An Indirect Spectrophotometric Method for the Microdetermination of Nitrogen (as ammonia)

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(Received 15th July, 1987, Revised 28th April, 1988)

Summary: A simple indirect spectrophotometric method for the determination of nitrogen (as ammonia) is described. The method is based on the fact that in a neutral medium the precipitation of nickel with dimethylglyoxime remains incomplete. After filtering off the precipitate, the filtrate contains unreacted nickel and dimethylglyoximate ions. Addition of ammonia to this filtrate produces an equivalent quantity of nickel-dimethylglyoximate which is extracted into chloroform and the absorbance of the extract is measured.

Introduction

Two spectrophotometric methods are usually employed for the determination of nitrogen as ammonia. First is the classical Nessler's method [1] and second is the Indophenol method [2]. Both methods are generally proceeded by the distillative separation of ammonia and have been used for a large variety of matrices [3-5]. However, Nesseler's method can be used for determining ammonia directly in natural waters [6].

A number of other spectrophotometric methods for ammonia estimation has been reported. Ammonia reacts with pyrazolone in pyridine to form a purple compound which is determined spectrophotometrically after extracting into carbon tetrachloride [7]. Zitomer and Lambert [8] determined ammonia by its reaction with hypochlorite to form trichloramine. The trichloramine is then reacted with a mixture of cadmium iodide and starch to give a blue complex. This method has been used for their determination of ammonia in blood [9].

In the present work, a simple indirect spectrophotometric method for ammonia determination is described. The method is based on the fact that precipitation of nickel ions with dimethylglyoxime remains incomplete in a neutral medium. After separating the precipitated nickel dimethylglyoximate, the filtrate contains the unconsumed nickel and oximate ions. From the saturated solution, nickel dimethylglyoximate can be precipitated on addition of basic species. The procedure has been used for the detection of basic ions such as carbonate, hydroxide and phosphate [10] etc.

In the described procedure, ammonia, distilled from ammonium sulphate, is brought into contact with the saturated solution and the resultant nickel dimethylglyoximate is extracted into chloroform. Absorbance of the extract is measured and plotted against ammonia (nitrogen) concentration.

Experimental

Apparatus

A Pye-Unicam SP 8-400 double beam UV/Vis Spectrophotometer with 10 mm glass cells was used for the absorbance measurements.

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Reagents

AnalaR grade chemicals and doubly distilled water (ammonia free) were used throughout this work.

Sodium hydroxide solution

40% aqueous solution of sodium hydroxide was prepared and boiled for 10-15 minutes to remove the traces of ammonia.

Nickel-dimethylglyoxime saturated solution

2.3 g Nickel sulphate hydrated, $NiSO_4.7H_2O$, (dissolved in 300 ml of water) was treated with 2.8 g of dimethylglyoxime (dissolved in 300 ml of ethanol). The red precipitate of nickel complex was allowed to stand for 30 minutes and then filtered. The filtrate was stored in a tightly stoppered bottle.

Standard ammonium sulphate solution

To prepare 1000 $\mu g\ ml^{-1}$ solution of nitrogen, 4.714 g of anhydrous ammonium sulphate was dissolved in 1000 ml water. This solution was further diluted ten times to give 1000 $\mu g ml^{-1}$ solution of nitrogen.

Calibration

Place 0.2 - 0.1 ml aliquot of ammonium sulphate solution (containing 20 - 100 µg nitrogen) in a 50 ml quickfit distillation flask. Dilute the solution to about 4 ml with water. Immerse the condenser outlet in a receiver containing 3 ml of the saturated solution of nickel dimethylglyoximate. Heat the distillation flask gently and add 2 ml of 40% sodium hydroxide solution. Boil the contents of the flask for 5 minutes so that all the ammonia is liberated. The solution in the receiver turns red.

Transfer the red solution from the receiver to a 50 ml separating funnel. Extract the nickel complex with two 5 ml aliquots of chloroform. Combine the two extracts in a 10 ml flask and make-up the volume with chloroform. Measure the absorbance against chloroform at 366 nm and plot against nitrogen concentration.

Discussion

The described procedure is based on the fact that nickel dimethylglyoximate can be completely precipitated from ammonical solution. In a neutral medium, the precipitation is incomplete especially when nickel salt of a mineral acid is treated with oxime. The clear filtrate in the later case, is a saturated solution of nickel dimethylglyoximate presenting the equilibrium:

$$Ni^{2+} + 2\ DH_2 \rightleftharpoons Ni\ (DH)_2 + 2H^+$$

(DH_2 = Dimethylglyoxime)

This saturated solution (pH≃2) is capable of reacting with all materials which consume H^+ ions and shift the equilibrium in the forward direction. Therefore, when basic species are brought into contact with this solution, an equivalent quantity of red nickel dimethylglyoximate is precipitated. In the present work, ammonia is distilled from ammonium sulphate solution by adding sodium hydroxide and absorbed in the saturated solution of nickel dimethylglyoximate. The resultant nickel complex is extracted and the absorbance of the extract is measured.

