

BIBLIOTEKET  
Danmarks Miljøundersøgelser  
Kals, Grenåvej 12, 8410 Rønde

# Diffusion Scrubber

## A Technique for Measuring Ammonia

NERI, Technical Report No. 99  
1994

Lise Lotte Sørensen, Kit Granby, Hans Nielsen &  
Willem A.H. Asman  
*Department of Emissions and Air Pollution*

Ministry of the Environment  
National Environmental Research Institute  
July 1994

## Data sheet

Title: Diffusion Scrubber  
Undertitle: A Technique for Measuring ammonia

Authors: Lise Lotte Sørensen, Kit Granby, Hans Nielsen & Willem A.H. Asman

Department: Department of Emissions and Air Pollution

Serial title and no.: NERI Technical Report No. 99

Publisher: The Ministry of the Environment. National Environmental Research Institute

Year of publication: July 1994

Figures: Bjarne Jensen, Lise Lotte Sørensen  
Technical assistance: Hans Nielsen, Bjarne Jensen  
Fieldwork: Lise Lotte Sørensen, Hans Nielsen, Kit Granby, Bjarne Jensen  
Laboratory assistance: Hans Nielsen, Bjarne Jensen  
Typist: Linda West Brogaard

Please quote: Sørensen, L.L., Granby, K., Nielsen, H. & Asman, W.A.H.  
(1994): Diffusion Scrubber - A Technique for measuring ammonia.  
National Environmental Research Institute, Denmark, 55 pp - NERI  
Technical Report No. 99

Reproduction permitted only when quoting is evident.

ISBN: 87-7772-138-1  
ISSN: 0905-815X

Printed by: Grønager's Bogtryk & Offset  
Circulation: 300  
Number of pages: 54

Price: Dkr. 70,00 (incl. 25% VAT, excl. freight)

For sale at: National Environmental Research Institute  
Department of Emissions and Air Pollution  
Postbox 358, Frederiksborgvej 399,  
DK-4000 Roskilde, Denmark  
Tel: + 45 46 30 12 00  
Fax: + 45 46 30 11 14

# Contents

Preface 5

Summary 7

Danish Summary 8

1 Introduction 9

2 The monitor system 11

2.1 The collection principles 11

2.2 Configuration of the monitor system 12

2.3 Constructing a diffusion scrubber 16

3 Test and conditions in the gas calibration system 21

3.1 Dilution of the calibration gas 21

3.2 Stability of the calibration concentration 22

3.3 Relative humidity of the calibration gas 24

4 Conditions in the analytical detection system 25

5 Influence of sampling conditions on the performance 26

5.1 Collection efficiency 26

5.2 Linearity 26

5.3 Temperature 28

5.4 Relative humidity 29

5.5 Blanks 31

5.6 Carryover 32

6 Detection limit, repeatability, and reproducibility 38

6.1 Detection criteria and detection limit 38

6.2 Repeatability and reproducibility 39

7 Intercomparison 43

7.1 Diffusion scrubber/denuder intercomparison 43

7.2 Diffusion scrubber/denuder intercomparison 44

7.3 Diffusion scrubber/filterpack intercomparison 46

7.4 Intercomparison of four  $\text{NH}_3$  sampling techniques 47

8 Summary and conclusion 51

References 52



## Preface

This work was conducted within the framework of the Danish Sea Research programme 90 and is a part of one of the authors Lise Lotte Sørensen's Ph.D. thesis: "Experimental study of the processes in air/sea exchange of gaseous nitrogen compounds". The purpose of this work was to develop a sensitive and accurate measurement technique to measure fluxes of ammonia to marine surfaces. The work was inspired by Prof. Purnendu Dasgupta, Texas Tech University, Lubbock, Texas, USA. Funding for this project was provided by the Danish Environmental Protection Agency, The Nordic Council of Ministers and the Danish Environmental Research Programme.



## Summary

The purpose of the presented work was to develop a sensitive and accurate measurement technique to measure fluxes of ammonia to marine surfaces. For this purpose an existing diffusion scrubber technique was further developed. The setup of the total monitor system including the collection device (the diffusion scrubber), the analytical detection system and the gas calibration system is described in details.

The sampling resolution time for this method is 10 minutes and the detection limit is estimated to be 0.01 ppbv. The response to the  $\text{NH}_3$  concentration is found to be dependent of the relative humidity in the ambient air and the temperature. The diffusion scrubber is calibrated by using a diluted  $\text{NH}_3$  cylinder gas, and the concentrations of the calibration gas were in the range 0.02 ppb to 2 ppb during test of the total monitor system. Sampling performed with the diffusion scrubber is compared to sampling performed by a filter pack, a diffusion denuder and a continuous flow denuder (AMANDA). The diffusion scrubber technique shows good agreement with the continuous flow denuder and the filter pack.

The diffusion scrubber technique can, in its present configuration, be used for flux measurements. Still the detection of concentrations by the technique corresponds to changes in temperature and relative humidity. These problems has to be sorted out in future work.

## Danish summary

Formålet med arbejdet var at udvikle en følsom og nøjagtig målemetode til målinger af ammoniakfluxe til marine overflader. For at opfylde dette formål blev en eksisterende diffusionsscrubber metode videreudviklet. Opbygningen af det totale monitoringsystem indeholdende opsamlingsenheden (diffusionsscrubberen), analysesystemet og gaskalibreringssystemet, er detaljeret beskrevet.

Opsamlingstiden for denne metode er 10 min. og detektionsgrænsen er beregnet til at være 0,01 ppbv. Signalstørrelserne for  $\text{NH}_3$ -koncentrationer viser sig at være afhængige af relativ fugtighed i den opsamlede luft og af temperaturen. Diffusionsscrubberen er kalibreret med en fortyndet  $\text{NH}_3$ -flaske, og koncentrationsområdet for kalibreringsgassen var 0,02 ppbv til 2 ppbv under de udførte tests. Opsamlinger foretaget med diffusionsscrubberen er sammenlignet med opsamlinger foretaget med filterpack, diffusionsdenuder og en annular våddenuder med kontinuert flow (AMANDA). Diffusionsscrubberteknikken viser god overensstemmelse med filterpack og den annulare våddenuder.

Diffusionsscrubberteknikken kan i sin nuværende udformning anvendes til målinger af fluxe. Metoden er dog følsom overfor temperaturændringer og for ændringer af den relative fugtighed. Disse problemer skal løses i kommende arbejde.



# 1 Introduction

The objective of the atmospheric part of the "Danish Sea Research Programme 90" was to estimate the deposition of nitrogen compounds to Danish coastal waters. Nitrogen is often a limiting factor for growth of algae at sea and the sea can act as a sink towards gaseous ammonia ( $\text{NH}_3$ ). Because deposition of  $\text{NH}_3$  cannot be measured directly using eddy-correlation due to the slow sampling rates of the sampling methods for  $\text{NH}_3$ , we chose to apply the gradient technique. The gradient technique infers the flux by assuming that the concentrations are spatially homogeneous and steady-state on time scales less than one hour, and that turbulent transport produces a measurable concentration gradient. Furthermore it is assumed that chemical reactions in the atmosphere will not influence the vertical concentration gradient caused by deposition. For ammonia typical concentrations in marine atmosphere will be low, about 0.5 ppb. The concentration difference measured by the gradient technique will be even smaller, i.e., 1-25% of this value. Small differences in concentrations yield the flux estimate and the ammonia detection method must therefore be very sensitive with high reproducibility. In the atmosphere above the sea surface the  $\text{NH}_4^+$  concentration will be higher than the concentration of  $\text{NH}_3$ . A method which measures  $\text{NH}_3$  at very low concentrations without influence from  $\text{NH}_4^+$  was necessary.

## *Filterpack methods*

The most commonly used method for sampling  $\text{NH}_3$  is the filter pack (*Williams et al., 1992*). Unfortunately this method has the disadvantage of a long sampling period and interferences due to  $\text{NH}_3$  evaporating from the particle filter placed in the inlet of the sampling device. *Williams et al. (1992)* used an oxalic acid coated filter pack in an intercomparison. The sampling time for the filterpack used was 2 hours and the detection limit was 0.036 ppb.

## *Denuder methods*

The denuder method (*Ferm, 1979*) does not have interferences from particles, but the sampling period is still long (two hours for high concentrations ( $> 1$  ppb) and longer for lower concentrations) and the sampling efficiency might change with the ambient temperature and relative humidity. The thermo denuder (*Keuken et al., 1989*) has a higher sampling rate (10 to 20 minutes) and a detection limit of  $0.1 \mu\text{g m}^{-3}$  ( $\approx 0.2$  ppb). In an intercomparison by *Williams et al. (1992)* a tungstic oxide denuder sampling/chemiluminescence detection system was used. The sampling time for this system is 10 minutes and the detection limit is 0.04 ppb.

## *Techniques with high sampling rate*

Only a few methods with very high sampling rates have been reported. *Williams et al. (1992)* used a photofragmentation/laserinduced fluorescence instrument in their intercomparison (average sampling time 5 min., detection limit 0.05 ppb), and recently a continuous-

flow denuder (AMANDA) was developed at Netherlands Energy Research Foundation (ECN, Petten, The Netherlands). The sampling rate is 1 minute and in an intercomparison (*Mennen et al. 1993*) the detection limit of this technique was estimated to be 0.07 ppb. During other experiments the detection limit was 0.009 ppb using the same technique (*Wyers et al. 1993*).

#### *The diffusion scrubber technique*

Recently also another sampler, a so called diffusion scrubber, was developed for the collection of trace gases (*Dasgupta, 1986; Dasgupta et al., 1988; Genfa et al., 1989*). The sampling/measurement method is semi-continuous and has no contamination problems from handling of the sample. The interferens from  $\text{NH}_4^+$  particles is also reported to be very low (*Genfa et al., 1991*). The detection limit of this instrument was estimated to be about 0.1 ppb (*Genfa et al., 1989*). We chose to develop this method further in order to obtain a lower detection limit so that a wide range of  $\text{NH}_3$  measurements could be made in the atmosphere over the sea.

The monitor system which we use consists of three parts: a diffusion scrubber (the sampling device), an analytical detection system and a calibration system. It is the purpose of the monitor system to separate the gas from the particles in a flow, to collect the gas and measure the concentration of the specific gas of interest. The principle of this sampler or diffusion scrubber (DS) is similar to the principle of the diffusion denuder, where the latter is a tube where the internal wall is coated with a suitable substance which acts as a sink for the gas of interest. The gas is separated from the particles due to the higher diffusion coefficient of the gases (*Ferm, 1979*). A diffusion scrubber consists of a tube with a water saturated microporous membrane tube centred along the axis of the outer tube. The air is sucked through the outer tube. During passage through the tube, ammonia will diffuse to the liquid in the membrane tube due to its solubility in water, so the ammonia is collected in the membrane, and not at the walls as in a diffusion denuder. The liquid is pumped into a fluorescence system for continuous on-line measurement of the sampled atmospheric ammonia. Because of direct flow to the analytical system there will be no contamination of the sample due to handling. Therefore it is possible to obtain a low detection limit by this method.

The analytical method for measuring samples of atmospheric ammonia is based on the reaction between o-phthaldialdehyde (OPA), a "reducing agent" and ammonia or primary amino acids to produce a fluorescent product (*Rapsomanikis et al. 1988*). Sulphite was chosen as the reducing agent because of the high selectivity for ammonia, low toxicity and because of the high fluorescence property (*Jacobs, 1987; Genfa and Dasgupta, 1989*). The fluorescent product is 1-sulfonatoisindole.

The diffusion scrubber is calibrated using a calibration gas having a known  $\text{NH}_3$  concentration. The calibration gas is prepared by diluting a known gas concentration from a gas cylinder. The gas is diluted with zero gas by controlling the flows very accurately. In the

following section the three parts of which the monitor system consist (the diffusions scrubber, the calibration system, the analytical system) is described. The calibration and analytical detection systems are tested before the three components of the monitor system is assembled. The test of the calibration system and the analytical detection system are described in section 3 and 4. The total system has been documented in terms of measured sensitivity to external parameters and precision of the equipment. The total systems sensitivity to external parameters is described in Section 5. Measured accuracy of the gradient is estimated by experimentally determining the reproducibility and repeatability of results, where reproducibility is the standard deviation of measurement scatter due to the method and repeatability is the standard deviation of measurement scatter due to the equipment. The reproducibility of the measurement system is reported in Section 6 and 7. Different intercomparisons with various  $\text{NH}_3$  measurement methods are described.

## 2 The monitor system

### 2.1 The collection principles

For the diffusion denuder/scrubber technique to function, a series of criteria must be met (*Ali et al., 1989*):

- the gas flow must be stable and laminar,
- the viscosity and temperature distribution within the gas flow must be homogeneous,
- any axial diffusion of the sampled gas must be insignificant in comparison to the sample flow,
- the collection surface should behave as an infinitely large sink towards the analyte, and
- adsorbate species should be neither created nor destroyed in the gas phase within the sampling device.

These five criteria are described in more detail in the following subsections.

### *Stable and laminar flow*

Complete separation of gas and particles only occurs if the gas flow is laminar. To determine if flow is laminar, one may apply Reynold's number  $R$  defined as:

$$R = \frac{vd}{\nu}$$

Where  $v$  is the flow rate ( $\text{m s}^{-1}$ ),  $d$  is the internal diameter of the tube (m), and  $\nu$  is the viscosity (for air at  $20^\circ\text{C}$ :  $1.5 \cdot 10^{-5} \text{ m}^2 \text{ s}^{-1}$ ). While there is no strict limit between laminar and turbulent conditions, the general rule is that the flow will always be laminar if the Reynold's number is less than 580 (*Engelund and Pedersen, 1982*).

### *Viscosity and temperature distribution within the gas flow*

If the viscosity or the temperature exhibits gradients within the gas flow, turbulence may be produced. The diffusion scrubber system was designed with thermostatic control and we assume the temperature conditions are homogeneous.

### *Axial gas flow*

If the axial diffusion is relatively high the laminar flow will be disturbed and turbulence may be produced. The axial diffusion is assumed to be insignificant in comparison to the sample flow. Although this issue has not been investigated, it is not expected adversely to influence the measurements.

### *Collection surface*

The size of the collection surface should be maximized so the sink will not be saturated. If saturation of the scrubber liquid occurs, an upper measurement limit will be reached. We have found linear response up to 3 ppb and *Harrison and Msibi (1994)* has measured concentrations at 30 ppb. We therefore assume that the sink is infinitely large in relation to the  $\text{NH}_3$  concentration in the marine atmosphere.

### *Loss of the analyte*

If the system has gas in equilibrium with the aerosol, the removal of the gas-phase component will result in a loss of material from the aerosol to the gas phase, and after continued passage through a denuder it might result in excess deposition in later denuder sections (*Eatough et al., 1985*). From previous investigations (*Ferm, 1979*) the interference from particulate  $\text{NH}_4^+$  release is considered to be negligible. The adsorption of the analyte on surfaces which are not analyzed has to be minimized by using material which is inactive towards  $\text{NH}_3$ . It might be possible that the  $\text{NH}_3$  will react by gas-gas interaction to form particles or by hydration of the gas molecule to form  $\text{H}_2\text{O} \cdot \text{NH}_3$  clusters (*Eatough et al., 1985*). This has not been investigated, but is discussed further in Section 3.3 and 5.2.

