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## Measurement of Reagent Blanks for the Determination of Ammonia and Silicate

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### Abstract

Simple analytical methods are described for the determination of ammonia and silicate originated only from reagents. Blank sources, other than that associated with reagents, cause a significant uncertainty to the corrected value and are important especially for the measurement of low concentrations of ammonia and silicate in fresh and sea waters.

### Introduction

The most sensitive analytical method for the determination of ammonia in unpolluted fresh and sea waters is required since its concentration is less than a few  $\mu\text{M}$ , even at probable maximum concentrations. Matsunaga and Nishimura (1974) described a rapid and sensitive method by spectrophotometry, in which ammonia is oxidized to nitrite by hypochlorite for 1 min, and then the nitrite is determined with sulfanilamide and N-1-naphthylethylenediamine. This method has been widely used as an analytical index of sea water (e.g. Parsons et al., 1984), and is not affected by the presence of organic compounds, such as amino acids, because of the shortened oxidation time.

However, this method has to be improved especially for the measurement of low concentrations of ammonia. For example, it is difficult to completely eliminate ammonia in distilled and deionized waters. Although the water is passed through a cation-exchange resin (hydrogen form) for the removal of ammonia, it is impossible to ascertain whether the water is essentially free of ammonia, in an open system, since residual ammonia from the laboratory readily dissolves in the water. Therefore, it is very important to differentiate the additional blank component not associated with the reagents in order to minimize the uncertainty of the ammonia value in the water.

Low concentrations of silicate have been determined by spectrophotometry employing the reduction of silicomolybdate with reducing reagents (Mullin & Riley, 1955; Parsons et al., 1984). In this determination, the distillation of water from a glass distillation system gives rise to silicate contamination. Furthermore, it is very difficult to completely remove the dissolved silicate even though it is passed through an ion exchange resin column.

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We discuss here a simple and accurate method for the determination of ammonia and silicate contaminants originated only from the reagents.

## Methods

### *Reagents*

#### 1. Reagents for determination of ammonia

Potassium bromide, 7 w/w % solution : Dissolve 35 g of potassium bromide in 500 ml of 2.5 M sodium hydroxide.

Sodium hypochlorite solution, 0.2 M : The concentration was determined by iodimetry. If the solution is stored in an amber bottle, the solution is stable for at least a week at room temperature.

Arsenite solution : Dissolve 1 g of arsenious oxide and 0.5 g of sodium hydroxide in 50 ml of water, and dilute to 500 ml with water.

Sulfanilamide solution : Dissolve 1 g of sulfanilamide in 100 ml of 3.5 M hydrochloric acid. This is stable for many months.

N-1-naphthylethylenediamine solution : Dissolve 0.1 g of N-1-naphthylethylenediamine dihydrochloride in 100 ml of water. Store the solution in an amber bottle. It is stable for a month.

#### 2. Reagents for determination of silicate

These reagents were prepared as follows (Parsons et al., 1984).

Molybdenum (VI) solution : Dissolve 4.0 g of ammonium paramolybdate,  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ , in about 300 ml of water. Add 12 ml of 12 M hydrochloric acid, mix and make to volume of 500 ml with water. Store the solution in a polyethylene bottle and keep out of direct sunlight.

Metol-sulfite solution : Dissolve 6 g of anhydrous sodium sulfite,  $\text{Na}_2\text{SO}_3$  in 500 ml of water and add 10 g of metol (p-methyl-aminophenol sulfate). When the metol has dissolved, filter the solution through a No. 1 Whatman filter paper and store it in a clean glass bottle which is tightly stoppered. This solution may deteriorate quite rapidly and erratically and should be prepared fresh at least once a month for use.

Oxalic acid solution : Prepare saturated oxalic acid solution by shaking 50 g of oxalic acid dihydrate,  $(\text{COOH})_2\cdot 2\text{H}_2\text{O}$ , with 500 ml of water. Decant the solution from the crystals for use ; the solution may be stored in a glass bottle and is stable indefinitely.

Sulfuric acid solution, 50 v/v % : Pour 250 ml of sulfuric acid (specific gravity : 1.82) into 250 ml of water. Cool to room temperature and make the volume to 500 ml with a little extra water.

Reducing reagent : Mix 100 ml of metol-sulfite solution with 60 ml of oxalic acid solution. Add slowly, with mixing, 60 ml of the 50 v/v % of oxalic acid solution. Add slowly, with mixing, 60 ml of the 50 v/v % sulfuric acid solution and make the mixture up to 300 ml with water. The solution should be prepared each time for immediate use.

All the reagents used were of analytical reagent grade. Waters used in the ammonia experiments were as follows. (1) distilled-deionized (mixture of cation and anion resins) water, (2) deionized water obtained by passing distilled-deionized water through cation-exchange resin in a hydrogen form in a room (open system).

(3) deionized water obtained by passing distilled-deionized water through the resin isolating the external atmosphere (closed system). Only distilled-deionized water was used for measurement of silicate.

#### *Analytical procedure*

##### 1. Procedure for ammonia

###### *Procedure I*

Take 25 ml of a water sample in a 50 ml stoppered Erlenmeyer flask and keep in a water bath at 30-40°C. Add 2 ml of the oxidizing solution and mix well. After 2 min, add 1 ml of the arsenite solution and mix well. Add 2 ml of the sulfanilamide solution, followed by 1 ml of N-1-naphthylethylenediamine solution. After 5 min, measure the absorbance at 543 nm with a 5 cm cell. By the same procedure, measure the blank absorbance using 25 ml of the each water.

