Direct spectrophotometric determination of ammonia in precipitation

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ABSTRACT

The method is based on the reaction of ammonium nitrogen with hypobromite in an alkaline medium. The excess of hypobromite is determined spectrophotometrically by adding an azo dye (Bordeaux B) solution, which is decolorized by hypobromite in acid solution. The influence of e.g. organic compounds is eliminated by allowing the whole reaction to proceed in acid solution also. The standard curve is a straight line up to 400 micrograms of ammonium nitrogen per liter, and the reaction is sensitive to 10 micrograms per liter, equal to 0.01 ppm, as determined in 25 ml of sample.

Introduction

The most extensively used colorimetric method for the determination of ammonia involves the use of Nessler's reagent, which generally requires rigid control of reaction conditions and reagent stability to prevent solution turbidity. The samples must be thermostated and measurements made after a fixed time plus minus a minute only. Finally, the Nessler reagent is in most cases not sensitive enough for a direct determination.

The method by KRUSE & MELLON (1953) based on the use of a pyridine–pyrazolone reagent and the extraction of the resulting purple system with carbon tetrachloride has excellent sensitivity. However, the reagent is very unstable and the extraction process time-consuming in routine work.

The reaction of ammonia with a phenol and hypochlorite reagent to give indophenol has been utilized by RILEY & SINHASENI (1957), ROSSUM & VILLARRUZ (1963) and MANN, JR. (1963), but the control of hypochlorite concentration as well as pH is critical.

Ammonia in water has been determined recently by ZITOMER & LAMBERT (1962) with a method based on the conversion of ammonia to trichloramine by treatment with hypochlorite, destruction of excess ClO^- with nitrite, and development of a blue color with a cadmium iodide linear starch reagent. This method is very sensitive, but the control of pH is critical and even trace amounts of bromine ion interfere.

Methods using hypobromite for the determination of ammonia were described in the last century already, and since then the reaction has been restudied by several investigators. For minute amounts of ammonia the reaction has been used by KROGH (1934) to determine ammonia after distillation, by HARVEY (1951) for nitrogen in organic matter, and by BULJAN (1951) in a direct determination of ammonia in sea water. Following the original procedure given by BULJAN the author could not get results, and that happened to STRICKLAND & AUSTIN (1959) too. The systems hypobromite–ammonia and hypobromite–Bordeaux B dye have been studied in detail, and a procedure has been developed for the direct spectrophotometric determination of ammonia in precipitation.

Reagents

Analytical reagent grade chemicals, low in nitrogen, and ammonia-free distilled water are required for the preparation of all solutions, with storage preferably in Jena or Pyrex glassware. Ammonia-free water can be prepared by distillation or ion exchange methods. Water prepared by these processes often retains about 5 to 10 micrograms of ammonium nitrogen per liter, and daily blanks should be run.

Bordeaux B dye solution. 150 mg of the dye is dissolved in one liter of 0.1 *N* acetic acid made up with ammonia-free water. A technical product (α-naphthene-azo-β-naphthol, 3–6 di-

sulfonic acid) from British Drug House Ltd. has been used in the investigation. Stored in a dark bottle the solution is stable for months.

Sodium hypobromite stock solution 0.1 N. Dissolve 10 g of sodium hydroxide in 500 ml of ammonia-free water. Keep the solution in a deep-freeze until ice is formed and then add with mixing 4 g, equal to 1.26 ml, of fluid bromine. Stored in a dark bottle and in a refrigerator the solution is stable for over a year.

Sodium hypobromite working solution 0.003 N. Dilute the stock solution with 0.3 *N* sodium hydroxide solution and store the solution cold in a dark bottle. One ml added to 5 ml of dye solution in 25 ml of ammonia-free water should result in a light brown color and have an absorbance of 0.280 to 0.350 determined according to procedure. If the normality is determined by titration with sodium thiosulfate solution, add a known amount of the hypobromite solution to 0.5 *N* acetic acid containing iodide. If a stronger acid is used, bromite and bromate will be simultaneously determined. Although the working solution is rather stable it must be checked daily.