## **2.2 Configuration of the monitor system**

### *Diffusion scrubber*

The diffusion scrubber consist of a 70 cm long tube (perfluoralkoxy (PFA)), 6 mm o.d., 1 mm wall. The PFA tube has a 60 cm long glass

jacket (i.d. 6 mm, o.d. 8 mm) in order to keep the PFA tube straight. A polypropylene membrane tube (Celgard X-20 400 micro porous membrane, 0.4 mm i.d., 0.03 mm wall, 0.065  $\mu\text{m}$  mean pore size, 40% surface porosity, Hoechst Celanese, Charlotte, North Carolina, USA) is centred within the PFA tube. Imbedded within the membrane tube is a nylon monofilament (0.26 mm o.d.). The air flow through the teflon tube is about 1.5 l  $\text{min}^{-1}$ . Construction of the diffusion scrubber is described in details in Section 2.3. The diffusion scrubber is shown in Figure 11.

### Analytical detection system

The diffusion scrubber and the analytical system is built into a temperature controlled box. The setup of the analytical system is shown in Figure 1. Before entering the membrane tube inside the diffusion scrubber, deionized water is cleaned for  $\text{NH}_3/\text{NH}_4^+$  by an ion exchange column (AG 50W-x4, Biorad Laboratories, Richmond CA, USA). The flowrate through the membrane tube is about 90  $\mu\text{l min}^{-1}$  and the liquid flows are carried by a peristaltic pump (U4-XV, Ventur Alitea AB, Uttran, Sweden). The water is stopped in the membrane for 10 minutes to collect ammonia. After the collection in the membrane, the sample is mixed with OPA (Sigma Chemical Co 10 mM) reagent (50  $\mu\text{l min}^{-1}$ ) in a mixing coil. The sulphite (sodium sulphite (p.a. Merck) 3 mM in phosphate buffer pH 11) reagent (50  $\mu\text{l min}^{-1}$ ) is then added before passing a heating coil. The reaction takes place in an electrical heating coil (90°C, i.d. 0.5 mm, length 1 m, stainless steel, Mikrolab, Aarhus, Denmark).

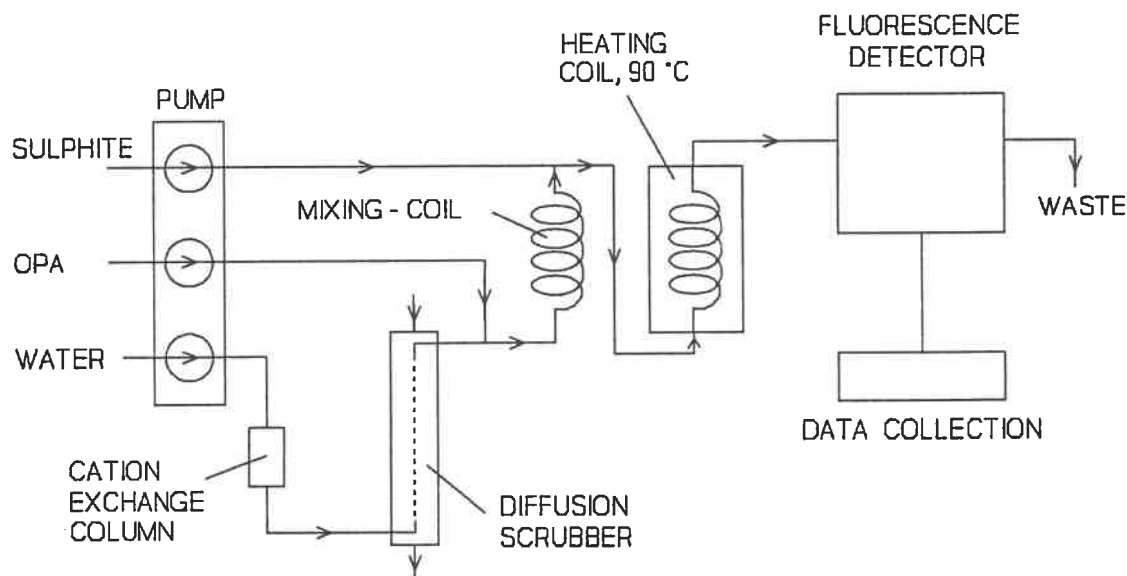


Figure 1. The analytical system.

The detection of the fluorescence compound from the reaction of OPA, sulphite and  $\text{NH}_3$  is performed on a fluorescence detector (fluoroMonitor™ III Filter Fluorometric Detector, LDC Analytical, Riviera Beach FL) with a 30  $\mu\text{l}$  flow cell. The wavelength of the excitation filter is 340-380 nm, and of the emission filter 418-700 nm. The chemical reaction is shown in Figure 2.

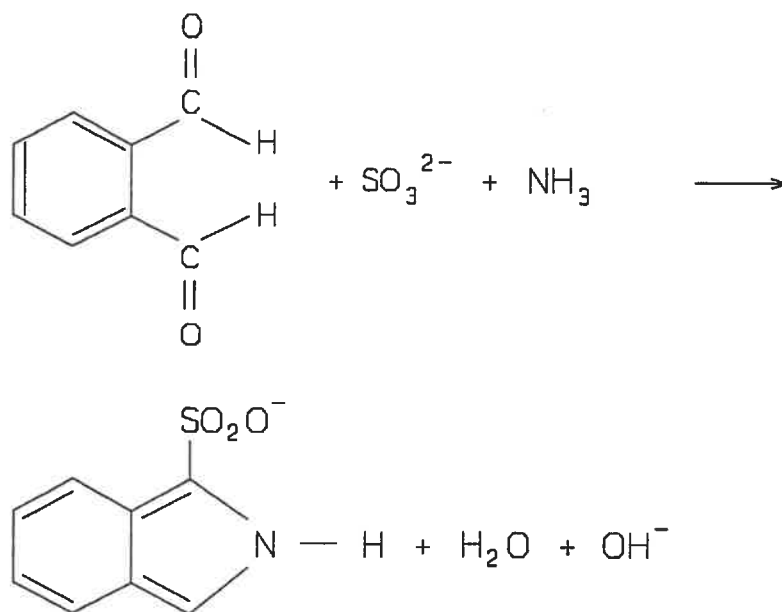


Figure 2. The reaction of OPA, sulphite and ammonia.

#### Gas calibration

To calibrate the system 30 ppm gaseous ammonia diluted to 0.1 ppb is used. The gas calibration system is shown in Figure 3. The dilution flows are controlled by mass flow controllers (5850TR/C1-C1C1D1, Brooks Instrument B.V., Veenendaal, The Netherlands). The flow from the cylinder holding the ammonia is controlled by a mass flow controller which gives up to 10  $\text{ml min}^{-1}$  (MF1). The gas is diluted with zero air from three other mass flow controllers (100  $\text{ml min}^{-1}$ , 2.5  $\text{l min}^{-1}$  (MF3) and 20  $\text{l min}^{-1}$ ).

The zero air is made by cleaning compressed air in a compressed air dryer (AD) (PS 1.0 MS, Novenco Anderberg A/S, Slagelse, Denmark). The dryer is a molecular sieve and adsorbs water and some gases like ammonia from the air. The process is accomplished using a compressed air filter (Model A, Walker Filtration, Washington DC, USA) placed in front of the air dryer to remove particles and oil from the compressor. After passing the air dryer, the zero gas is split into three different flows: two to mix with the calibration gas and one to clean the diffusion scrubber. The  $\text{NH}_3$  gas flow and the zero air flow to the box is controlled by nozzles (N1, N2). The nozzles dilute the calibration concentration 10 times.

The mass flow controllers in the calibration system work at a certain pressure and there are a pressure drop over the flow controller. The flow through the nozzles also depends on the air pressure. Because of this the air pressure has to be well known and stable. To get stable and well known pressures two precision regulators (PR1, PR2) and two back pressure regulator (BP1, BP2) (GH30 series, CONOFLOW regulators & controls, St. George, S.C., USA) are used.

The calibration gas is humidified by humidification of the zero air before the last dilution step, which takes place inside the diffusion scrubber box. The zero air is humidified by the use of two water bubblers (W1, W2). The gas is blown over the surface in the bubblers.

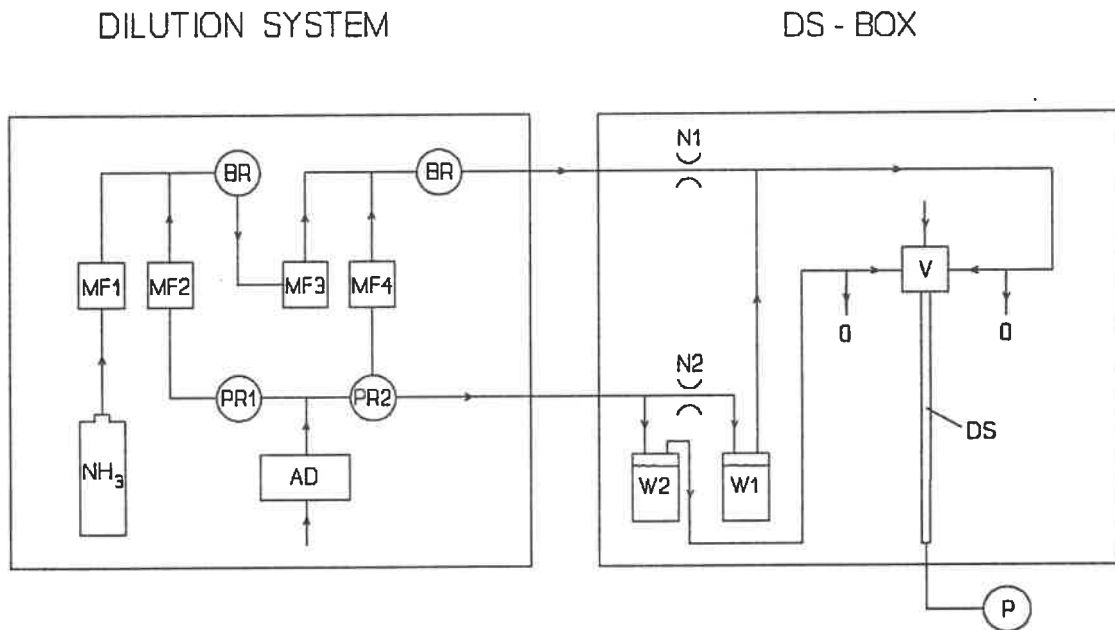


Figure 3. The calibration system and the diffusion scrubber system. MF1-MF4: Mass flow controllers, PR1-PR2: Precision regulators, BR: Back pressure regulators, AD: Air dryer, V: Valve, DS: Difusion scrubber, W1-W2: water bubblers, N1-N2: Nozzles, P: Pump.

The tubes used for the gasflows are Dekabon manufactured by Dekoron, Type 1300, Dekabon, Metal/Plastic, EATON, Industrial Polymer Products Division, Aurora, Ohio, USA. The Dekabon tube

is an aluminum tube with a high density polyethylene jacket and an inner ethylene copolymer coating. To have a straight inlet from the sample air to the diffusion scrubber a ball plug PTFE valve (V) is used (AVS-DANMARK A/S, Hedehusene, Denmark).

*Controlling the sample time duration*

The whole system is run automatically by a programmable controller (PLC) (IDEC IZUMI CORPORATION, Osaka, Japan). The ball valve and the pump are connected to the PLC. The PLC is programmed so the liquid flow is stopped for 10 minutes and injected for 10 minutes. The valve runs calibration, sample or zero gas loads for 10 minutes and zero gas during the 10 minutes of injection. The schedule for injections and loads is shown in Figure 4.

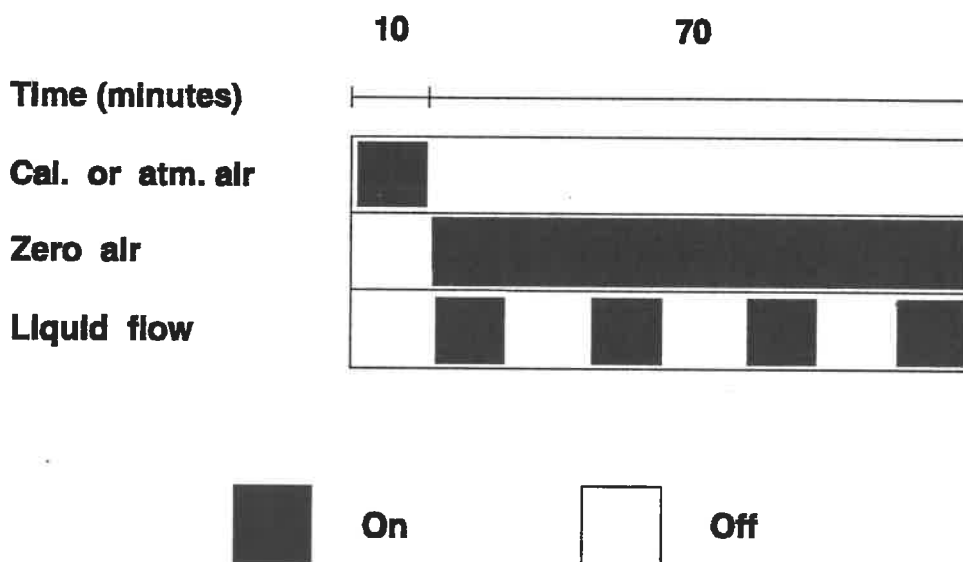


Figure 4. Time cycle for load of calibration gas, zero air and atmospheric air. The cycle also shows when the liquid in the membrane tube is stopped or flows.

### 2.3 Constructing a diffusion scrubber

The tube is made of a 60 cm long glass tube with i.d. 6 mm, o.d. 8 mm. At a distance of 5 cm from the ends of the tube and on opposite sides of the cylinder 2 holes, 1.5 mm d. are drilled. 70 cm of teflon (perfluoralkoxy (PFA) teflon) tube 6 mm o.d., 1 mm wall is drawn through the glass tube until 5 cm of PFA tube is protruding from the ends. With a needle (1 mm d.) two holes are perforated through the PFA tube at the same position as the holes in the glass jacket. A piece of silicone tube is put around the PFA tube in both ends and into the glass tube to make sure the holes will keep their positions (Figure 5).



