with potassium acetate – acetic acid solution for two reasons. First, unless there are a large number of nuclei of the nitrate present, the direct titration is very slow and tedious. Secondly, the addition of an excess of potassium acetate was effective in quenching immediately the nitrolysis reaction that was under investigation.