Standard ammonium nitrogen solution. Dissolve 382 mg of anhydrous ammonium chloride in ammonia-free water and dilute to 1.0 liter (1 ml = 100 micrograms of nitrogen). Prepare standard solutions by appropriate dilution of the stock solution.

Fundamental reactions

The oxidation of ammonia with hypobromite proceeds according to the equation: $2NH_3 + 3BrO^- \rightarrow N_2 + 3Br^- + 3H_2O$. The reaction is complete at a pH higher than 9. At pH 8 90 per cent, at pH 6.5 50 per cent and at a pH of 3 to 5 about 20 per cent of the ammonia present reacts with the hypobromite. By adding 1 ml of the hypobromite working solution to 25 ml of rain water the pH always rises to about 11.8 and buffering the samples is not necessary.

Hypobromite is a general oxidizing agent which attacks not only ammonia, but also other compounds, especially those of organic origin. It was first thought such substances were absent in precipitation and consequently the ammonia was determined with the alkaline reaction only. However, a comparison of the amounts obtained in this way with those found by the direct nesslerization, Table 3, showed in most cases much higher values for the hypobromite reaction. Therefore, the influence of other compounds reacting with hypobromite is estimated by adding the reagents to the sample in reverse order, and the absorbance so obtained is subtracted from the absorbance measured after the alkaline reaction.

The excess of hypobromite is estimated spectrophotometrically by adding the acid Bordeaux B dye solution. The oxidation of the azo-dye is regular at pH 4.5 to 5.5, and a pH of 4.8 to 4.9 is always reached with the concentrations used.

General procedure

Transfer 25.0 ml aliquots of standard solutions or samples (filtered through silica cotton if necessary) into two 50 ml beakers. Add to one beaker 5.0 ml of the Bordeaux B solution, and then to both while stirring 1.0 ml of the hypobromite working solution by means of an all-glass syringe (Krogh type). Allow the ammonia present to react with the hypobromite in the second beaker for 3 to 4 minutes and then add with stirring 5.0 ml of the dye solution. Measure the absorbance of the solutions after 15 to 25 minutes in 5 cm cells at 525 mμ using air as reference. Spectrophotometer in this investigation was the Beckman, model B. The difference in extinction values gives the amount of ammonia present.

Results and Discussion

Concentration and stability of reagents

The concentrations of the reagents have been chosen to cover the amount of ammonium usually found in precipitation. The standard curve is a straight line up to 400 micrograms of nitrogen per liter when the acid reaction in ammonia-free water has an absorbance of 0.280 to 0.350 according to procedure. Typical standard values are given in Table 1, and plotted up to 100 micrograms per liter in Fig. 1.

The hypobromite working solution can be used for several weeks, as a small decomposition causes a parallel displacement in the alkaline and the acid curves only, leaving the slope of the 0-curve unchanged.

In an earlier stage of the investigation the dye solution was added as an one ml portion

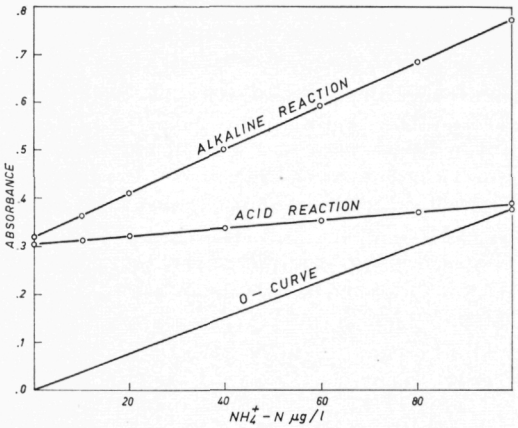

FIG. 1. Standard curves based on the values in Table 1.

with a syringe, however, occasionally negative 0-values were obtained. This fact was most certainly due to inaccuracy of the syringe, as the dye solution is very strong in color.