A linear calibration, shown in Fig. 1, is obtained when aliquots of ammonium sulphate solution, containing nitrogen in the range of 20 - 100 µg, were taken. No difference in the absorbance values of the extracts has been noticed when measurements were made against a compensatory blank and

Table-1

Nitrogen Containing Sample	Nitrogen Calculated in sample aliquot	Nitrogen Content Found by described method	by reference method	Reference method
Ammonium Chloride	100 g	98.5 g	98.0 g	Nessle Method.
Ammonium nitrate.	100 g	97.2 g	98.8 g	Nessle Method
Ammonium Sulphate	50 g	49.5 g	49.4 g	Nessle Method.
Thio Urea	70 g	71.7 g	68.7 g	Indophenol Method
Urea	70 g	68.8 g	68.5 g	Indophenol Method
Maize.		1.45%	1.53	Kjeldahl Titration
Rice		1.65%	1.57	Kjeldahl Titration
Wheat		1.84%	2.02	Kjeldahl Titration

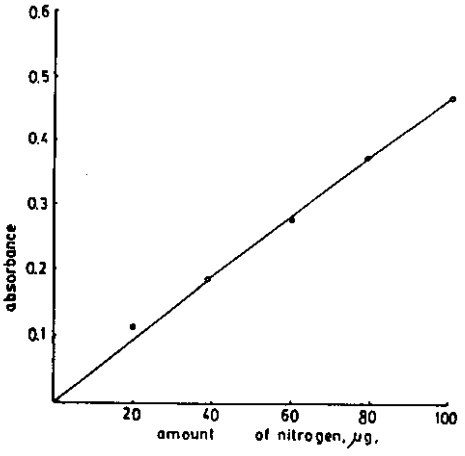

Fig.1: Calibration Group

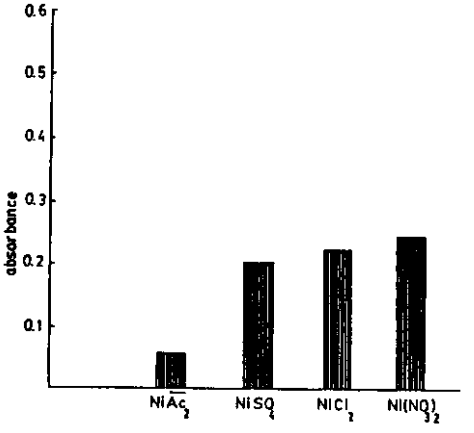

Fig.2: Absorbance obtained from equimolar nickel salts

chlofororm. During the distillation process, the concentration of sodium hydroxide affected the procedure significantly. 2 ml of 40 - 50% sodium hydroxide solution gave the optimum results for the calibration range. Similarly when the total volume of the reagents in the still exceeded 7 ml, a slow and poor recovery of ammonia has been found. To check the performance of various nickel salts, solutions of nickel dimethylglyoximate were prepared from different nickel salts and used for equivolume samples. As shown in Fig. 2, the absorbance was found in the order.

$$Ni(NO_3)_2 > NiCl_2 > NiSO_4 > Ni(CH_3COO)_2$$

The exceptionally low value of the absorbance found in the case of nickel acetate is probably due to the fact

that when nickel acetate reacts with dimethylglyoxime in aqueous medium, acetate ions detain H^+ ions (due to low dissociation constant of acetic acid) and most of the nickel ions react with dimethylglyoxime radicals to form nickel dimethylglyoximate leaving a little nickel in the filtrate.

To check the applicability of the described method nitrogen (as ammonia) is determined in ammonium salts, organic compounds and grain samples. Ammonium salts were directly treated with sodium hydroxide whereas organic compounds and grain samples were first digested with sulphuric acid to yield ammonium sulphate. Each sample was also analysed by a reference method. The results obtained by the described procedure as well as by reference methods are summarized in Table 1. Most of the results are in well agreement with each other. The relative standard deviation calculated for eight equivolume samples of ammonium sulphate is 2.82.

The described procedure provide itself adequately sensitive, precise and accurate. If the nickel-dimethylglyoximate saturated solution is stored in a tightly stoppered bottle it can be used for more than a week. The method is relatively quicker than a number of other spectrophotometric methods used for this purpose. As ammonia is to be distilled off from the sample, the procedure is free from interference. The sensitivity of the method can still be improved by using long-path cells and improving the extraction system. The method can be used for ammonia determination and by employing the Kjeldahl digestion, organic compounds, biological materials and other nitrogeneous compounds can also be analysed for nitrogen.

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