

**Ammonia and ammonium
over the southern Baltic
Sea. Part 1. Preparation
of aerosol and air samples
for the determination
of ammonia by the
indophenol method**

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Abstract

1997 saw the start of a study into the spatial and temporal changes in the chemical composition of the atmosphere over the littoral and offshore waters of the Baltic Sea. Collection of samples and their subsequent chemical analysis was preceded by meticulous laboratory experiments concerning the validation and adaptation of the analytical procedures. The colorimetric indophenol blue technique was used to analyse the aerosol samples for the concentration of ammonium ions and the air samples for their gaseous ammonia. The samples were collected with PTFE-filters and Whatman 41 filters coated with 5% orthophosphoric acid. This acid enhances the aerosol sampling efficacy but reduces the pH of the reaction in which indophenol is formed. The pH of the aerosol samples thus had to be raised, and this in turn required an alteration to the original procedure prior to ammonia determination. It was demonstrated that the addition of 0.1 N KOH to the filters coated with H_3PO_4 increases the pH of the reaction medium to the required level of $pH = 8-11.5$ and does not substantially influence the precision of the determination; the error of the modified procedure was of the order of 5.2%.

Air samples for the determination of gaseous ammonia were collected with annular denuders. Oxalic acid and citric acid are the usual impregnating agents. In the present experiments oxalic acid was used for denuder impregnation; it turned out to be more effective than citric acid under the conditions of the southern Baltic Sea.

The complete text of the paper is available at <http://www.iopan.gda.pl/oceanologia/>

The detection limit of the indophenol blue method in these laboratory experiments was $0.045 \text{ mmol dm}^{-3}$. The respective relative standard deviations (RSD) within the range of higher and lower concentrations were 0.64% and 4.53%.

1. Introduction

For a better understanding of climate change in the coastal zone it is very important to monitor the processes in which gases in air and marine salts in aerosols participate. Significant constituents in this respect are ammonia in the air and the ammonium ion in aerosols. The colorimetric indophenol method for ammonia determination is well established and commonly applied in marine chemistry and atmospheric precipitation analyses (Grasshoff et al. 1983, Sopauskiene & Budvityte 1993, Falkowska et al. 1999). Recommended by HELCOM¹, this sensitive method was used in studies carried out within the BASYS² international project (1996–99), which have been continued up to the present day. Since chemical analysis of atmospheric samples operates on very small volumes of aerosols or air, the original analytical procedure had to be validated with a reduced volume of analyte and checked step by step from the sampling to the colorimetric determination in order to ascertain whether the reduction in volume affected the analytical error.

Aerosol samples were collected using a filter pack (Fig. 1) with 2 types of filters each 47 mm in diameter: PTFE-filters of 5 mm pore size, and Whatman 41 filters. First, the air passes through the PTFE-filter, which adsorbs large suspended particles ($\phi > 1 \mu\text{m}$), then through the Whatman 41 filter. The impregnated surface of the latter filter collects the suspended fraction of small particles ($\phi < 1 \mu\text{m}$) and also the gaseous ammonia. The PTFE-filter is made of non-flammable, high-quality material, resistant to mechanical breaking. With its hydrophobic and chemically inactive surface, aerosol adsorption by this material is 99.99% effective (Appel et al. 1984, Markaki et al. 2003). Because of the high quality properties of the PTFE-filters, only Whatman 41 filters were tested in the experimental part of the study.

Gaseous ammonia was collected in annular denuders 430 mm in length and 13.6 mm in diameter (Fig. 2). The denuders contain embedded closed vials ($l = 375 \text{ mm}$ and $\phi = 10 \text{ mm}$). The efficiency of collection in denuders depends to a great extent on the impregnation agent and may range from 3% with Al_2O_3 to 100% with oxalic or citric acid (Behlen 1996). When air

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Fig. 1. Filter pack for aerosol collection used in the tests and measurements



Fig. 2. Denuders for gaseous ammonia collection used in the tests and measurements

passes through a denuder impregnated with oxalic or citric acid, gaseous ammonia reacts with the acid, so that the form actually analysed is the ammonium ion.

The indophenol method for determining ammonia in air and aerosol samples is based on the formation of an indophenol blue pigment during the reaction of phenol and hypochlorite in the presence of ammonia. In an alkaline medium (pH = 8–11.5) a chloramine is first obtained. This then reacts with the surplus hypochlorite and with the phenol forms quinone chloramine in the presence of catalytic quantities of sodium nitroprusside. Quinone chloramine further reacts with surplus phenol to produce indophenol. The blue coloration is due to the dissociated form of indophenol. The prime task of the tri-sodium citrate buffer used here is to bind magnesium and calcium ions into complexes, thus preventing the precipitation of their hydroxides and carbonates in the alkaline reaction medium. Since the analytical details of the method lie beyond the scope of this article, they will not be discussed further. The reader is referred to Grasshoff et al. (1983) and Falkowska et al. (1999).

The pH of the reaction medium plays an important role in the indophenol method of ammonia determination. At pH exceeding 11.5 the oxidation of ammonia to nitrite is not complete, and the concentrations of the blanks are not reproducible; the latter show a greenish coloration instead of a clear blue one. At pH below 8, the reaction fails to start at all.