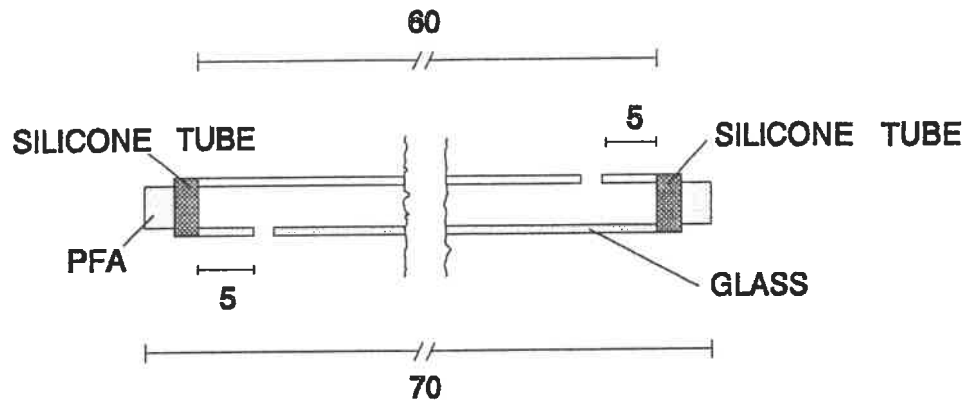


Figure 5. The PFA tube is kept in the glass tube by two pieces of silicone tubes.

A 90 cm long nylon monofilament 0.26 mm o.d. is inserted in a 70 cm long polypropylene membrane. In both ends of the membrane 10 cm of the nylon string is protruding. In one of the holes in the glass/PFA tube a nylon loop is inserted and the membrane with the nylon is inserted in the PFA tube through one of the holes. The membrane is pushed through the tube until the end of the membrane is protruding from the end of the tube. The membrane should go through the nylon loop (Figure 6).

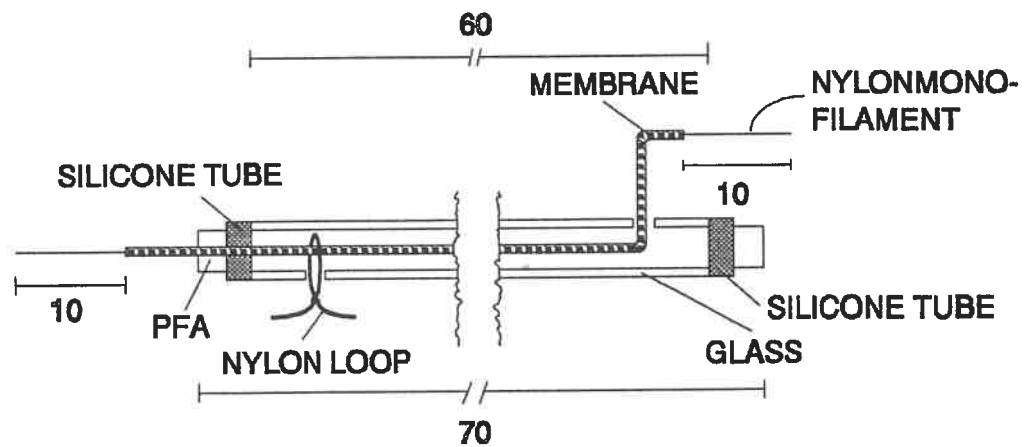


Figure 6. The glass/PFA tube with the membrane and the nylon loop.

The membrane is drawn out through the hole in the tube using the loop. About 10 cm of the membrane and 20 cm of the nylon filament is protruding from the holes in the tube. Now the membrane is

drawn in such that 2 cm of it protrudes from the hole in the other in (Figure 7).

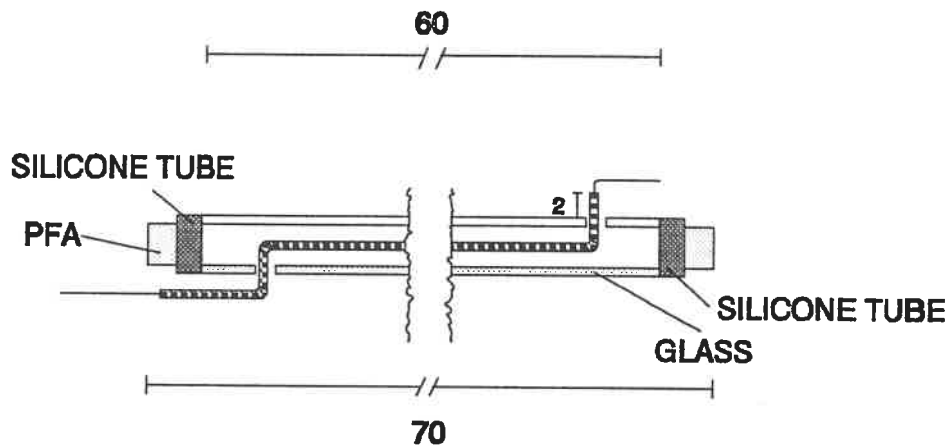


Figure 7. The membrane is placed in the tube.

The longest end of the membrane is inserted in a 18 cm long PVC tube i.d. 0.45 mm (from a wire) until 1.5 cm of the nylon filament is protruding from the end. 0.5 cm downwards from the PVC tube a small amount of cyanoacrylate glue is put onto the membrane (extract of the cyanoacrylate glue did not show elevated ammonia concentrations compared to blanks) (Figure 8).

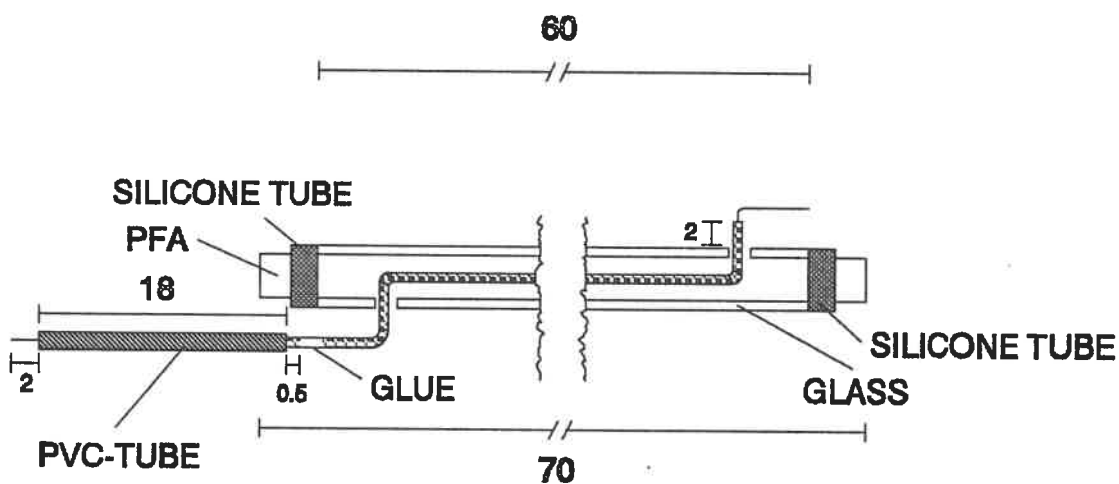


Figure 8. The PVC tube is going to be secured to the membrane.

The PVC tube is now pushed (carefully) downwards until it sticks to the membrane. It should be checked that the glue is dry, then the membrane and PVC tube are now pulled into the tube until 20 cm

of the membrane is protruding from the other hole in the tube (Figure 9).

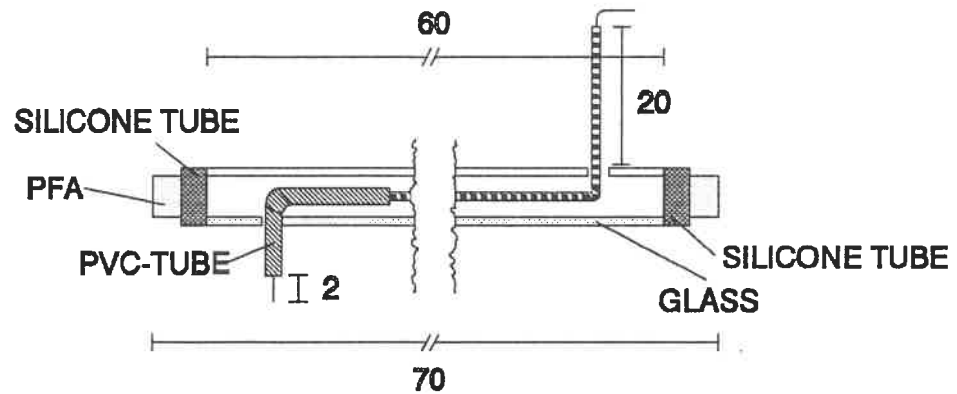


Figure 9. The membrane and the PVC tube is placed in the tube.

The membrane end is inserted in another PVC tube (18 cm, i.d. 0.45 mm). The PVC tube is pushed down until 1.5 cm of the nylon filament is protruding from the end of the PVC tube. 0.5 cm downwards from the PVC tube, a small amount of glue is put on to the membrane. Again the PVC tube is pushed downwards until it sticks to the membrane (Figure 10).

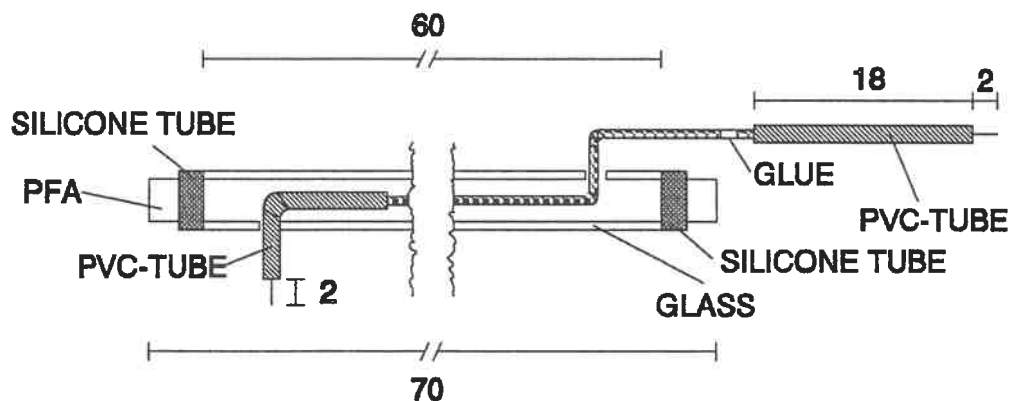


Figure 10. The other end of the membrane is inserted to a PVC tube.

Now the membrane is carefully pulled so the 13 cm of the PVC tubes protrude from both ends, and the membrane is now axial and horizontally centred in the scrubber tube. The PVC tubes are secured with tape and glued with silicone rubber adhesive (Figure

11). The diffusion scrubber has to dry for about 12 hours and will then be ready to use. Making one diffusion scrubber takes 15 minutes for an experienced person.

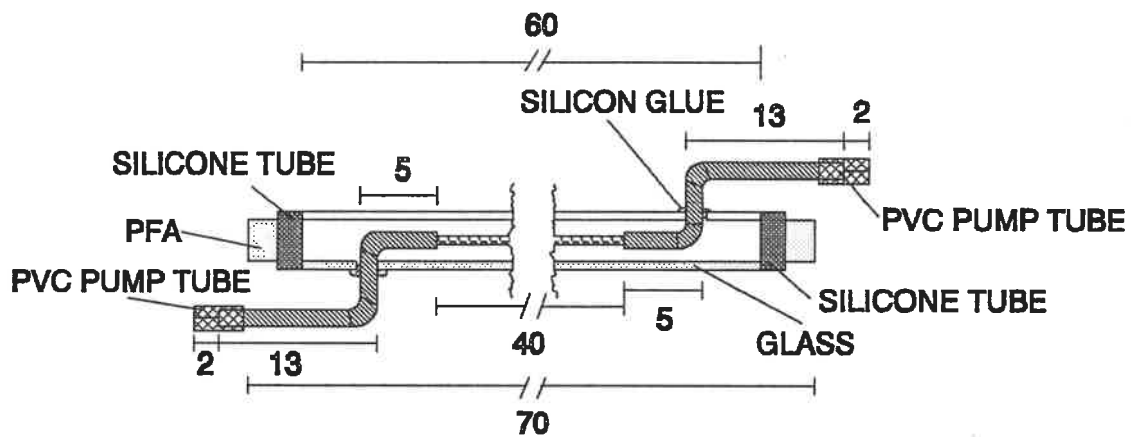


Figure 11. The final diffusion scrubber.

### **3 Test of and conditions in the gas calibration system**

The  $\text{NH}_3$  concentration of the calibration gas has to be well known, stable, and exhibit a relatively fast response to step-changes in calibration concentrations in order to change the calibration gas when the sample gas concentration level changes. Physical parameters such as temperature, pressure and relative humidity must be the same for the calibration gas as for the sample gas to compare the responses from the two gasses; this is discussed further in Section 5. The accuracy of the calibration concentration depends on the precision of the dilution and on the accuracy of the concentration of the cylinder gas.

#### **3.1 Dilution of the calibration gas**

A very accurate dilution system is chosen to make small and accurate dilutions of the gas flow. The system makes it possible to change the calibration concentrations by changing the dilution flows.

The dilution system consists of four mass flow controllers and one nozzle. The precision and linearity of the mass flow controllers and the precision of the nozzles are measured.

In order to change the calibration concentrations the flows of the mass flow controllers must be well known. Each mass flow controller was measured at 20 different flow settings. The linearity of the flow changes is shown in Figure 12. The relative standard deviation of the mass flow controllers is measured to be 1% at the limits of the flows and otherwise 0.1-0.4%. Each flow setting was measured six times in order to estimate the standard deviation.