SENSITIVITY AND PRECISION

In Table 2 triplicate analyses of standards and samples are given. The "ammonia-free" water used for the standard solutions contained in this case 7 micrograms of nitrogen per liter, which is a very common amount for these waters. The difference in absorbance is here 0.027 and this value also gives the sensitivity of the method. By using 7 cm cells the lower limit will be about 2 micrograms of nitrogen per liter.

TABLE 1. *Determination of ammonia in standards.*

25 ml of sample, 1 ml of hypobromite solution and 5 ml of dye solution. Absorbance measured in 5 cm cell at 525 mµ. Reference air.

NH_4^+–N µg/l	Alkaline react. ε_1	Acid react. ε_2	ε_1–ε_2	0-curve
0	0.320	0.305	0.015	0.000
10	.365	.315	.050	.035
20	.413	.322	.091	.076
40	.505	.340	.165	.150
60	.595	.355	.240	.225
80	.685	.372	.313	.298
100	.780	.390	.390	.375
200	1.235	.470	.765	.750
300	1.690	.555	1.135	1.120
400	2.150	.640	1.510	1.495

TABLE 2. *Triplicate determination of ammonia in standards and samples.*

	Alkaline react. ε_1	Acid react. ε_2	ε_1–ε_2	N found µg/l
NH_4^+-free water	0.330	0.302	0.028	7.4
	.328	.303	.025	6.5
	.340	.317	.027	7.2
40 µgN/l added	0.510	0.330	0.180	47.5
	.520	.344	.176	46.5
	.525	.341	.184	48.5
Sample 1	0.493	0.448	0.045	12.5
	.490	.446	.043	11.5
	.498	.456	.042	11.0
Sample 2	1.050	0.600	0.450	120.
	.055	.595	.460	121.
	.045	.605	.440	118.

The values in Table 2 also give the precision of the method, which is estimated to ±10 per cent in the 5 to 50 microgram range and ±5 per cent in the 50 to 400 microgram range.

INTERFERENCE

The interference of diverse organic compounds has already been mentioned, and also how these errors have been eliminated. In precipitation samples there are no other ions present in amounts causing any significant interference. Even a visible precipitation of calcium or magnesium hydroxide has no effect on the recovery of ammonia, as it will redissolve when the acid dye solution is added. Iodide ions ex-

TABLE 3. *Determination of ammonia in rain water samples with hypobromite and with Nessler reagent.*

Sample	Alkaline react. only	According to method	Nessler
	N found in µg/l		
1	25	12	15
2	47	28	30
3	92	50	45
4	115	94	90
5	112	106	100
6	159	120	115
7	173	135	145
8	256	242	240
9	370	352	360

ceeding 50 micrograms per liter have a small positive effect; however, such large amounts have not been found in natural precipitation.

Comparison with direct nesslerization

Nine rain water samples collected in different parts of Finland have been analyzed for their ammonia content as follows: (i) with hypobromite in alkaline solution only, (ii) according to procedure and (iii) with Nessler reagent. The results are given in Table 3. In the direct nesslerization 100 micrograms of ammonium nitrogen per liter were added to the first four samples as to overcome the sensitivity limit of Nessler reagent when measuring the color in 7 cm cells.

The values show an excellent agreement between the two methods and also the necessity of given procedure with a reaction in acid solution too.

Most certainly the values also prove the existence of organic compounds in natural precipitation.

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НЕПОСРЕДСТВЕННОЕ СПЕКТРОФОТОМЕТРИЧЕСКОЕ ИЗМЕРЕНИЕ АММОНИЯ В ОСАДКАХ

Метод основан на реакции азотнокислого аммония с солью бромноватистой кислоты в щелочной среде. Излишек бромноватистой соли определялся спектрофотометрически с помощью добавления раствора азокрасителя, который обесцвечивался солью бромноватистой кислоты в кислом растворе. Влияние, например, органических соединений исключалось тем, что вся реакция происходила также в кислом растворе. Стандартная кривая является прямой линией, возрастающей до 400 μг азотнокислого аммония на один литр. (При определении в 25 μл пробы реакция чувствительна к 10 μг на литр, что равняется 0,01 ppm.)