Indirect Determination of Ammonia by Atomic Absorption Spectroscopy

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Summary: An indirect atomic absorption method is described for the determination of ammonia. The method is based on the reduction of silver ions with ammonia in presence of manganese (II) ions. The unconsumed silver, in solution, is determined by atomic absorption spectroscopy. A number of related factors have been studied and the procedure is employed for the determination of ammonia obtained from nitrogen containing compounds.

Introduction

A considerable number of elements, mainly non-metals, exhibit their principal resonance lines in the vacuum ultraviolet region. Hence these elements and their compounds are not directly determinable by atomic absorption spectroscopy. Nitrogen is one of such elements which can not be directly determined by conventional atomic absorption methods. However indirect procedures have been reported for different nitrogen-containing ions such as nitrates [1,2], cyanides [3] and thiocyanates [4].

For ammonia only a few methods based on atomic absorption spectroscopy are available in the literature. Danchik [5] et al. have shown that the co-precipitation of ammonium molybdophosphate with a known amount of the thallium molybdophosphate followed by dissolution of the precipitate provides the basis for an indirect atomic absorption procedure for ammonia determination. The absorbance of dissolved molybdate was measured at 313.2 nm in an air-acetylene flame. The method is non-selective as many metals are precipitated as molybdophosphates. Mitsui and Fujimura [6] reported a method based on the enhancement effect of ammonia on the atomic absorption of silver in air-acetylene flame. The recovery range was 98-100% but calcium and zinc interfered. The enhancement of the zirconium absorbance at its 360.1 nm line by ammonia in a dinitrogen oxide-acetylene flame has been employed by Bond and Willis [7] for estimating ammonia. Phosphate and a number of other nitrogen-containing compounds interfered the determination.

In this work a relatively simple and sensitive method with less interferences is described for ammonia determination. The method is based on the reduction of silver (I) ions by ammonia in presence of manganese (II) ions. After the black precipitate of maganese dioxide and reduced silver has been removed, the unconsumed silver in the solution is determined by atomic absorption spectroscopy.

Experimental

Equipment

A Varian AA-1275 single beam atomic absorption spectrophotometer with standard silver hollow cathode lamp was used. Absorbance of silver was measured at 328.1 nm in a medium air-acetylene flame.

Silver (1) Solution

0.850 g silver nitrate was dissolved in 500 ml chloride-free water and and stored in a dark bottle. A fresh 1 x 10^{-3}M solution of silver was prepared by diluting this solution before use.

Manganese (II) Solution

0.051 g of anhydrous manganese sulphate was dissolved in 1000 ml of distilled water.

Standard Ammonia Solution

To prepare 0.1 mg/ml ammonia solution 0.388 g of anhydrous ammonium sulphate was dissolved in water and diluted to 1000 ml.

Sodium hydroxide Solution

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

Calibration Procedure

Place 0.2 - 1 ml aliquot of ammonium sulphate solution (containing 20 - 100 μg of ammonia) in a 25 ml round bottom quickfit distillation flask. Dilute the contents to about 4 ml with water. Immerse the condenser outlet in a receiver containing 2.5ml of $1\text{x}10^{3}$ M silver solution and 2.5 ml of 1×10^{-3}M manganese solution. Heat the distillation flask gently and add 2 ml of 40% soidum hydroxide solution. Boil the contents of the flask for 5 minutes so that all the ammonia is liberated. The solution in the receiver turns black. Remove the receiver and filter the solution through Whatman No. 41 filter paper. Collect the filtrate in a 50 ml flask. Make up the volume with water and measure the silver absorbance at 328.1nm. Prepare a calibration using different volumes of ammonia solution.

Results and Discussion

A semi-linear calibration line, shown in Fig.1, was obtained when 20 - 100 μg of ammonia were condensed from appropriate volume of ammonium sulphate solution. The range of calibration could be further lowered by using dilute solutions of the reagents but probability of errors increased significantly possibly due to formation of silver oxide. However sensitivity of the method could be increased by improving the distillation system.

The method has been found adequately accurate when a number of inorganic and organic nitrogen-containing compounds were analysed by the described method as well as with Indophenol method [8]. Precision of the method was determined by analysing eight equivolume samples of ammonium sulphate solution (each containing 100 μg of ammonia). The relative standard deviation obtained was 2.6%.

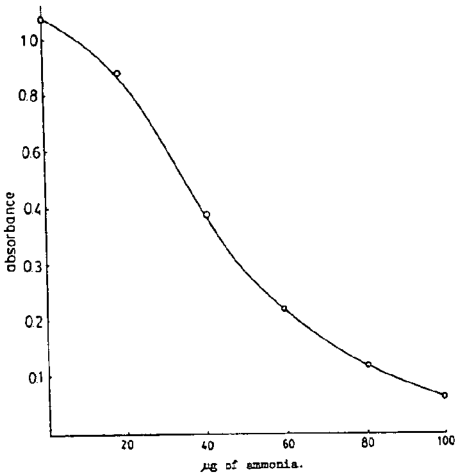

Fig.1: Calibration for ammonia.

Effect of Manganese Concentration

To check the effect of manganese concentration ammonia was distilled from a fixed quantity of ammonium sulphate and passed through solutions containing different quantities of manganese but same volume of silver solution. The results obtained, shown in Fig. 2 reveal that at lower concentrations of manganese (less than half the molar concentration of silver) relatively higher values of silver absorbance were obtained. However when manganese concentration was increased upto a certain level the silver absorbance became constant. Stochiometric calculations indicated that manganese and silver react in 1:2 molar ration. High concentrations of manganese did not produce any adverse effect.

