

DETERMINATION OF NITROGEN (AS AMMONIA) BY INDIRECT TURBIDIMETRIC METHOD

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A simple indirect turbidimetric method for the determination of nitrogen (as ammonia) is described. The method is based on the formation of yellowish-green fine suspension of zinc-oxinate when ammonia vapours are absorbed by a saturated solution of zinc and oxinate ions. The precipitation is stabilized with *n*-propanol and absorption of the sol is measured.

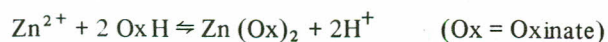
Key words: Turbidimetry; Nitrogen determination; Ammonia determination.

INTRODUCTION

Spectrophotometrically ammonia is usually determined either by Nessler's method [1] or by Indophenol method [2]. Both methods are generally preceded by the distillative separation of ammonia and have been used for a large variety of matrices [3-5]. A number of other inorganic and organic reagents has also been used for the spectrophotometric estimation of ammonia [6-8].

Turbidimetry is an identical technique to visible spectrophotometry but could never get parallel significance because of its limited precision. The major difficulty arises in turbidimetric procedures is to maintain the reproducibility of collidal suspension. Our previous work revealed that adequate precision in turbidimetric results can be achieved by optimizing certain physical parameters like stirring time, choice of surfactant and temperature of the sol [9]. This has also been reported that the sensitivity of the turbidimetric methods can be improved by producing coloured suspension instead of white turbidity [10].

In the present work a simple indirect turbidimetric method is described for ammonia determination. The method is based on the fact that when 8-hydroxyquinoline (oxine) is added to a basic solution of zinc salt there is quantitative precipitation of the light yellow zinc oxinate which displays a yellow green fluorescence in ultra-violet light [11]. The precipitation of zinc oxinate from neutral solutions of zinc salts is incomplete because of the rapid establishment of the equilibrium:



Accordingly if a solution of a zinc salt is treated with an excess of oxine and the precipitate is removed by filtration, the clear filtrate consists of the zinc oxinate equilibrium solution, from which fluorescent zinc oxinate can be precipitated by contact with ammonia vapours.

In the described procedure, ammonia distilled from ammonium salt is brought into contact with clear zinc-oxinate equilibrium solution. The resultant fine suspension of zinc-oxinate is stabilized with *n*-propanol and absorption of the sol is measured.

EXPERIMENTAL

Absorbance were measured on a Pye-Unicam SP8-400 double beam UV/V is spectrophotometric with 10 mm glass cells. Anhydrous ammonium sulphate, 0.471 g, was dissolved in 100ml and solution was further diluted 10 times. An aliquot of ammonium sulphate solution (containing 20-100 μ g of nitrogen) was placed in 20ml distillation flask. The solution was diluted to about 5ml with water. The condense outlet was immersed in a receiver containing 4ml of zinc-oxinate solution (prepared by mixing of 1% zinc chlorides solution and 1% oxine solution). The distillation flask was heated gently and 2ml of 40% sodium hydroxide solution was added. Contents of the flask were boiled for 2 minutes so that all the ammonia was liberated. The solution in the receiver turned turbid.

The turbid solution was transferred to a 100ml flask. To this 2ml *n*-propanol was added to the flask and volume was made up to the mark with water. The solution was shaken thoroughly and absorbance was measured at 430 nm against a compensatory blank.

RESULTS AND DISCUSSION

In turbidimetry the measurement in principle is the same as for the spectrophotometric methods. The only difference is that instead of homogeneous coloured solutions, collidal suspensions obstruct the incidence light. The applications of turbidimetry are limited because of scant precision of results. However our previous work showed that adequate reproducibility in turbidimetric results can

be achieved by careful optimization of certain physical parameters [9].

In present work a fine yellowish-green colloidal suspension of zinc-oxinate is produced by trapping ammonia vapour in zinc-oxinate equilibrium solution. The suspension is stabilized with *n*-propanol and its absorbance is measured.

Choice of surfactant. A number surfactants like ethanol *n*-propanol, glycerol and 2% gelatine solution were employed for stabilizing the colloidal suspension. The best results were obtained with *n*-propanol. Gelatine solution produced an additional white turbidity, especially in solutions with less zinc-oxinate suspension glycerol proved itself a tolerable stabilizer but entrapped air bubbles very often which created problems in absorption measurements. Ethanol and *n*-propanol were equally good in stabilizing the turbidity in start but on keeping the solution for more than five minutes the turbidity in ethanol started to settle down. The suspension stabilized with *n*-propanol showed constant absorption for more than seven minutes and more precise results have been obtained in this case. This has also been noticed that 2ml of *n*-propanol were quite adequate to stabilize 10ml of the suspension.

Effect of time. Effect of time was checked by measuring the absorbance of different stabilized suspensions after different intervals of time. The suspensions were stabilized with ethanol and *n*-propanol. As shown in Fig. 1, in the case of ethanol absorbance was depressed significantly after five minutes of stabilization. However with *n*-propanol the suspension showed constant absorbance for more than seven minutes. Another difference which has been noticed in the case of two surfactants is that depression in absorbance with time is considerably mild in the case of propanol. This experiment reveals the rate of setting the turbidity for two surfactants, which is significantly lesser in the case of *n*-propanol.