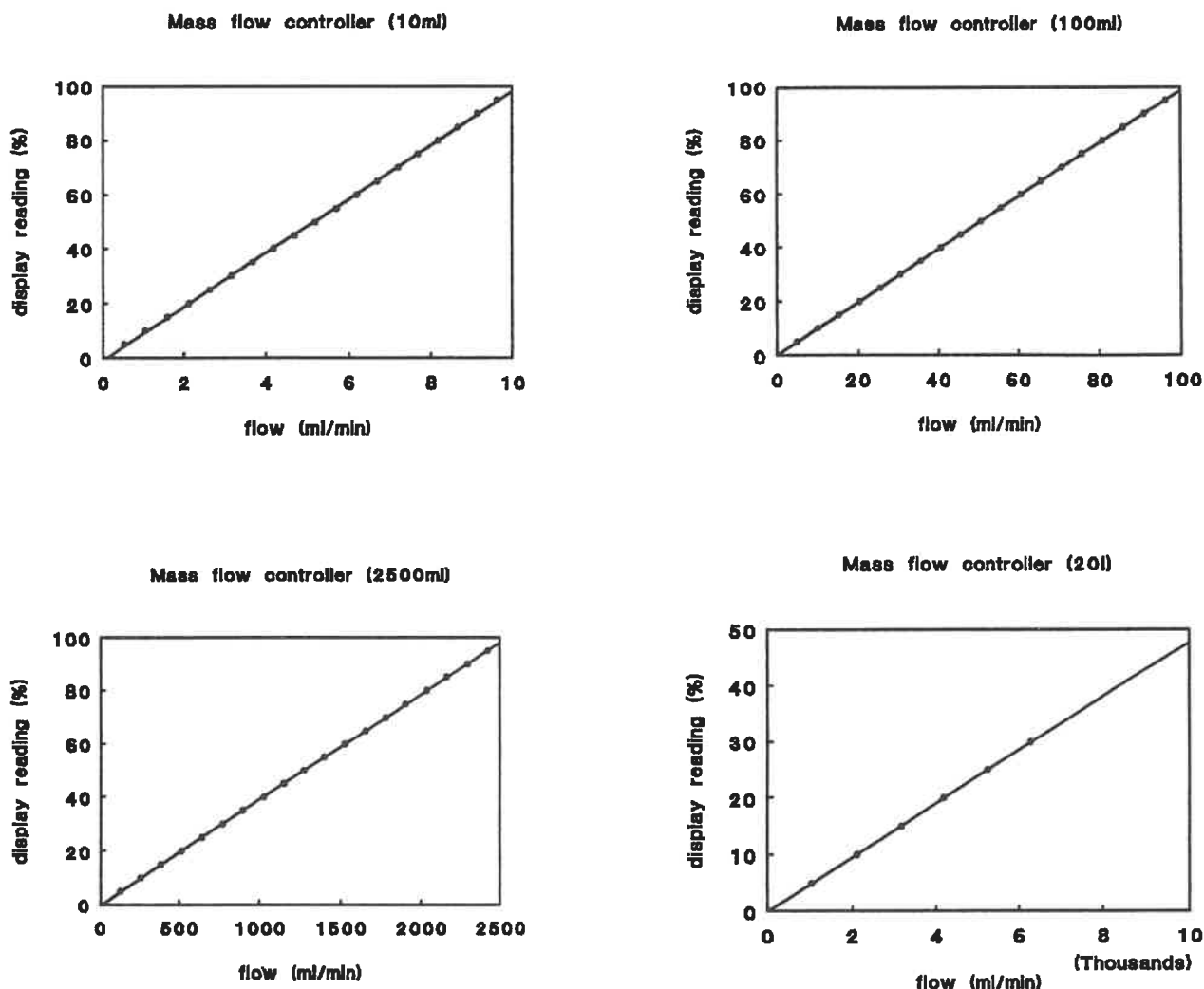


Figure 12. Calibration curves for the four mass flow controllers. The setting of the mass flow controllers is plotted against results from flow measurements

The last dilution step using nozzles must also be accurate and stable. Since the flow through the nozzle depends on pressure, the pressure must be stabilized by a precision regulator. Flows through the nozzles are measured and the relative standard deviation of the flow rate never exceeds 0.5%. The dilution by the nozzle is 1:10. The flows in the system are measured before each sampling period, at least one time during the period, and again at the end of the period.

### 3.2 Stability of the calibration concentration

The stability of the ammonia concentrations depends not only on the stability of the concentration of  $\text{NH}_3$  in the gas cylinder but also on the material which is used for tubes massflow controllers and surfaces, which the gas is in contact with. If the material is porous,  $\text{NH}_3$  from the environment will diffuse into the system which may result in a high and fluctuating background. It is also possible for

the material to absorb or adsorb ammonia. These conditions will cause a long period for the system to get into equilibrium with an  $\text{NH}_3$  concentration.

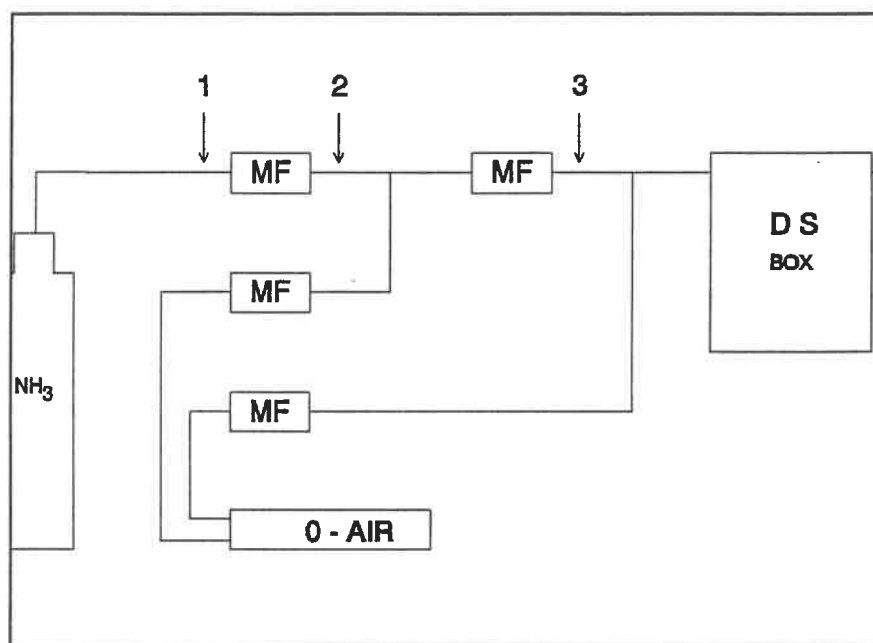


Figure 13. Measurement points (1,2,3, and 4) for control of the  $\text{NH}_3$  concentration, MF; mass flow controllers, DS box; diffusion scrubber box.

*Measured  $\text{NH}_3$  concentration in the calibration system*

The  $\text{NH}_3$  concentration in the gas cylinder was measured in order to determine the exact concentration before dilution. The methods used were based on collecting the gas in 0.1M oxalic acid solution in three impingers in a row and sampling by diffusion denuders coated with oxalic acid. The  $\text{NH}_3$  concentrations in the dilution system have been measured at points between the mass flow controllers and in the overflow from the diffusion scrubber. The sampling points are shown in Figure 13. The results can be seen in Table 1. The sampling show no loss of  $\text{NH}_3$  in the calibration system, but the denuder sampling in January 1993 shows higher measured  $\text{NH}_3$  concentrations than expected. This may be explained by a contamination from a high  $\text{NH}_3$  background.

*Table 1.* Measured concentrations of NH<sub>3</sub> in the calibration system using denuders or impingers. The concentrations are measured at the points; 1, 2, 3 and 4 shown in Figure 13.

Date of measurement	Sampling device	Collection efficiency (%) of the sampling device	Sampling point (ref.to Fig.13)	Measured concentration of the calibration gas	Expected concentration of the calibration gas
Jan. 93	denuder (n=2)	94.3 ± 4.6	4	0.55 µg N m <sup>3</sup> ± 0.07	0.46 µg N m <sup>3</sup>
Jan. 93	denuder (n=2)	83.85 ± 14.9	4	0.27 µg N m <sup>3</sup> ± 0.01	0.11 µg N m <sup>3</sup>
Mar. 93	denuder (n=3)	95.8 ± 6.5	4	1.3 µg N m <sup>3</sup> ± 0.3	1.39 µg N m <sup>3</sup>
Oct. 92	bubbler (n=2)	100	1	20.25 mg N m <sup>3</sup> ± 2.4	21.43 mg N m <sup>3</sup>
Oct. 92	bubbler (n=2)	100	3	23.26 mg N m <sup>3</sup> ± 2.19	21.43 mg N m <sup>3</sup>
Feb. 92	denuder (n=3)		4	1.05 µg N m <sup>3</sup> ± 0.16	1,21 µg N m <sup>3</sup>
Feb. 92	denuder (n=3)		4	1.3 µg N m <sup>3</sup> ± 0.05	1.2 µg N m <sup>3</sup>
Feb. 92	denuder (n=3)		4	0.98 µg N m <sup>3</sup> ± 0.14	1.2 µg N m <sup>3</sup>
Feb. 92	denuder (n=3)		4	0.93 µg N m <sup>3</sup> ± 0.12	1.2 µg N m <sup>3</sup>
Feb. 92	denuder (n=3)		4	1,21 µg N m <sup>3</sup> ± 0.11	1.2 µg N m <sup>3</sup>
Feb. 92	bubbler (n=3)	100	3	28.29 µg N m <sup>3</sup> ± 0.5	29.39 µg N m <sup>3</sup>

### 3.3 Relative humidity of the calibration gas

Humidifying the calibration gas introduces the question whether the concentration of the NH<sub>3</sub> gas will remain unchanged. When the zero gas is humidified there will be water molecules present in the gas. Theoretically these H<sub>2</sub>O molecules and the NH<sub>3</sub> molecules will combine with a hydrogen bond. This means the diffusion coefficient for ammonia/water clusters will differ from the coefficients for ammonia (Genfa *et al.*, 1989; Eatough *et al.*, 1985). However experiments estimating diffusion coefficients at various relative humidities showed no difference in diffusion coefficients (Spiller, 1989).

The humidification has to take place in the zero gas before the last dilution step. It is not possible to humidify the final calibration gas because the ammonia then will be trapped in the humidification system.



## 4 Conditions in the analytical detection system

The fluorescence signal is influenced by the following reaction parameters:

- concentration of  $\text{NH}_3$ ,
- concentration of OPA,
- concentration of sulphite,
- pH of the reaction (pH of the sulphite/buffer solution),
- reaction temperature,
- reaction time (the length of the reaction coil).
- concentration of interferant species (amines).

We have not made specific tests of the analytical detection system because it is already well documented by other authors. Some of the tests which have been performed is summarized in this section.

### *Test of the analytical system*

*Genfa and Dasgupta (1989)* showed that the highest fluorescence system response is produced at pH 11.0, reaction temperature 85°C, OPA concentration 10 mM, and sulphite concentration 3.0 mM.

The detection of the reaction product is influenced by excitation/emission conditions. *Genfa and Dasgupta (1989)* found the maximum emission and excitation wavelength to be 425 nm and 365 nm respectively. The signal is also influenced by dispersion of the sample in the system.

The dispersion of the sample in the analytical system, can be minimized by optimizing the dimensions of the flow injection analysis (FIA) system, inclusive knotted mixing coils and connections. *Jeppesen and Hansen (1991)* showed that the length of the reaction coil did not have a significant influence compared to the influence of pH, temperature and OPA concentration. In an optimized flow system the selectivity for  $\text{NH}_3$  is good and the interference from amines is small (*Jeppesen and Hansen, 1991*).

The product of OPA and sulphite is not stable (*Jeppesen and Hansen, 1991*). Sulphite adds to most aldehydes to form a bisulphite addition product (*Morrison and Boyd, 1973*). Therefore OPA is carried to reaction with  $\text{NH}_3$  in a mixing coil before sulphite is added.

## 5 Influence of sampling conditions on the performace

The diffusion scrubber system has been tested to see how various parameters influence the sampling and analysis of the  $\text{NH}_3$ .

### 5.1 Collection efficiency

Collection of  $\text{NH}_3$  is not 100% effective in a diffusion scrubber. The collection efficiency will depend on the length of the membrane, atmospheric pressure, temperature and relative humidity (*Genfa et al., 1989; Dasgupta and Lindgren, 1989*). Decrease in efficiency is suggested to be due to deposition of particulate matter on the membrane (*Simon et al., 1991*), but investigations (*Genfa et al., 1991*) have shown that deposition of particles in the diffusion scrubber is small. Due to the collection efficiency dependence on varying parameters the efficiency is difficult to predict and therefore it is important to calibrate often.

### 5.2 Linearity

The concentration of  $\text{NH}_3$  in the atmosphere can be estimated by comparing the detected signal with a calibration curve. It is difficult to generate a calibration curve for the diffusion scrubber system because the collection efficiency is not constant due to change in temperature, atmospheric pressure and relative humidity. The sensitivity of the analysis decreases in time due to oxidation of the sulphite. This will also cause a change in the detected signal.

#### *Measurements of calibration curves*

Calibration curves have been made by adding calibration gases to three different monitor systems. Each concentration was added for 2 days. All systems were placed under the conditions in which they are normally to be used. This means the temperature has not been stable because of heating from the sun over a diurnal cycle and the background concentration correspondingly changes.

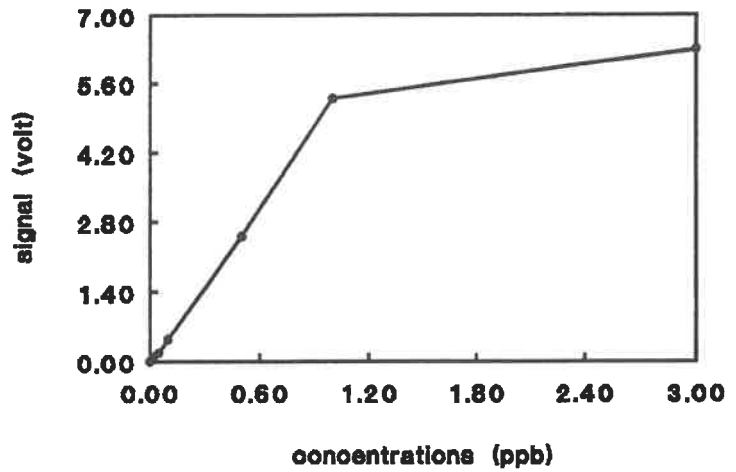


Figure 14. Calibration curve for the diffusion scrubber. The measurements has been carried out over more than one week. The bend is due to a decrease in the collection efficiency with time.

Figure 14 shows the decrease in collection efficiency and sensitivity between 1 ppb and 3 ppb. At this point the diffusion scrubber has been sampling for more than one week. It was not possible to change the scrubber during the run because a new scrubber would have a different collection efficiency. The first week of sampling shows that the system exhibits a linear response over the range of 0.02 ppb to 1 ppb. Other measurements shows linearity between 0.5 ppb and 3 ppb. The linearity can be seen in Figure 15. The scatter at each point is due to change in temperature and decrease in collection efficiency, and decrease in the sensitivity of the analysis.

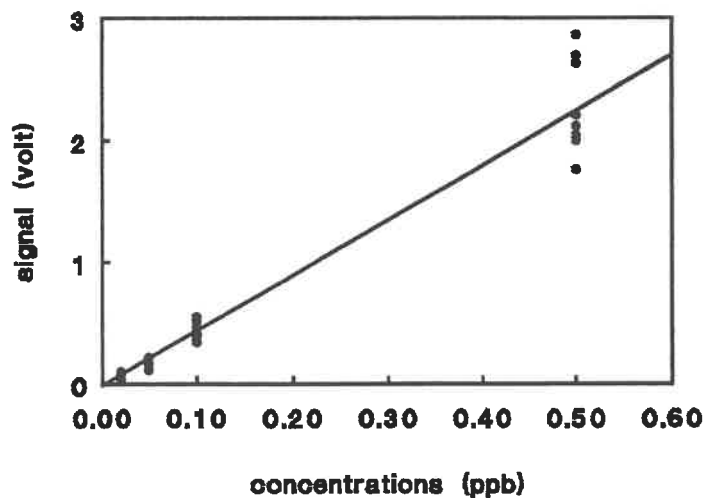


Figure 15. Calibration curve. The system has been loaded with 4 different calibration concentrations (0.02, 0.05, 0.1 and 0.5ppbv) for 1 day each.

Because of the change in collection efficiency and sensitivity, calibration gas is added every 3 hours. The calibration concentration used is attempted to be at the same concentration level as the sample air.