Because the filters and denuders were pre-impregnated with acid for better sampling efficiency, it proved necessary to raise the pH of the reaction medium to ensure the formation of indophenol. The methodological correction therefore applied to the analytical procedure of the aerosol or air sample handling prior to the actual determination by the indophenol method. A series of experiments was carried out to determine: (1) the effect of acid impregnation of the filters/denuders on the reaction medium, on the effectiveness of the adsorption of the aerosol and gaseous components, and on the resulting concentration of the ammonium ion to be analysed; (2) whether the addition of KOH to increase the pH of the reaction medium affected the ammonia concentration and the reproducibility of the measurements.

2. Laboratory experiments

2.1. Limit of detection (LoD) of the indophenol method

According to the definition, the limit of detection is a number expressed in units of concentration (or amount) that describes the lowest concentration level (or amount) of an element that an analyst can identify as statistically different from an analytical blank (Long & Winefordner 1983). LoD was

evaluated statistically by 14 repetitions of a blank sample concentration (milli-Q water with the addition of procedural reagents), after which the standard deviation of the measurements was calculated (see Table 1).

Table 1. Determination of the detection limit of the indophenol method based on blank measurements

Characteristics	Concentration [$\mu\text{mol dm}^{-3}$]
n	14
mean	1.074
SD	0.015
max	1.099
min	1.049

Symbols: n – number of replicates, mean – mean concentration calculated with equation $C = (A - 0.0025)/0.0596$; $R^2 = 0.9992$, SD – standard deviation, min – minimum, max – maximum.

Assuming that $\text{LoD} = 3 \times \text{SD}_{\text{bl}}$ (EURACHEM 2000), SD_{bl} calculated from 14 measurements was 0.015 and $\text{LoD}_{\text{NH}_3} = 0.045 \mu\text{mol dm}^{-3}$. This is the same value as that given in Grasshoff et al. (1983). To achieve the requisite precision of measurements, the analysed concentrations have to be higher than the detection limit of the method.

2.2. Precision of the analytical method in the high and low concentration ranges

The precision of the analytical method in the high and low concentration ranges allows the analytical error to be determined. Chemical analysis of experimental samples was carried out under stable laboratory conditions. In general, 12 independent samples of a standard solution of ammonium ion were analysed over low and high concentration ranges, where the low concentration was set at $< 0.8 \mu\text{mol dm}^{-3}$ and the high one at $> 6.0 \mu\text{mol dm}^{-3}$. Each sample was analysed with two replicates. The relative standard deviation within the low concentration range of ammonia lay at 4.53%, but within the high concentration range it reached only 0.64%.

2.3. Selection of the introductory procedure prior to chemical analysis by the indophenol method

All Whatman 41 filters were rinsed three times with de-ionised water (milli-Q) and then dried. The experiment included 4 groups of filters, with 15 filters examined in each group:

- **Groups I and II:** impregnated with 5% H_3PO_4 p.a. and dried. The filters were inserted into airtight polypropylene bottles.
- **Groups III and IV:** the filters were impregnated with 5% H_3PO_4 p.a., then with a standard solution of NH_4^+ reaching a concentration of $10 \mu\text{mol dm}^{-3}$ and dried. The filters were then inserted into airtight polypropylene bottles.

Immediately after desorption by agitation in an ultrasonic bath for 45 min., ions from the Whatman 41 filters were introduced into de-ionised water (always 0.014 dm^3). In groups II and IV prior to analysis, 0.1 cm^3 of 0.1 N KOH p.a. was added to the samples to increase the reaction pH to between 8 and 11.5. Such prepared filter samples were analysed using the indophenol blue method to determine the ammonium ion. Every sample was analysed twice using 3.5 cm^3 of eluant.

The results obtained in group IV indicated that this procedure was the most appropriate for sample preparation prior to the analysis by the indophenol method of ammonia in aerosol samples collected on Whatman 41 filters (Table 2). The results best fitted the concentration of the applied standard ($10 \mu\text{mol dm}^{-3}$), and the analytical error of the modified method was around 5.2%. Without the addition of KOH, the analyte concentration obtained was nearly 50% less.

Table 2. Results of ammonia determination by the indophenol method in aerosol samples collected on Whatman 41 filters using different procedures of sample preparation prior to analysis

No.	Test characteristics	n	Concentration [$\mu\text{mol dm}^{-3}$]				pH
			mean	SD	max	min	
1	filters impregnated with H_3PO_4	15	0.042	0.019	0.059	0.010	3
2	filters impregnated with H_3PO_4 plus KOH	15	0.050	0.012	0.066	0.025	10.8
3	filters impregnated with H_3PO_4 plus NH_4^+ ($C = 10 \mu\text{mol dm}^{-3}$)	15	4.076	0.762	5.160	3.062	3
4	filters impregnated with H_3PO_4 plus NH_4^+ ($C = 10 \mu\text{mol dm}^{-3}$) plus KOH	15	10.077	0.526	11.032	9.421	10.5

Symbols: A – absorbance, SD – standard deviation, min – minimum, max – maximum, mean C – concentration calculated with equation $C = (A - 0.0025)/0.0596$; $R^2 = 0.9992$.

