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SPECTROPHOTOMETRIC DETERMINATION OF SODIUM AZIDE

Part I. Indirect Colorimetry

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The redox reaction between sodium azide and ceric ammonium nitrate has been spectrophotometrically applied to the determination of sodium azide with satisfactory results (accuracy: ± 0.2%). It has been shown that the present method has advantages over the usual titrimetric and gasometric determination of the azide.

INTRODUCTION

Sodium azide forms the basic raw material for the manufacture of explosive azides like those of lead and silver. The azide normally used in these processes must be of the highest purity (above 99.5%) as the preclusion of heavy metal ions and other hazardous impurities is of paramount significance. Consequently, it is desirable to analyse the raw material quickly and precisely.

The conventional oxidizing and reducing agents are not very satisfactory with sodium azide solutions owing to the latter's low reactivity. Thus, whereas, iodine oxidises the azide only in the presence of a catalyst [1], permanganate gives complex and variable results [2]. The oxidation of azide with hypochlorous and nitrous acids is, no doubt, quantitative [3], but the standard solutions of these acids are very unstable. The reaction of azides with ceric salts in acid solution, as depicted below, is quantitative, stoichiometeric and rapid.

$$2NaN_3+2Ce(NH_4)_2(NO_3)_6 \rightarrow$$
$$2NaNO_3+4NH_4NO_3+2Ce(NO_3)_3+3N_2$$

This is, therefore, the basis for the quantitative determination of sodium azide and is one of the two routine methods employed for its assay [4], the other being argentimetric determination in neutral media [5] requiring special care as the silver azide formed is highly explosive.

The ceric salt method utilises oxidimetry with ceric ammonium nitrate and provides the following three alternatives:

(i) Hydrazoic acid, as liberated by acidification of the sample, reacts with a known excess of ceric ammonium nitrate solution and the excess of the reagent is back–titrated with ferrous ammonium sulphate using nitroferroin as the indicator [6].

(ii) A known excess of standard ceric ammonium nitrate is added to the azide sample directly and then the excess is back–titrated as in (i) above [7].

(iii) The azide is added to a known excess of ceric ammonium nitrate resulting in the liberation of nitrogen which is measured gasometrically [8].

Based on the reaction of ceric ammonium nitrate and azide a fourth alternative has been evolved and is the basis of a spectrophotometric assay method of the azide which is given in the present paper. The principle of the method is described in the present study.

The spectrophotometric absorbance of a standard ceric ammonium nitrate solution is noted at the wavelength of maximum absorbance (390 nm). Known quantities of sodium azide are added to a fixed volume of standard ceric salt solution which should have ceric content more than equivalent to the amount of sodium azide. The absorbance of the ceric salt solution falls as a result of the reaction with sodium azide and the decrease in absorbance is noted. A standard curve for concentration *vs* absorbance is plotted for the unreacted ceric ammonium nitrate. The unknown sample is now allowed to react with the same volume of standard ceric salt solution as used previously and the absorbance is noted. The amount of unreacted ceric salt corresponding to this absorbance is obtained from the plot above and this is subtracted from the original amount present in the volume used. The difference is the amount of ceric ammonium nitrate which reacted with sodium azide and is equivalent to the amount of the later. The experimental details of the method are given below:

MATERIALS AND METHOD

Standard solutions of ceric ammonium nitrate with concentrations ranging from 10×10^{-5} ML^{-1} to 80×10^{-5} ML^{-1} were prepared by dissolving appropriate amounts of the salt in 2 N sulphuric acid. Absorbances for various concentrations in this range were noted on a Beckmann DB spectrophotometer and a concentration *vs* absorbance graph was plotted (Fig. 1). A straight line passing through the origin was obtained thereby establishing the validity of the Lambert—Baeyer law for the system.

A standard solution 60×10^{-5} ML^{-1} each of sodium azide and ceric ammonium nitrate was prepared and aliquots from 1 to 9 ml of the former were allowed to react with a fixed volume (10 ml) of the later. The spectrophotometric absorbances due to the unreacted excess of ceric salt were noted in all the cases and a concentration *vs* absorption graph was plotted (Fig. 2). It was again a straight line passing through the origin and almost coinciding with the first standard line as obtained in Fig. 1.

In the prevalent titrimetric method for the assay of the explosive azides like those of lead and silver it is necessary that the reducible interferences such as dextrin and polyvinyl alcohol be eliminated. This is achieved by acidifying the sample and distilling the hydrazoic acid which is estimated by method (i) mentioned above. To find out whether or not the present method can be extended to such cases, the same approach was utilised in the spectrophotometric method as here too the chemical reaction is the same.