### 5.3 Temperature

*Change in response with changing temperature*

As mentioned the sampling efficiency of the diffusion scrubber is influenced by temperature (Genfa et al., 1989). The fluorescence response increases with increasing temperature in the diffusion scrubber box. The temperature in the diffusion scrubber box is measured, while a constant concentration of calibration gas is sampled. It is clearly seen from Figure 16, that the signal closely tracks changes in temperature. The relative humidity was not controlled during the experiment but varied between 60% and 90%. This will also effect the signal. Change in relative humidity will change the conditions and then the ratio of concentration to temperature will change. This might explain the change in the response/temperature ratio in Figure 16.

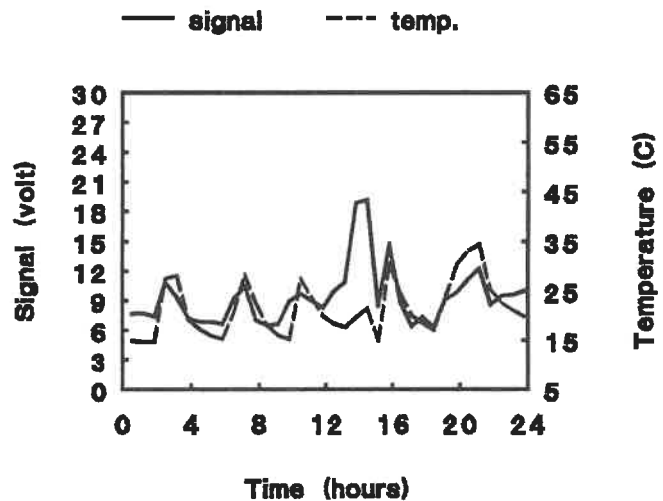


Figure 16. Temperature is measured in the sampling device during sampling. The fluorescence signal from the sample and the temperature is shown.

*Discussion of temperature dependency*

At increasing temperatures the membrane pores may be more open, which will cause a higher sampling efficiency and therefore a higher response. The increase in signal at increasing temperature can also be due to evaporation of water from the membrane tube which leads to an increase in  $\text{NH}_3$  concentration. Furthermore an increase in the temperature will cause a higher diffusivity, which will be even higher if the temperature increase cause dissociation of

hydrated  $\text{NH}_3$ . Collection of the component will then be more effective. Evaporation will cause diffusion of water vapour away from the membrane (Genfa et al., 1989). This may inhibit diffusion of gas towards the membrane. Therefore a decrease in sampling efficiency and in signal would be expected at higher relative humidities.

## 5.4 Relative humidity

*Change in response with changing relative humidity*

The fluorescence response from two calibration concentrations at different relative humidity was measured. The results are shown in Figure 17 and Figure 18.

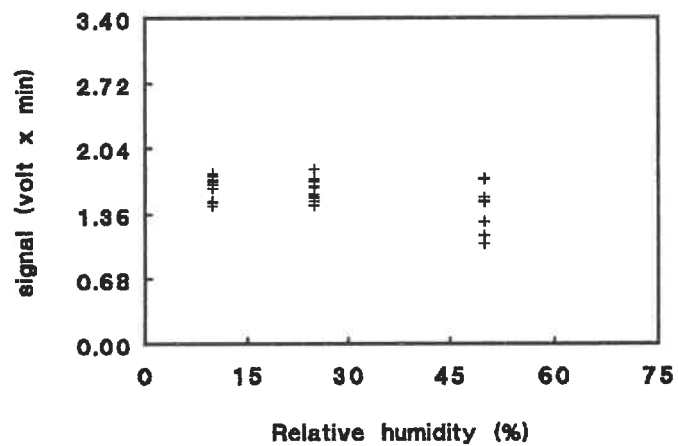


Figure 17. The fluorescence signal from calibration gas at 0.5 ppbv concentration at three different relative humidities (10, 25 and 50%)

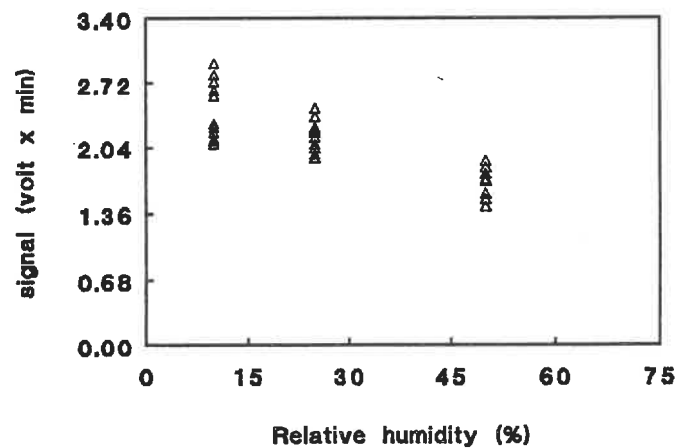


Figure 18. The fluorescence signal from calibration gas at 2 ppbv concentration at three different relative humidities (10, 25 and 50%)

The response seems to decrease with increasing relative humidity. This was also found by *Genfa et al. (1989)*. This can be caused by less evaporation of water from the membrane at higher relative humidity. Another explanation is, that  $\text{NH}_3$  will be hydrated and then have lower diffusion coefficient as suggested in Section 3.3 (*Genfa et al., 1989; Eatough et al., 1985*).

*Evaporation of sample liquid*

The water in the scrubber membrane will evaporate during "stopped flow". The amount of evaporated water from the membrane will be a function of temperature, relative humidity, and length of time in which the flow is stopped.

The water loss from the membrane was determined by adding sodium chloride (NaCl) to the scrubber liquid and collecting the scrubber liquid from the outlet of the diffusion scrubber for 2 minutes. The evaporation from the membrane during collection will cause an increase of the concentration of NaCl. The samples were collected after 20 minutes of "stopped flow" and after continuous flow at relative humidities of 20, 40 and 60 % (temperature 296 K). The water losses were determined from the chloride concentrations which were measured by ion chromatography. The results are shown in Table 2.

Table 2. Water losses from the membrane during sampling (296 K)

	Continuous flow	Flow stop for 20 min.
20 % RH	9 $\mu\text{l}$	57 $\mu\text{l}$
40 % RH	4 $\mu\text{l}$	46 $\mu\text{l}$
60 % RH	3 $\mu\text{l}$	33 $\mu\text{l}$

The accuracy of the results measured with continuous flow is limited because the results are calculated as the differences between two large figures. The water losses from the membrane during the 20 minutes "stopped flow" are high. The water loss caused by evaporation will vary so the water losses of 30-60  $\mu\text{l}$  at relative humidities of 60-20% may give an unsteady response (reduced repeatability), therefore the "stopped flow" period was set to 10 min. This is assumed to reduce the water losses by a factor of 2, i.e. 15-30  $\mu\text{l}$ , at relative humidities of 60-20% (296 K).

*Discussion of dependency of the relative humidity*

The membrane in the diffusion scrubber is not a closed system, so the evaporated liquid will be replaced in the membrane with liquid from the connected tubes.

The loss of water is small compared to the total liquid system due to mixing of the sample carrier liquid with the reagents (reagents flow are 100  $\mu\text{l min}^{-1}$ , sample flow is 90  $\mu\text{l min}^{-1}$ ). At RH 25% there is 4% less sample liquid, due to evaporation, than at RH 50%.

The change in fluorescence response from 50% RH to 25% RH is 30% at concentration 2 ppb (Figure 17) and 14% at concentration 0.5

ppb (Figure 18). The higher measured difference in fluorescence response could be explained by the formation of  $\text{NH}_3 \cdot \text{H}_2\text{O}$  clusters. Further investigations of dependency of relative humidity has to be carried out.

## 5.5 Blanks

Zero air sampled with stopped water flow gives a background signal. This signal can be caused by various conditions: residual  $\text{NH}_3$  concentration in the analytical system (the water is difficult to purify 100%) and/or in the zero air (the zero gas is difficult to purify 100%); and/or carry over from the previous injection of calibration gas or atmospheric air. These conditions were investigated and are described in the following subsection.

### *$\text{NH}_3$ in the analytical system*

To investigate the conditions responsible for the background concentration of  $\text{NH}_3$  derived from the analytical system (the water and the reagents), we conducted an experiment with three diffusion scrubber systems which were run simultaneously. The first system measured the atmospheric concentrations as a control during the test (DS1). The second system was loaded with zero gas, in the following referred to as DS2. The diffusion scrubber in the third system, referred to as DS3, was plugged in both ends so air could not diffuse into it.

The DS2 system loaded with zero gas showed small detector responses and the DS3 system, which was not loaded with gas, also showed small response peaks. This indicates  $\text{NH}_3$  in both the analytical liquid systems. We also found the response from both systems (DS2 and DS3) to decrease with time. After 24 hours the diffusion scrubber in the DS2 system was plugged and the diffusion scrubber in the DS3 system was now unplugged, and the DS3 system was loaded with zero gas. The detector responses were low for systems DS2 and DS3, and the signals decreased with time until a constant level was reached. The change of signals with time for DS3 and DS2 is shown in Figure 19.

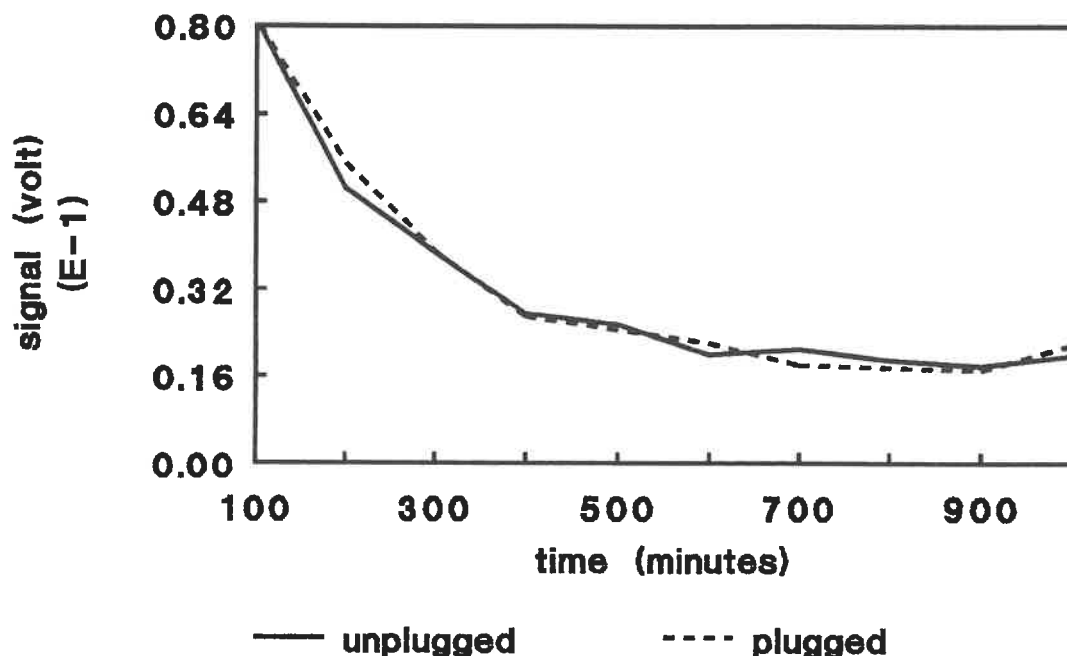


Figure 19. Background signals from a plugged and an unplugged diffusion scrubber.

The decrease in signals is due to change in temperature and decrease in residual  $\text{NH}_3$  in the systems. Since the response signals for the plugged and unplugged systems have the same magnitude and behaviour, it seems likely that the background concentration detected is the result of  $\text{NH}_3$  in the analytical system. The contribution from the background concentration is assumed to be the same for the calibration gas sample as for the atmospheric air sample.

## 5.6 Carryover

### *Carryover after calibration gas sample*

Figure 21 shows the fluorescence signals after sampling atmospheric air, zero gas and calibration gas. The peaks 2, 12 and 21 are calibration gas and the small peaks in between are zero gas. After loading a calibration gas, a memory effect or carryover was observed in the following zero gas response. To investigate this carryover three systems were set up to do parallel simultaneous sampling. The first system was loaded with gases using the following cycle: calibration gas for 10 minutes and then three times zero gases each for 10 minutes. The two other systems were loaded for 10 minutes with calibration gas holding the same concentration and then zero gas was loaded for 24 hours.

The carryover after the calibration gas is small. We found carryover after different calibration concentrations to be less than 10%. It is also found that a higher concentration generally



corresponds to less relative carryover. When the background (zero signal) is high variation in zero responses makes the carryover becomes undetectable. The carryover is not detectable on the third zero gas response, which means the system is cleaned after three zero gas samples.

Carryover is most likely due to the adsorption of  $\text{NH}_3$  or  $\text{NH}_4^+$  in the teflon valves. The conclusion is supported by previous tests (Williams *et al.*, 1992) which showed uptake of  $\text{NH}_3$  in teflon. The valve should therefore be made from stainless steel or PFA.

*Carryover after atmospheric sample*

After loading with atmospheric air, the carryover is larger than for the calibration gas and is very unstable. A typical value of carryover is 25% at 5 ppbv. Very high concentrations will give a considerable contribution to the following sample because the three zero gas injections are not able to "clean" the system. We speculate that the higher carryover for atmospheric gas might be due to particle deposition in the DS or the inlet valve.

Sampling at lower sampling time has shown relative less carryover, so to minimize the carryover effect the sampling time should be lower. It is possible to sample only for 1-5 minutes at relatively high concentrations.

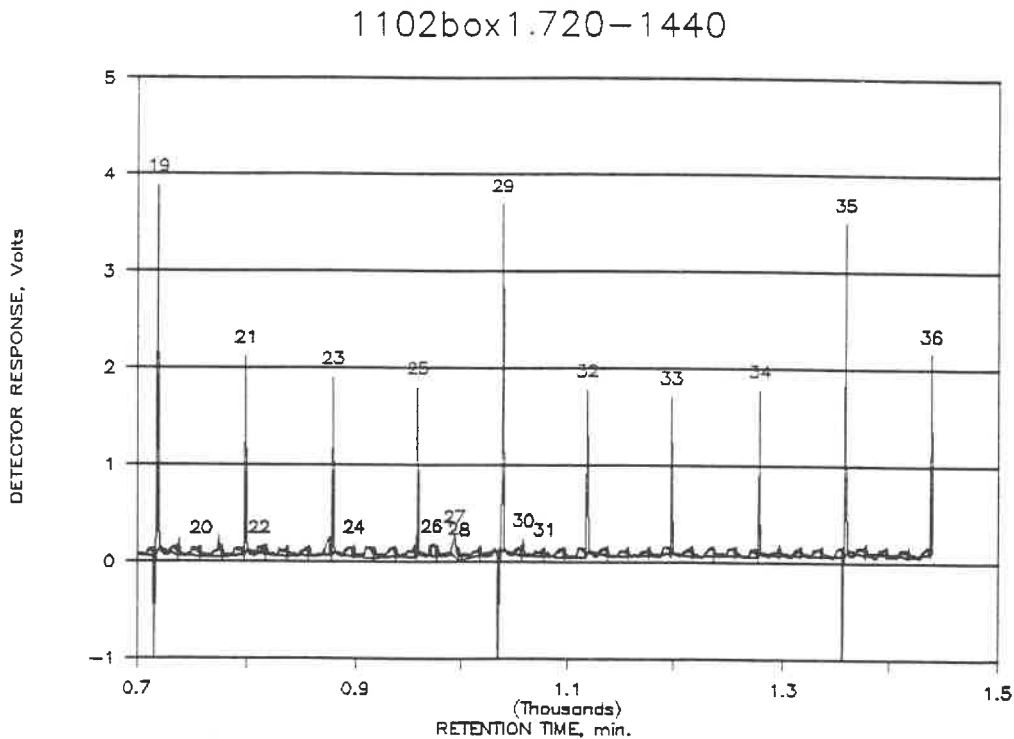


Figure 20. Signals from sampling with a diffusion scrubber having a filter in the inlet. The peaks 19, 29 and 35 are calibration gas; the peaks 21, 23, 25, 32, 33, 34 and 36 are atmospheric air, and the small peaks are zero air.