Filters impregnated with 5% H_3PO_4 p.a. (first group) were treated as blanks, this being the standard procedure prior to sample collection. The blank for Whatman filters was set at $0.042 \pm 0.019 \mu\text{mol dm}^{-3}$.

3. Experiments including environmental sample collection

The air samples were collected in Gdynia on the roof of the building of the Institute of Oceanography, c. 20 m a.s.l., above the crowns of the adjacent trees. The building is situated 1 km from the shore of the Gulf of Gdańsk. Adsorption efficiency tests of the substances used to impregnate the denuders were carried out in 24 h cycles.

3.1. Selection of the impregnating substance

Denuders allow the determination of gaseous components of atmospheric air. A commonly used technique, it minimises errors in the first stage of sample collection (Possanzini et al. 1983, Appel et al. 1988, Eatough et al. 1988, Perrino et al. 1988, Harrison & Kito 1990, Andersen & Hovmand 1994). Air flow through the denuder is laminar. The inner walls of the tube are coated with the agent, which selectively absorbs the molecules of the analysed gas. The most frequently used impregnating substances to absorb gaseous ammonia are citric acid (Vossler et al. 1988, Brauer et al. 1989) and oxalic acid (Appel et al. 1988, Eatough et al. 1988, Andersen & Hovmand 1994). The effectiveness of absorption was assumed to reach 100% at $\text{pH} = 6.3$ for oxalic acid and at $\text{pH} = 1.7$ for citric acid, if the analysis was done by ion-exchange chromatography (Behlen 1996).

Prior to environmental sample collection with denuders, a test was run to compare the efficacy of oxalic and citric acids as impregnating agents in the indophenol method. The measurement unit consisted of two denuders, one impregnated with oxalic acid, the other with citric acid. Before the measurements they were carefully washed in water containing acetone, rinsed three times with de-ionised water, then dried. The denuders were divided into two groups – one group was impregnated with a 2% solution of oxalic acid, the other with a 2% solution of citric acid. In each case the impregnating mixture contained a 1% solution of glycerol (to increase the viscosity of the coating agent) and quartz powder (to provide visual evidence that the denuder was properly impregnated). The denuders were dried again following impregnation.

The preparation of the denuders and the analytical procedure followed the same steps for all samples. The impregnated denuders were placed in a box protecting them from extreme weather conditions (rain, strong wind) and were connected to the air pump by polyethylene tubing. Recorded by gas-meter readings and regulated by the critical orifice, the air flow through

the two denuders was stable, reaching respective values of $0.672 \text{ m}^3 \text{ h}^{-1}$ and $0.705 \text{ m}^3 \text{ h}^{-1}$ for the denuders impregnated with citric and oxalic acid. After 24 h, air pumping was terminated. The denuders were washed out using 0.014 dm^3 de-ionised water, then shaken for 30 min to dissolve the ammonium salt. The resulting solution was poured into polyethylene bottles, which were then closed tightly. The solution from each denuder was divided into 3 sub-samples, then analysed with the indophenol blue method.

Oxalic acid turned out to be the more efficient absorber of ammonia, nearly 45% more so than citric acid. Moreover, the precision of the measured 3 sub-samples was better in the case of oxalic acid (0.012) than with citric acid (0.017). Because it acidified the impregnate to a higher pH (6.3) – the pH of citric acid was only 1.7 – the error in the indophenol method was much lower. Ferm (1986), too, has indicated oxalic acid as the more effective absorber of gaseous ammonia in temperate geographical latitudes.

3.2. Precision of NH_3 analysis in samples collected with denuders

Ammonia concentrations were determined in samples collected in 10 measurement cycles lasting 24 h each with the use of 2 denuders impregnated with oxalic acid. The pre-collection procedure and sample handling before chemical analysis by the indophenol method followed the steps described in section 3.1. Both denuders were connected in parallel to the same air pump. Air flow was $0.672 \text{ m}^3 \text{ h}^{-1}$ through denuder A, and $0.705 \text{ m}^3 \text{ h}^{-1}$ through denuder B. On completion of this process, the denuders were rinsed with 0.014 dm^3 of de-ionised water, and the ammonia in the eluate determined by the indophenol method. The mean relative error for these two denuders installed in parallel was calculated at 3.35% (range: 1.02–4.90%).

4. Conclusions

- The application of the indophenol method for determining ammonia in aerosol samples collected on Whatman 41 filters impregnated with acids requires, besides the standard procedure, the addition of 0.1 N KOH to raise the reaction pH to 8–11.5. The experiments showed that the addition of 0.1 N KOH does not affect the concentration of ammonia, and the analytical error of the modified method at 5.2% can be regarded as satisfactory.
- Oxalic acid proved to be the more effective absorbing agent for environmental sample collection. In denuders impregnated with this acid the absorption of ammonia was 45% more efficient than in those impregnated with citric acid. The mean relative error for the two denuders impregnated with oxalic acid installed in parallel in the measurement set was 3.35%.

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