Thus, a known weight of sodium azide was distilled with sulphuric acid and the hydrazoic acid liberated was absorbed into a standard solution (known excess) of ceric ammonium nitrate. The absorbance due to the unreacted excess of ceric salt was noted and the amount of the azide found out indirectly and the result was in a very close proximity with that obtained by the direct reaction of the azide with ceric ammonium nitrate.

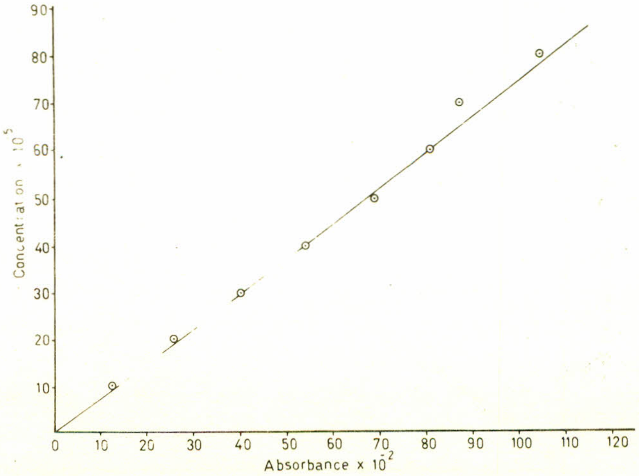

Fig. 1. Absorbance vs concentration line for $Ce(NH_4)_2(NO_3)_6$.

DISCUSSION

The two methods that are in general use at present are the titrimetric methods, one using the redox system and the other argentimetric. Compared to the titrimetric methods, in particular the argentimetric one, the spectrophotometric method eliminates the formation of hazardous silver azide. Once a standard line has been drawn the process of estimation involves only the reaction of sodium azide with a known excess of ceric ammonium nitrate and finding the absorbance due to the unreacted excess of the ceric salt. The exact amount of the azide reacted with the ceric salt is thus calculated indirectly. An assessment of the accuracy and reliability of the present method is given in Table 1

Table 1. Precision of the spectrophotometric method.

Volume of sodium azide (ml)	Concentration of sodium azide $ML^{-1}\times10^{-5}$	Absorbance $\times10^{-2}$	Concentration of unreacted ceric ammonium nitrate (from graph) $ML^{-1}\times10^{-5}$	Original concentration of ceric ammonium nitrate $ML^{-1}\times10^{-5}$	Concentration of ceric ammonium nitrate reacted with sodium azide (i.e. concentration of sodium azide estimated) $ML^{-1}\times10^{-5}$	Percentage difference
10	5.000	32.5	25.00	30.00	5.00	0.00
12	5.454	28.5	21.81	27.27	5.46	0.11
14	5.833	25.0	19.18	25.00	5.82	0.22
16	6.153	22.0	16.93	23.07	6.14	0.21

Volume of ceric ammonium nitrate solution ($60\times10^{-5}ML^{-1}$) used = 10 ml.

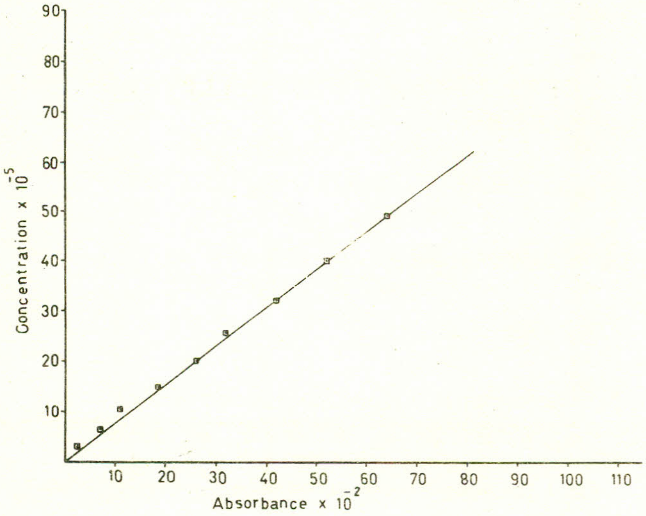

Fig. 2. Absorbance vs concentration line for unreacted $Ce(NH_4)_2(NO_3)_6$.

The method gives reliable results with hydrazoic acid and can, therefore, be used for other azides as well. However, as the method is based on a redox system, interferences from other reducing agents can be completely reduced by isolating the azide by treating the mixture with a mineral acid and distilling off the hydrazoic acid formed.

Further ceric ammonium nitrate solution has excellent keeping qualities as no appreciable change occurs even when the solution is kept at the waterbath temperature for 8 hr and exposed to light. Therefore, a stock solution once prepared can be used for a number of experiments over a sufficient long time.

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