*Carryover caused by particles*

Figure 20 shows the signals from sampling with a diffusion scrubber having a filter in the inlet to avoid the interference from particles. The peaks 19, 29 and 35 is calibration gas sampling. The zero gas peaks (blanks) are very small and no carryover can be observed.

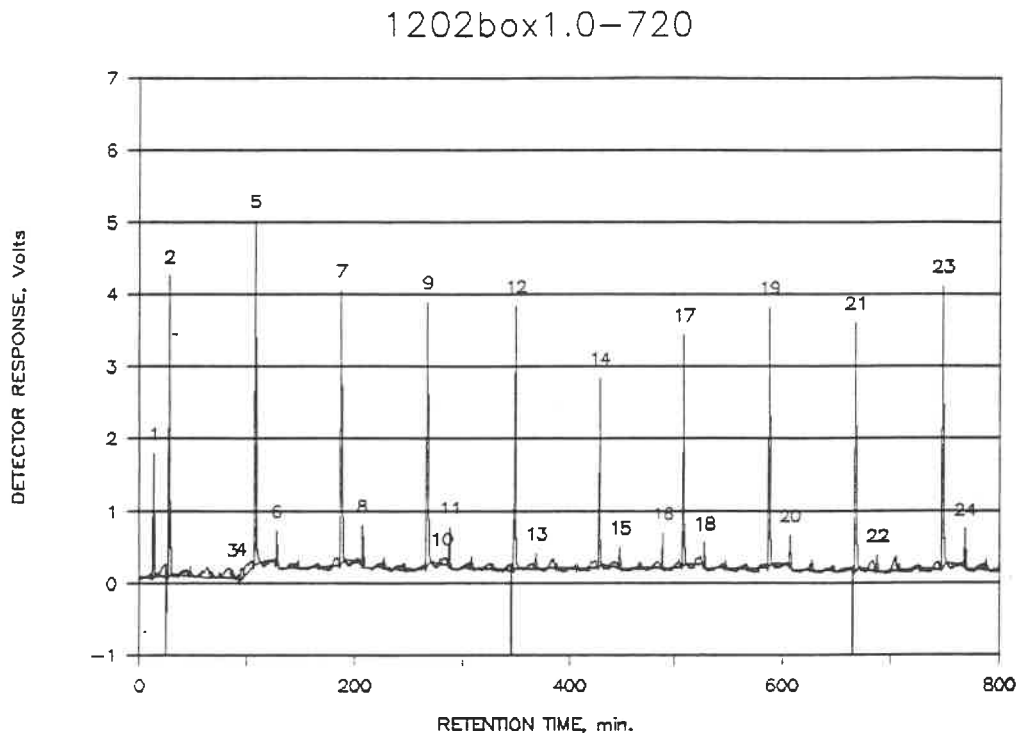


Figure 21. Signals from sampling with a diffusion scrubber. The peaks 2, 12 and 21 are the calibration gas; the peaks 5, 7, 9, 14, 17, 19, and 23 are atmospheric air, and the small peak, (i.e. 6, 8, 11 and 13) are zero air.

On Figure 21 the filter was removed from the inlet and it is clear that there is a much higher zero gas peak right after the atmospheric air sample. This leads to the conclusion, that particles deposited in the inlet valve is the source of the carryover.

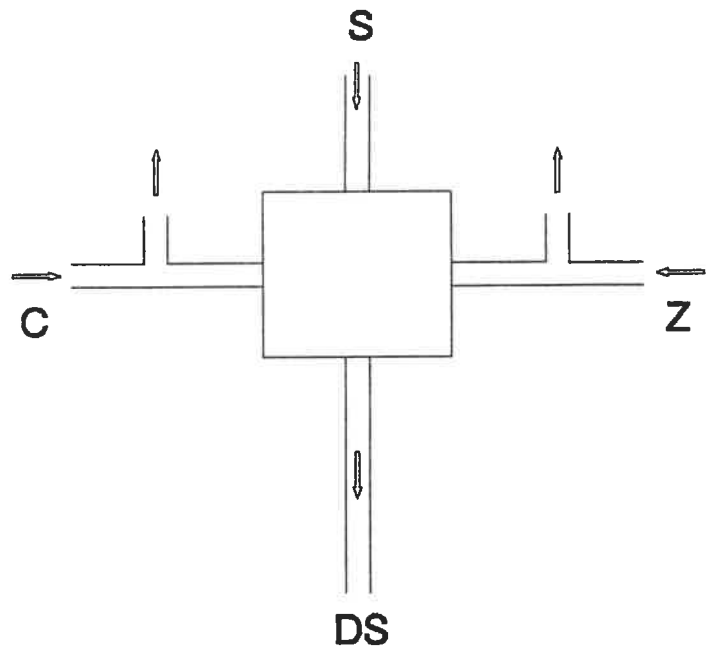


Figure 22. Inlet konfiguration with PTFE valve, S = sample air, C = calibrationgas, Z = zerogas, DS = diffusion scrubber

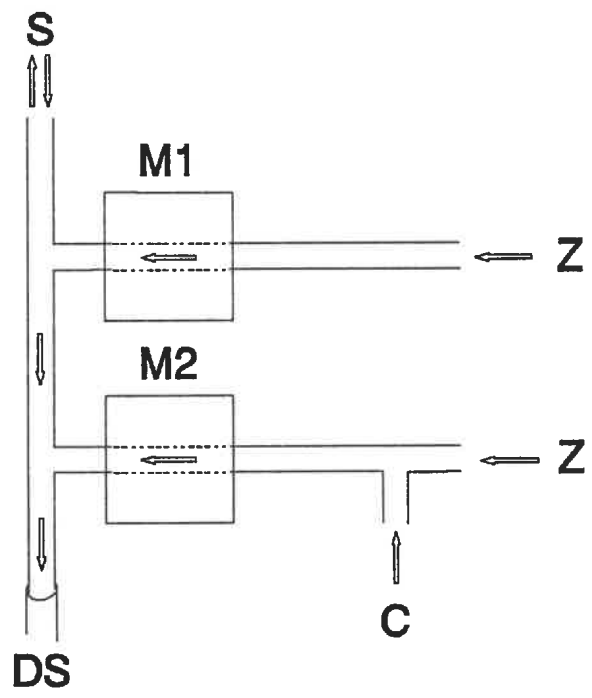


Figure 23. Inlet configuration with stainless steel valves. M1 + M2 solenoid valves in stainless steel, S = sample air, C = calibrationgas, Z = zerogas, DS = diffusion scrubber

The inlet configuration with a teflon ball valve, which is shown in Figure 22, was applied in the diffusion scrubber system from August 1991. Before this, a different inlet configuration with stainless steel solenoid valves was used. Using this inlet the atmospheric air was sampled directly in the diffusion scrubber without getting in contact with valves. This configuration is shown in Figure 23.

The reason for changing this configuration was that the inlet was also the outlet for overflow of humidified calibration gas. The calibration gas condensed in the outlet/inlet when the temperature outside was lower than the temperature of the calibration gas.

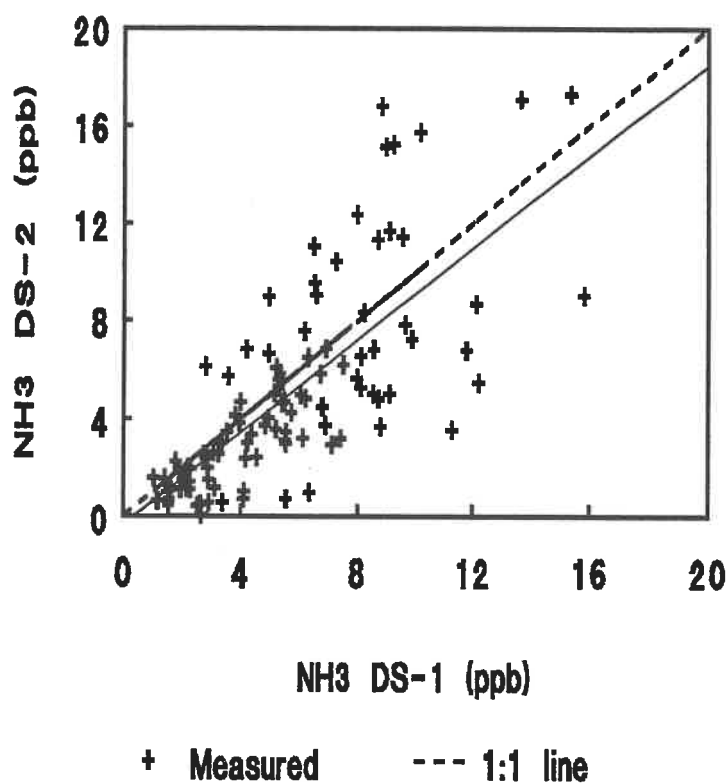


Figure 24. Results obtained with a diffusion scrubber system with a straight inlet and stainless steel valves against results obtained with a diffusion scrubber with teflon valve inlet.

An intercomparison of two diffusion scrubber systems, having two different inlet configurations was carried out. The relative humidity was controlled very carefully, so the relative humidity of the calibration gas was slightly lower than the relative humidity of the atmosphere, to avoid condensation in the outlet. The result is shown in Figure 24. A good correlation was obtained between the two diffusion scrubber systems, but the system with the teflon ball valve showed slightly higher concentrations, which might be due to evaporation of NH<sub>3</sub> from particles deposited in the inlet valve. This

might also be the reason for the scatter on the results. The intercomparison was carried out at the same time as an intercomparison between the diffusion scrubber and other sampling techniques. This intercomparison is described in Section 7.4. It was found, during this intercomparison, that the results obtained by the device, with the straight inlet and the stainless steel valves, correlated better with the results obtained by the other techniques. It is preferred to use the device with the straight inlet because measurements obtained by this will give less carryover, which again leads to a better precision of the measurement of the  $\text{NH}_3$  concentration. To use this device a better regulation of the humidification or a heating system to warm up the inlet, to avoid condensation of water in the inlet, is needed.

## 6 Detectionlimit, repeatability and reproducibility

The diffusion scrubber system has been tested for sensitivity and its potential use.

### 6.1 Detection criteria and detection limit

The detection limit (DL) is estimated from:

$$DL = t_{0.95}(f) \cdot S_B \cdot 2 \cdot \sqrt{1 + \left(\frac{1}{n_B}\right)}$$

$t_{0.95}$  = student's t-test statistic for 95% confidence level

$f$  = degrees of freedom

$S_B$  = standard deviation of the blank values

$n_B$  = number of blanks

Table 3. Detection limits for two diffusion scrubber systems, during three different field experiments at the Island Anholt in the Kattegat. All concentrations are in ppbv.

	June 1991	March 1992		June 1992	
		1.week	2.week	1.week	2.week
DS-box 1		0.01	0.03	0.05	0.1
DS-box 2	0.25	0.02	0.09	0.05	0.1

To estimate the detection limit, using data representing a wide variety of conditions,  $\text{NH}_3$  measurements obtained from a field experiment at the island Anholt in the Kattegat Strait between Denmark and Sweden were analyzed. The estimated detection limits varied from 0.01 ppbv to 0.25 ppbv. The different detection limits obtained are shown in Table 3. The correlation coefficient between the detection limit and the concentration in the atmospheric air was calculated to determine if the high detection limit corresponds to high atmospheric concentrations. No correlation was found. We found that high background concentrations in the analytical system are responsible for high detection limits. During longer filed experiments the water used as sampling liquid in the diffusion scrubber and for making reagents will collect  $\text{NH}_3$ , and the  $\text{NH}_3$  in the analytical system will increase with time. The lowest concentration of calibration gas we have measured by the diffusion

scrubber system is 0.02 ppb, which is shown in Figure 15. We illustrate the detection of low concentrations using four days of measurements at Anholt (see Figure 25).

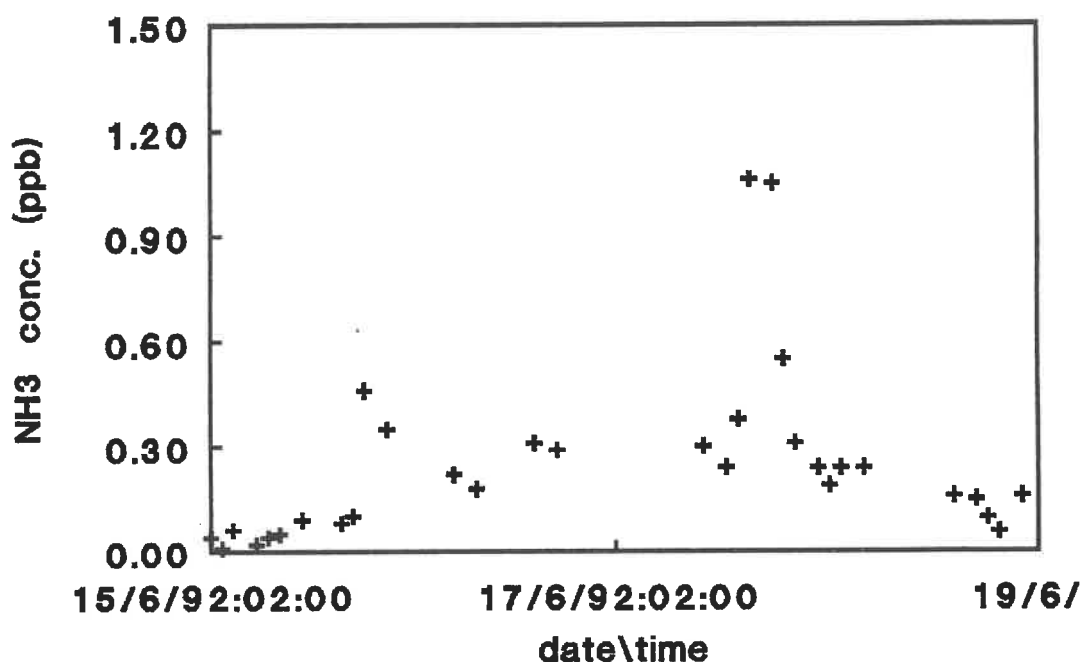


Figure 25.. Ammonia concentrations measured at a coastal sampling site at the Island Anholt in the Kattegat strait between Denmark and Sweden

To keep the detection limits low, it is necessary to keep the analytical system clean with respect to  $\text{NH}_4^+$ . For field experiments the water has to be transported in glass bottles with ion exchange materials. The ion exchange column in the diffusion scrubber system has to be regenerated regularly. Because of very different detection limits, this has to be estimated before every period of sampling.