###### *Procedure II (determination for ammonia included in reagents only)*

Take 2 ml of the oxidizing solution in a 50 ml stoppered Erlenmeyer flask and keep in a water bath at 65-75°C for 5 min. Add 1 ml of the arsenite solution and mix well. Add 25 ml of water, followed by 2 ml of the sulfanilamide solution and 1 ml of N-1-naphthylethylenediamine solution. After 5 min, measure the absorbance at 543 nm with a 5 cm cell.

##### 2. Procedure for silicate

###### *Procedure III*

Silicate in a sample solution was determined by a slightly modified method of Parsons et al. (1984).

Take 10 ml of molybdate solution to a 50 ml polyethylene bottle. Add 25 ml of a sample to the bottle and mix by inverting. Allow to stand for 10 min, but not for more than 30 min. Add the reducing reagent and allow the solution to stand for 2-3 hr to complete the reduction. Measure the absorbance at 810 nm with a 5 cm cell. Procedure IV (determination for silicate included in reagents only)

Take 10 ml of molybdate solution to a 50 ml polyethylene bottle, followed by 15 ml of the reducing reagent and mix immediately. Allow the solution to stand for 2-3 hr, and then add 25 ml of water and mix well. Measure the absorbance at 810 nm with a 5 cm cell.

### Results and discussion

The ammonia recoveries for the procedures I and II were studied by the addition of 200  $\mu$ l of  $2.5 \times 10^{-4}$  M ammonium chloride to the bottles (final concentration 2  $\mu$ M). The procedure I gave a constant maximum absorbance at the temperature range from 30 to 40°C. On the other hand, the absorbance by the procedure II increased with the increase of temperature and attained a constant maximum value at 65-80°C but, at 35°C, was considerably lower than that by the procedure I (Fig. 1). At the temperature range from 65 to 80°C, the oxidation time more than 3 min gives a constant absorbance.

The results of the reagent blanks for three different types of waters are shown in Table 1, according to the procedures I and II. The procedure I results in higher absorbance than the procedure II because of the oxidation of ammonia contained in the waters and the reagents used. The absorbance obtained by the procedure II

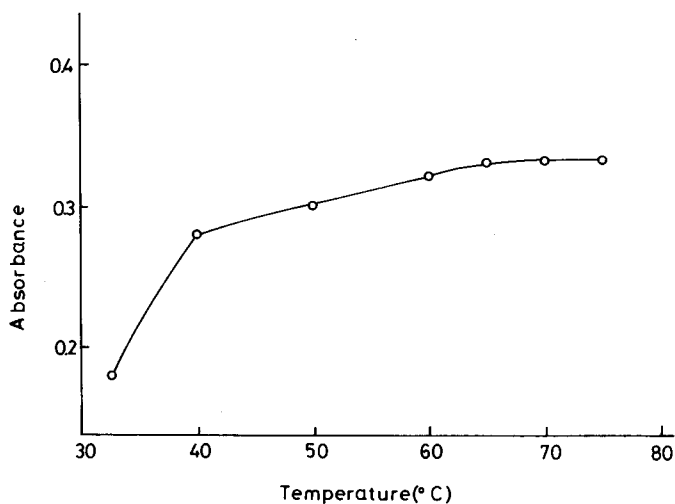


Fig. 1. Effect of temperature on ammonia recovery by procedure II  
Oxidation time was 5 min in all temperature. At 32°C, the absorbance is low even if the oxidation time was 10 min.

Table 1. Measurement of blanks for ammonia by procedures I and II.

	Procedure I	Procedure II
Absorbance		
(1)Distilled-deionized water	0.045±0.005	0.008±0.002
(2)Deionized water(open system)	0.038±0.003	0.010±0.003
(3)Deionized water(closed system)	0.016±0.002	0.008±0.002

Table 2. Measurement of blanks and 6 μM silicate by procedures III and IV

Procedure III		Absorbance				
blank value	0.040,	0.030,	0.030,	0.035,	0.043	0.036±0.006
net value	0.305,	0.304,	0.296,	0.310,	0.307	0.304±0.005
Procedure IV		Absorbance				
blank value	0.015,	0.019	0.010,	0.015,	0.018	0.015±0.003
net value	0.292,	0.310,	0.307,	0.297,	0.303	0.302±0.007

originates only from the reagents. The ammonia recovery for the procedure II, by addition of 200 μl of  $2.5 \times 10^{-4}$  M ammonium chloride, was in good agreement with that for the procedure I.

In case of the determination of silicate, the blank (distilled-deionized water) and 6 μM silicate (addition of 200 μl of  $7.5 \times 10^{-4}$  M silicate) were determined by

both the procedure III and IV (Table 2). There is no significant difference between two methods for the determination of  $6 \mu\text{M}$  silicate. However, the blank values by the procedure III were slightly higher than those by the procedure IV, which indicates that the elevated blank values by the procedure III resulted from silicate contained in the reagents and the water used, instead of the sample solution.

In conclusion, these methods are very reliable for the determination of small amounts of ammonia and silicate. Namely, ammonia and silicate contained only in the reagents can be determined according to the procedure II and IV, respectively.

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