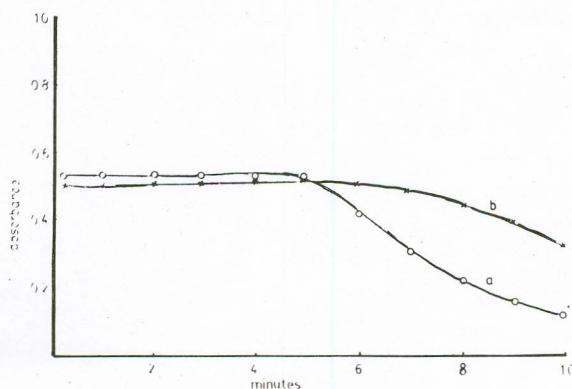


Fig. 1. Effect of time on absorbance.

a-Ethanol; b- *n*-propanol.

Effect of zinc salt. In order to attain the optimum conditions for maximum turbidity various nickel salts were employed to prepare zinc-oxinate equilibrium solution. Only zinc chloride showed a promising behaviour in this respect. Zinc sulphate solution did not produce any insoluble complex with oxine. Similarly no precipitation occurred when ammonia vapours were passed through a solution of zinc sulphate and oxine. Zinc nitrate yielded insoluble zinc-oxinate but on filtering a colourless filtrate was obtained which did not give any turbidity with ammonia. These experiments indicated that zinc sulphate does not react with ethanolic oxine solution whereas the filtrate obtained in the case of zinc nitrate could not develop equilibrium with oxinate ions as developed by zinc chloride.

Calibration and samples. As shown in Fig. 2, a linear calibration graph with a little intercept along Y-axis was obtained for ammonia evolved from 20-100 μg of nitrogen taken as ammonium sulphate. When the absorbance of the suspension was recorded against the clear light green filtrate slightly high values were obtained in the region 422-445 nm. Hence all the absorption measurements were made at 430 nm.

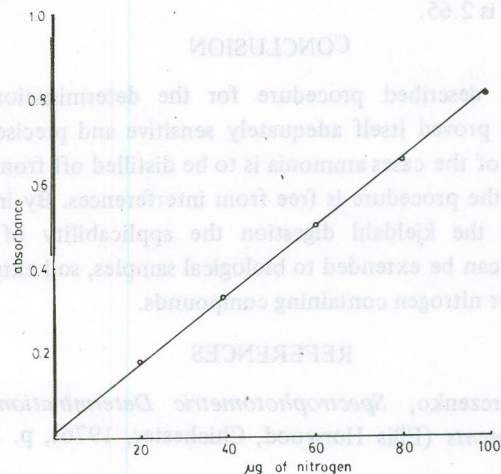


Fig. 2. Calibration for nitrogen.

To check the applicability of the proposed method, nitrogen (as ammonia) is determined in ammonium salts, organic compounds and grain samples. Ammonium salts were directly treated with sodium hydroxide in the distillation flask and the ammonia produced was determined. The nitrogen containing organic compounds and grain samples were first digested with sulphuric acid to yield ammonium sulphate. Then a suitable liquor of the digested mixture was boiled with sodium hydroxide to get ammonia. Each sample was also analysed by a reference method. The results obtained by the described method as well as by the

Table 1. Comparison of results for nitrogen determination in various samples.

Nitrogen containing sample	Taken	Nitrogen content found		Reference method used
		By described method	By reference method	
Ammonium sulphate	60.00 μg	58.5 μg	58.0 μg	Indophenol method [2]
Ammonium nitrate	40.00 "	41.0 "	40.5 "	"
Ammonium chloride	20.00 "	20.2 "	21.2 "	Nessler's method [1]
Urea	50.00 "	57.7 "	59.4 "	"
Thiourea	25.00 "	24.8 "	25.00 "	"
Biacetyldioxime	25.00 "	25.00 "	25.5 "	Indophenol method
Maize		1.48%	1.52%	Kjeldahl titration
Rice		1.67%	1.58%	"
Wheat		1.87%	2.02%	"

reference methods are summarized in Table 1. It is evident from the table that the results obtained for the lesser quantities of the samples are more precise and in well agreement with each other. The relative standard deviation calculated for eight equivolume samples of ammonium sulphate is 2.65.

CONCLUSION

The described procedure for the determination of nitrogen proved itself adequately sensitive and precise. As in most of the cases ammonia is to be distilled off from the sample, the procedure is free from interferences. By incorporating the kjeldahl digestion the applicability of the method can be extended to biological samples, soil extracts and other nitrogen containing compounds.

REFERENCES

1. Z.Mrczenko, *Spectrophotometric Determination of Elements* (Ellis Horwood, Chichester, 1976), p. 394.
2. D.F. Boltz, *Colorimetric Determination of Nonmetals* (John Wiley & Sons, Chichester, 1978), p. 210.
3. N.T. Crosby, *Analyst*, **93**, 406 (1968).
4. M. Buck and H. Stratmann, *Z. Anal. Chem.*, **213**, 241 (1965).
5. R.N. Heistand, *Anal. Chem.*, **42**, 903 (1970).
6. F. Zitomer and J.L. Lambert, *Anal. Chem.*, **34**, 1738 (1962).
7. F.R. Seta and B.E. Tamagno, *Anal. Chem.*, **42**, 1443 (1970).
8. M.H. Hashmi, A.L. Ajmal and A. Rashid, *Mikrochim. Acta*, 860 (1960).
9. J. Anwar, A. Firdous and Z. Kirmani, *J. Chem. Soc., Pakistan*, **7**, 219 (1985).
10. Ref. 1, p 19.
11. F. Feigi, W. Anger and R.E. Desper, *Spot Tests in Inorganic Analysis* (Elsevier Publ. Co., London, 1972).