## 6.2 Repeatability and reproducibility

The reproducibility is expressed by the statistical scatter in results obtained when analyzing the same sample with different diffusion scrubber systems. The repeatability represents statistical scatter in results obtained when analyzing the same sample with the same diffusion scrubber. To obtain gradient measurements with the diffusion scrubber system, the reproducibility is more important than the absolute concentrations as it shows the precision of the gradient. A small standard deviation of the repeatability implies a decrease in the frequency of the calibration of the monitor system.

### Repeatability

The repeatability is estimated as the relative standard deviation of a constant calibration concentration measured by the same system. The standard deviations of the repeatability is shown in Table 4. The

standard deviation is generally high but higher in the summer measurements, which is due to a big temperature variation.

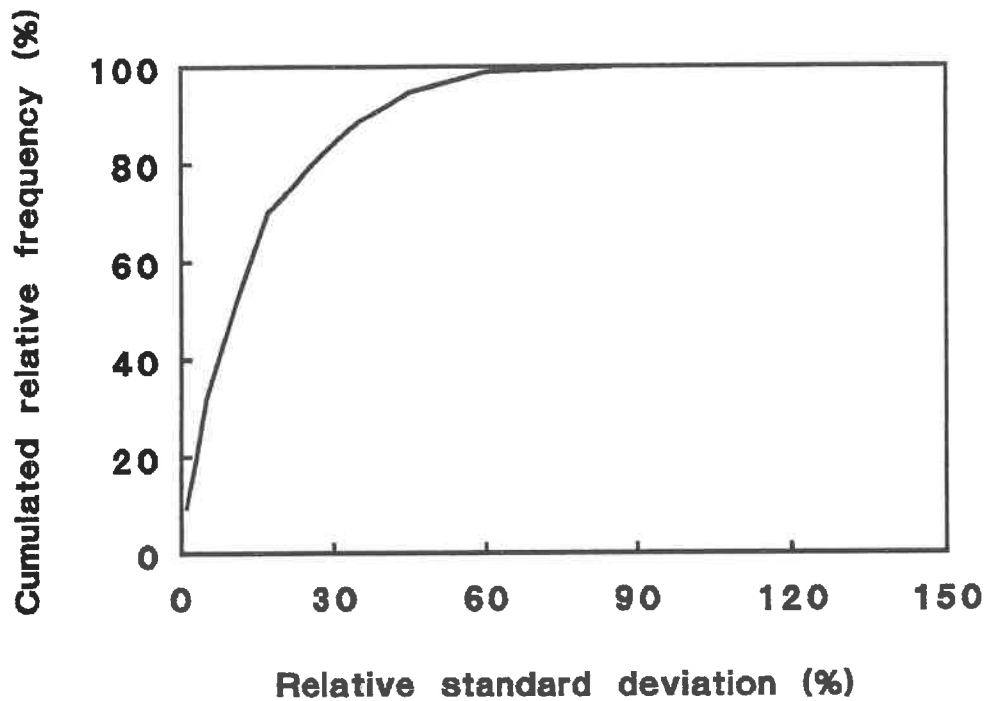
*Table 4.* The standard deviation of repeatability measured at Risø, Roskilde and during a field experiment at the island Anholt in the Kattegat Strait.

Repeatability (%)				
Box 1	Box 2	Exp.site	Period	Cal. conc. (ppbv)
5	15.5	Risø	12. may 1992	0.1
16.5	51	Risø	21. may 1992	0.1
64.8	-	Anholt	14. june 1992	0.05
65.9	-	Risø	31. july 1992	0.05
32.8	-	Risø	25. - 29. nov. 1992	1
38.2	-	Risø	27. nov. 1992	1
9.27	-	Risø	28. nov. 1992	1
5.6	27.2	Risø	29. nov. 1992	1
32.9	(-)	Risø	9. - 12. mar. 1993	2
(-)	40.1	Risø	10. - 13. mar. 1993	2

### *Reproducibility*

The reproducibility is estimated as the relative standard deviation on the NH<sub>3</sub> concentrations, measured by two systems, and it has been estimated during various measurement periods. The number of samples is 181. The total of the measurements can be seen in Figure 26.





*Figure 26.* The relative standard deviation in results obtained from sampling with two diffusion scrubber instruments. The samples were taken at Risoe in Roskilde, Denmark and at Anholt. It shows that 80% of the samples has a relative standard deviation of the reproducibility less than 35%

In Figure 26 it is shown that 50% of the samples obtained from two diffusion scrubber systems have a relative standard deviation of reproducibility less than 15%. A better reproducibility was obtained from data collected during a field experiment at the island Anholt in the Kattegat Strait between Denmark and Sweden. This is shown in Figure 27, and here we find that 50% of the measurements have a relative standard deviation less than 9%. This low standard deviation might be due to a more stable temperature during the sample period. Furthermore the  $\text{NH}_3$  concentration at this sampling site is very constant while there is no local source which can give rise to sudden high peak concentrations. At high fluxes the difference in concentrations in the gradient can be more than 25%, which suggest that the diffusion scrubber technique can easily be applied where high fluxes are expected.

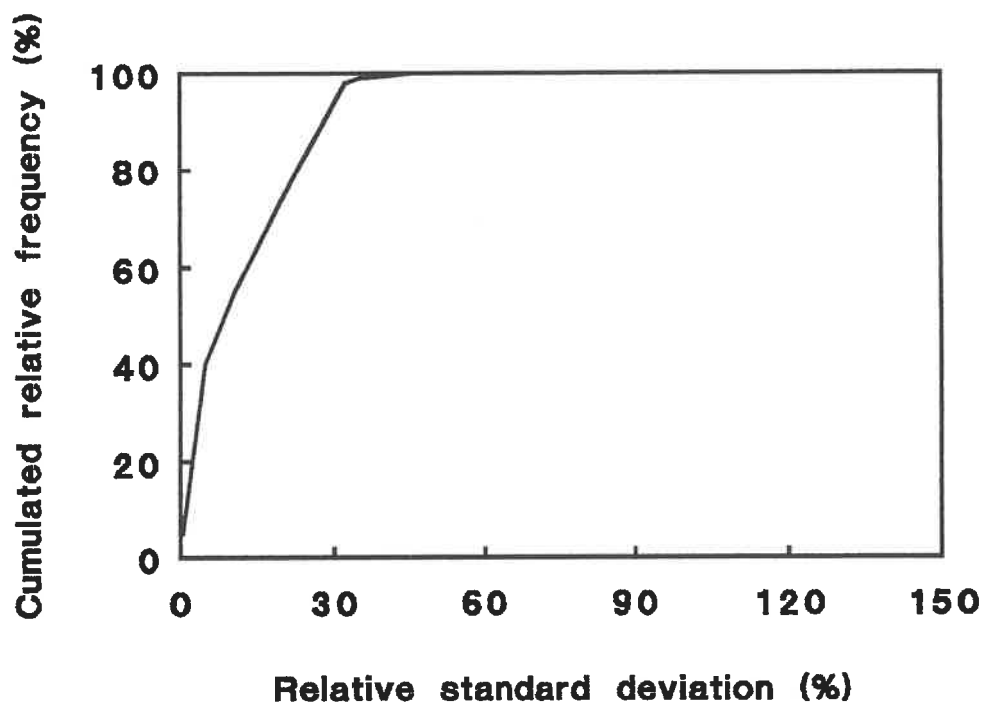


Figure 27. The relative standard deviation in results obtained from sampling with two diffusion scrubber instruments. The samples were taken at Anholt. It shows that 80% of the samples has a relative standard deviation of the reproducibility less than 25%

## 7 Intercomparison

### 7.1 Diffusion scrubber/denuder intercomparison (March 1992)

Two diffusion scrubber systems with teflon ball valve inlets and two diffusion denuders (*Ferm, 1979*) were set up to measure the  $\text{NH}_3$  concentrations in the ambient air in March 1992 at NERI, Roskilde. The diffusion scrubber sampled for 10 minutes every 70 minutes. The denuders sampled for 3x4 hours from 8:00 to 20:00 and for 12 hours during the nights. The results obtained by the two different techniques, are plotted against each other in Figure 28.

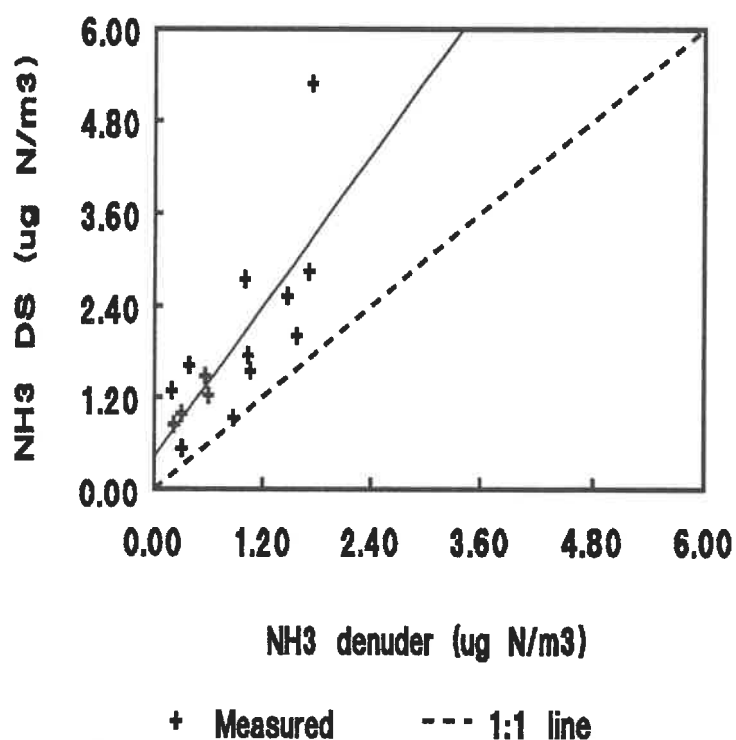


Figure 28. Results obtained with a diffusion scrubber instrument having teflon valve inlet against results obtained with a denuder (March 1992). The full line is the best fit.

The results show that the diffusion denuder yielded smaller values than the diffusion scrubber. We speculate that the larger values obtained from the diffusion scrubber could be due to particle deposition in the system, though this was expected to be negligible while the  $\text{NH}_4^+$  concentration was low (about the same level as the

NH<sub>3</sub> concentration) during the sampling period. The efficiency of the diffusion denuder was not investigated.

## **7.2 Diffusion scrubber/denuder intercomparison (February 1993)**

Two diffusion denuders (*Ferm, 1979*) and one diffusion scrubber system were set up to measure the NH<sub>3</sub> concentration in the ambient air in February 1993 at NERI, Roskilde. To avoid interferences from particles on the measurements, particle filters were put on the inlet of all three collection devices. The diffusion denuders were changed every 8 hour. When the denuders were changed the particle filters at all three devices were also changed. The results are shown in Table 5.

Table 5. Atmospheric NH<sub>3</sub> measurements at Risoe, Roskilde. Datetim1 is the sampling start time, Datetim2 is the sampling end time. conc1 and conc2 is the NH<sub>3</sub> concentration measured by the use of diffusion denuders which sample for 6 to 18 hours, conc3 is the NH<sub>3</sub> concentration measured by the diffusion scrubber system.

Datetim1	Datetim2	conc1 (ppbv)	conc2 (ppbv)	conc3 (ppbv)
09feb93:15:07	09feb93:15:17	.	.	1.06
09feb93:16:27	09feb93:16:37	.	.	0.95
09feb93:17:47	09feb93:17:57	.	.	0.90
09feb93:20:10	10feb93:14:00	0.01	~0.00	.
09feb93:20:27	09feb93:20:37	.	.	1.07
09feb93:21:47	09feb93:21:57	.	.	0.91
09feb93:23:06	09feb93:23:16	.	.	0.86
10feb93:01:46	10feb93:01:56	.	.	0.83
10feb93:03:06	10feb93:03:16	.	.	0.75
10feb93:04:26	10feb93:04:36	.	.	0.76
10feb93:07:06	10feb93:07:16	.	.	0.70
10feb93:08:26	10feb93:08:36	.	.	0.67
10feb93:09:46	10feb93:09:56	.	.	0.81
10feb93:12:09	10feb93:12:19	.	.	0.97
10feb93:13:29	10feb93:13:39	.	.	1.64
10feb93:14:00	10feb93:20:05	0.03	0.62	.
10feb93:14:49	10feb93:14:59	.	.	0.89
10feb93:17:28	10feb93:17:38	.	.	0.72
10feb93:18:48	10feb93:18:58	.	.	0.58
10feb93:20:05	11feb93:08:10	~0.00	~0.00	.
10feb93:20:08	10feb93:20:18	.	.	0.57
10feb93:22:48	10feb93:22:58	.	.	0.6
11feb93:00:08	11feb93:00:18	.	.	0.53
11feb93:01:28	11feb93:01:38	.	.	0.54
11feb93:04:08	11feb93:04:18	.	.	0.52
11feb93:05:28	11feb93:05:38	.	.	0.48
11feb93:06:48	11feb93:06:58	.	.	0.42
11feb93:08:10	11feb93:14:20	0.02	~0.00	.
11feb93:09:28	11feb93:09:38	.	.	0.74
11feb93:10:48	11feb93:10:58	.	.	0.79
11feb93:14:20	11feb93:20:05	~0.0	0.09	.
11feb93:14:47	11feb93:14:57	.	.	0.76
11feb93:16:07	11feb93:16:17	.	.	0.7
11feb93:17:27	11feb93:17:37	.	.	0.56
11feb93:20:05	12feb93:08:10	~0.00	~0.00	.
11feb93:20:07	11feb93:20:17	.	.	0.71
11feb93:21:27	11feb93:21:37	.	.	0.62
11feb93:22:47	11feb93:22:57	.	.	0.59
12feb93:01:27	12feb93:01:37	.	.	0.59
12feb93:02:46	12feb93:02:56	.	.	0.56
12feb93:04:06	12feb93:04:16	.	.	0.51
12feb93:06:46	12feb93:06:56	.	.	0.52

The values obtained by the diffusion scrubber are higher than the values obtained by the diffusion denuders. Very little or nothing has been collected by the diffusion denuders.

Values obtained by the diffusion scrubber will be too high if the concentration in the calibration gas, which is used as a reference measurement in the diffusion scrubber technique, is lower than expected. Previous investigations showed no loss of  $\text{NH}_3$  in the calibration system (see Section 3.2).

Concentrations measured by the diffusion scrubber will be estimated too high if the relative humidity of the calibration gas is much higher than the relative humidity in the atmospheric sample. Figure 20 shows the signals from the diffusion scrubber measurements during part of the measurement period. From the figure it is clear that, even though the estimation of the concentration is too high, the atmosphere contains  $\text{NH}_3$ . The results obtained by the diffusion denuders seem strange. Only one denuder sample shows a result which can be compared to the results obtained by the diffusion scrubber. This suggests that the coating of the denuders may have been bad.