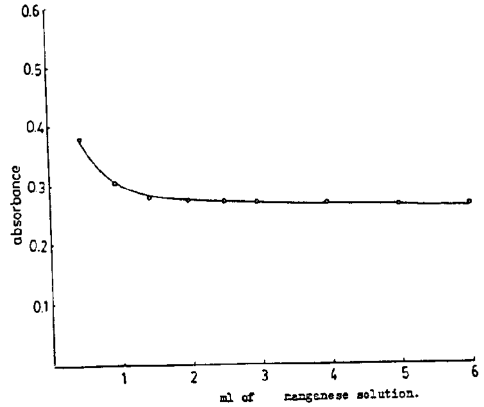

Fig.2: Effect of manganese concentration.

Table 1: Effect of different ions on ammonia determination.

Interferring anion	in excess	taken as	ammonia found mg	Interferring Cation	in excess F	taken	ammo found μg
Chloride	Five fold	Sodium	78.5	Barium	Five fold	Nitrate	81.0
Acetate	Ten fold	Sodium	86.4	Calcium	Ten fold	Chloride	78.2
Nitrite	Ten fold	Potassium	85.2	Zinc	Ten fold	acetate	86.2
Nitrate	Ten fold	Sodium	84.5	Magnesium	Ten fold	Sulphate	85.5
Sulphide	Five fold	Sodium	79.0	Copper	Five fold	Sulphate	89.4
Carbonate	Ten fold	Sodium	84.2	Aluminium	Five fold	Nitrate	84.4
Bromide	Ten fold	Potassium	85.0	Nickel	Ten fold	Nitrate	85.5
Thiosulphate	Ten fold	Sodium	86.2	Lead	Five fold	Nitrate	78.0
When collected from ammonium sulphate solution without any other ion.							85.0

Table 2: Ammonia determined in inorganic compounds and fertilizer samples

Sample	Wt. of sample in 250 ml of solution	Ammonia, (in 1 ml of sample solution) μg				
			(Average) found by			
		Calculated from the Sample taken	No. of determination	Described method	No. of determination	Indephenol method
Ammonium Sulphate	0.063 g	65.0	3	63.5	3	64.2
Ammonium Nitrate	0.096 g	82.0	3	81.0	3	82.4
Ammonium Chloride	0.063 g	80.0	4	75.0	4	78.2
Urea	0.032 g	72.0	3	73.5	3	72.5
Thiourea	0.0369 g	64.0	3	65.0	3	65.0
Ammonium Phosphate	0.062 g	85.0	5	87.2	5	84.7
Diammonium hydrogen	0.087 g	90.0	3	87.5	3	86.0

Effect of Silver Concentration

To check the effect of silver concentration different volumes of silver solution were used to prepare the calibration for 20 - 100 μg of ammonia. As shown in Fig. 3, by varying the silver concentration a significant change has been found in the slope of the calibration line. When the molar concentration of silver was equal to the maximum concentration of ammonia there was not much different in the absorbance. Contrarily when conentration of silver was less than half of the concentration of ammonia calibration line intercepted the x-axis very shortly. This showed that silver was not enough to consume ammonia completely. Calibration with workable slope was obtained when silver to ammonia ratio was 3:4. This reveals that in order to get a good calibration for a given range of ammonia the concentration of silver has to be adjusted.

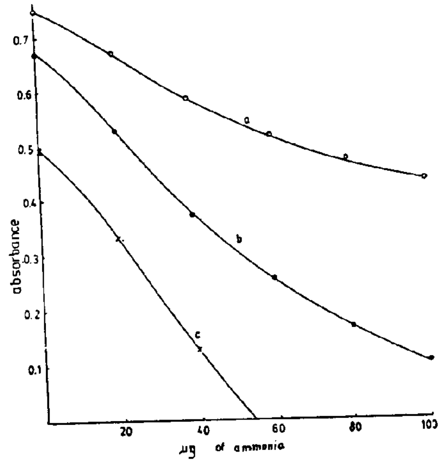

Fig.3: Effect of silver concentration Silver/ammonia mol.ratio: a:1:1, b:3:3, C;2:5

Interferences

To check the possible interferences a number of ions were added in five and ten folds alongwith the ammonium solution. The anions were added as sodium and potassium salts whereas cations were employed as acetates and sulphates. Table 1 shows the effect of these ions. Among the anions only chloride and sulphide had a slight effect on the determination. Both of these ions caused a slight enhancement in the silver absorbance which may be attributed to a little depletion in ammonia liberation. Other anions did not leave any significant effect on the absorbance.

As for as cations were concerned barium and lead have shown a little positive effect on the silver absorbance whereas copper depressed the abosrbance slightly. Other cations like nickel, zinc, iron, magnesium, aluminium and calcium did not show any appreciable effect.

Samples and Conclusion

Ammonia from a number of fertilizer samples and inorganic salts was determined by the described procedure as well as by the reference method. The results obtained by both methods are summarised in Table 2. As can be seen from the Table most of the results reasonably agree with each other.

The procedure described in this work proved itself a simple, sensitive and adequately accurate method for ammonia determination. For obtaining a good calibration line the adjustment of the silver to ammonia concentration ratio is required. However higher concentrations of manganese does not have any significant effect on the determination. The method can be safely employed for the determination of ammonia from a number of matrices such as fertilizers, soil samples and sewerage water samples. The procedure can also be extended for the determination of nitrogen in nitrogen-containing samples by incorporating Kjeldahl digestion.

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