### **7.3 Diffusion scrubber/filterpack intercomparison**

During field experiments at a coastal station at the island Anholt in between Denmark and Sweden (i.e., two weeks in March 1992 and two weeks in June 1992), the  $\text{NH}_3$  concentration was measured by the use of filters and the diffusion scrubber system with a teflon ball valve. The results have been plotted against each other in Figure 29.

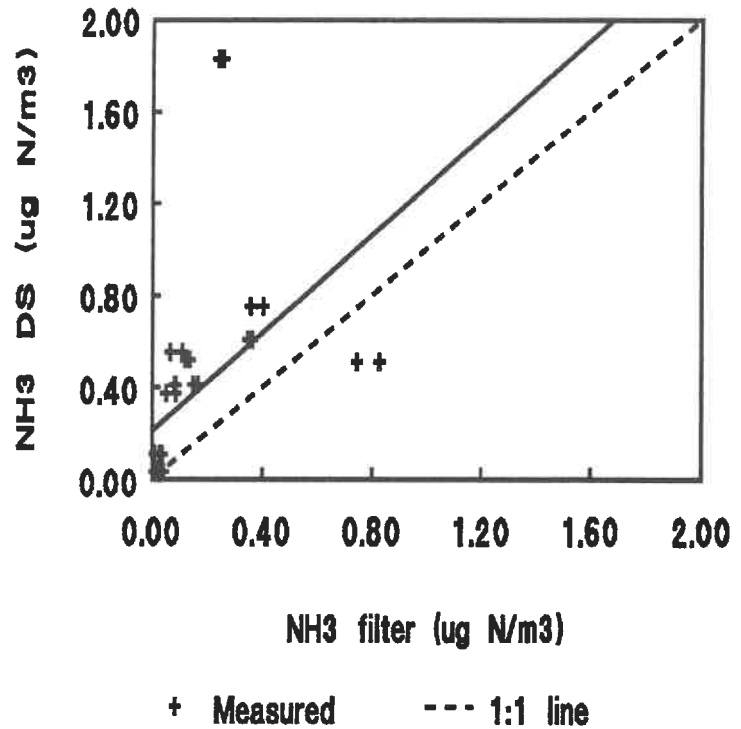


Figure 29. Results obtained with a diffusion scrubber instrument against results obtained with a filter pack system (Anholt, March/June, 1992). The full line is best fit.

The plot in Figure 29 shows lower  $\text{NH}_3$  values obtained with the filters. Previous experiments (Harrison and Kitto, 1990; Appel *et al.*, 1988) indicate overestimation of the  $\text{NH}_3$  concentration when using the filterpack techniques. This is due to volatilization of  $\text{NH}_4\text{NO}_3$  and  $\text{NH}_4\text{Cl}$  at the front filter. The experiments by Harrison and Kitto, (1990) and Appel *et al.* (1988) are all performed in rural sites. The aerosols at a coastal station will have a different composition, and this might give rise to collection of  $\text{NH}_3$  at the front filter. The higher values obtained with the diffusion scrubber system could also be due to  $\text{NH}_3$  evaporating from particles sampled in the inlet valve.

#### 7.4 Intercomparison of four $\text{NH}_3$ sampling techniques

An intercomparison was performed in March 1993 at Roskilde, Denmark, with four different methods: one diffusion scrubber system with the straight inlet which is described in Section 5.6.3, one filterpack system (Asman *et al.*, 1993), one diffusion denuder (Ferm,

1993; Wyers *et al.*, 1993). The diffusion scrubber system was sampling atmospheric air for 10 minutes having 70 minutes between every sample due to three times zero air sampling and four times injections. The filterpack samples and the denuder samples were performed with sampling time at 24 hours. The data obtained by the diffusion scrubber is averaged over 24 hour to be compared with the filterpack samples and the denuder samples. The results obtained by the different techniques are plotted in Figure 30, 31 and 32. The diffusion scrubber is the reference method and is shown at the y-axis.

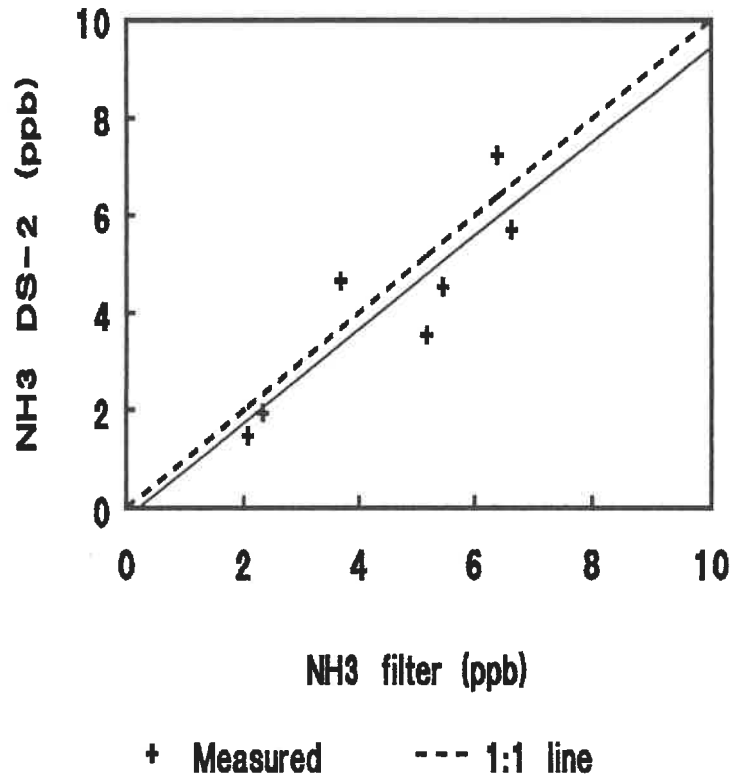


Figure 30. Results obtained with the DS-2 system (system with straight inlet and stainless steel valves) against results obtained with a filter pack (February 1993). The full line is the best fit.



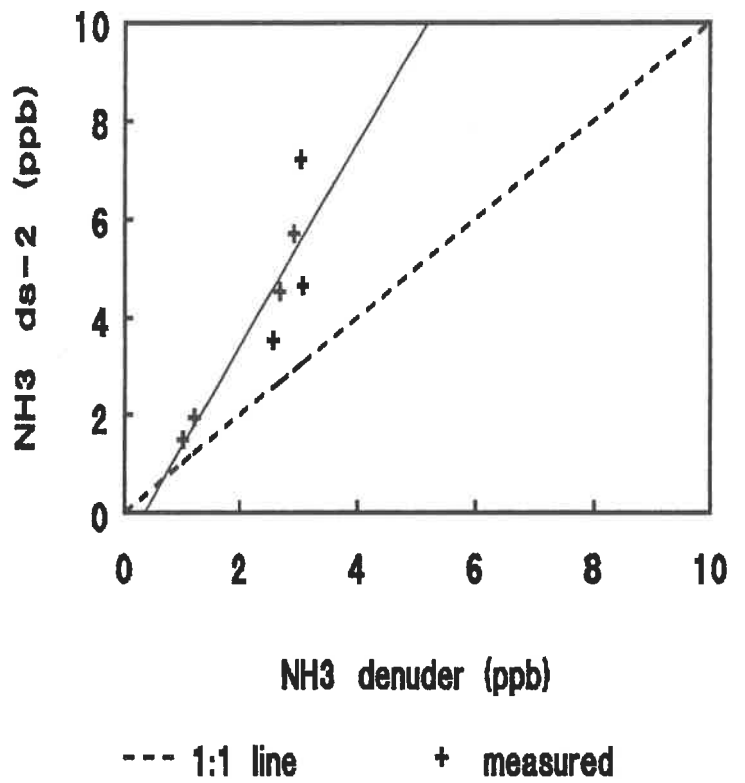


Figure 31. Results obtained with the DS-2 system (Diffusion scrubber with straight inlet and steel valves) against results obtained with a denuder (February 1993). The full line is the best fit.

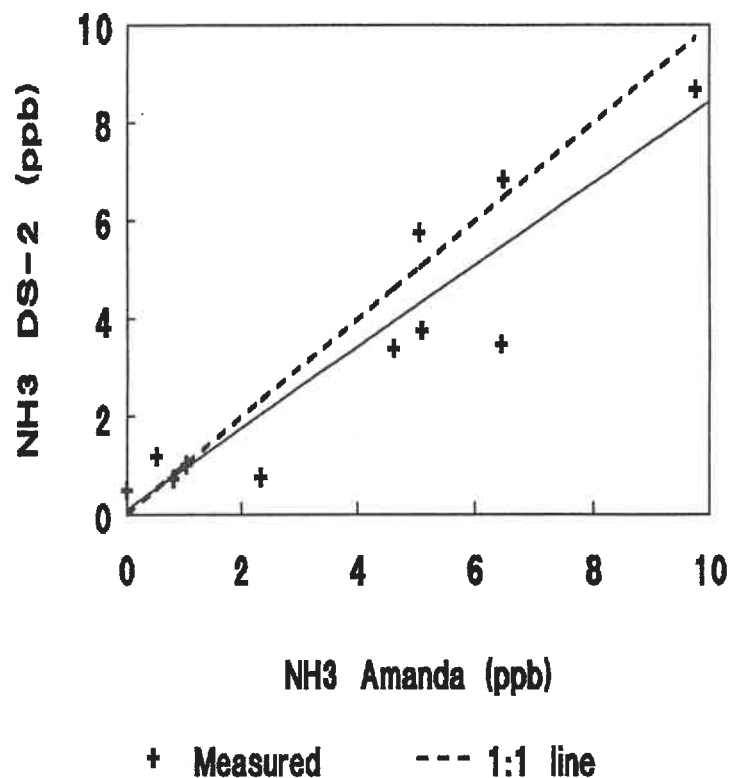


Figure 32. Results obtained with the DS-2 system (diffusion scrubber with straight inlet and stainless steel valves) against results obtained with the AMANDA system. The full line is the best fit.

A good correlation was obtained comparing the diffusion scrubber system and AMANDA ( $r=0.927$ ). A slightly higher concentration was measured by the AMANDA system, which could be due to particles deposited in the AMANDA sampling device. The difference could also be due to too low relative humidity on the calibration gas, which will give a relative higher signal from the calibration concentration and cause an underestimation of the atmospheric sample for the diffusion scrubber. The filterpack system showed good correlation with the diffusion scrubber system ( $r=0.88$ ). As mentioned in section 7.3 an overestimation of  $\text{NH}_3$  will often occur using filterpacks (Harrison & Kitto, 1990). The volatilization of the particles will increase with increasing temperature.

The results obtained by the diffusion denuder technique were much lower than the results obtained by the diffusion scrubber system. There is no obvious explanation for this. We speculate that ammonia might be collected in the inlet of the diffusion denuder (the inlet is not analyzed) or the sampling efficiency is smaller than expected.

## 8 Summary and conclusion

We find that the diffusion scrubber system is capable of achieving a very low detection limit (0.01 ppb) at low sampling time (10 minutes). With the low detection limit, the system has the potential for monitoring trace gas concentration over the sea during conditions of large temporal variability. The reproducibility of the diffusion scrubber method is on average 15%. This reproducibility is reasonably good and the system can be easily and routinely used for gradient measurements depending on the requirement to the standard deviation on the results and on the size of the flux.

Most of the tests has been carried out using a diffusion scrubber device where the atmospheric sample flows through a teflon ball valve inlet. There would not be a big difference in test results obtained with this device and results obtained with a diffusion scrubber with a straight inlet and a sample flow directly in the diffusionscrubber. Results obtained with the two devices will mainly differ when particles are present, and most of the tests has been carried out using a particle free calibration gas. However, the teflon valve might absorb  $\text{NH}_3$  from the calibration gas, which might cause bigger standard deviation on the repeatability. Changing the inlet configuration will result in less carryover, which will give a better repeatability. Further, it will be possible to have more frequent measurements if there is less carryover.

To obtain a more stable system and a better reproducibility, first the dependency of temperature and relative humidity has to be well known. Further investigations, where the relative humidity and the temperature are controlled parameters, have to be carried out. Experiments to examine formation of hydrated  $\text{NH}_3$  and dependency on hydration for the diffusion coefficient of  $\text{NH}_3$ , should also be carried out. The temperature might be stabilized by improving the thermostatic system in the diffusion scrubber box.

A steady and low detection limit can be obtained by keeping the sampling liquid clean (i.e. by storing it in glass bottles with ion exchange material during field experiments).

Collection efficiency should be further investigated. If a more stable and well controlled collection efficiency could be achieved, it would be possible to increase the frequency of atmospheric samples.

## References

*Ali, Z., Thomas, C.L. P. & Alder, F. (1989):* Denuder tubes for sampling of gaseous species. *Analyst* 114, 759-769.

*Appel, B.R., Tokiwa, Y., Kothny, E.L., Wu, R. & Povard, V. (1988):* Evaluation of procedures for measuring atmospheric nitric acid and ammonia. *Atmospheric Environment* 22, 1565-1573.

*Asman, W.A.H., Sørensen, L.L., Berkowicz, R., Granby, K., Nielsen, H., Jensen, B., Runge, E., Lykkelund, C. (1994):* Dry deposition processes (in Danish: Processer for tørdeposition). Under the series "Marine Research from the Danish Environmental Protection Agency". In press.

*Dasgupta, P.K., Dong, S., Hwang, H., Yang, H. & Genfa, Z. (1988):* Continuous liquid-phase fluorometry coupled to a diffusion scrubber for the real-time determination of atmospheric formaldehyde, hydrogen peroxide and sulfur dioxide. *Atmospheric Environment* 22, 949-963.

*Dasgupta, P.K. & Lindgren, P.F. (1989):* Inlet pressure effects on the collection efficiency of diffusion scrubbers. *Environ. Sci. Technol* 23, 895-897.

*Dasgupta, P.K., McDowell, W.L. & Rhee, J. (1986):* Porous membrane-based diffusion scrubber for the sampling of atmospheric gases. *Analyst* 111, 87-90.

*Eatough, D.J., White, V.F. & Hansen, L.D. (1985):* Hydration of nitric acid and its collection in the atmosphere by diffusion denuders. *Anal. Chem* 57, 743-748.

*Engelund, F.A. & Pedersen, F.B. (1982):* *Hydraulik*, Danish Technical University, Lyngby, Denmark.

*Ferm, M. (1979):* Method for determination of atmospheric ammonia. *Atmospheric Environment* 13, 1385-1393.

*Genfa, Z. & Dasgupta, P.K. (1989):* Fluorometric measurement of aqueous ammonium ion in a flow injection system. *Anal. Chem* 61, 408-412.

*Genfa, Z., Dasgupta, P.K. & Yung-Sung, C. (1991):* Design of a straight inlet diffusion scrubber. Comparison of a particle transmission with other collection devices and characterization for the measurement of hydrogen peroxide and formaldehyde. *Atmospheric Environment*, 25A, 2717-2729.

Genfa, Z., Dasgupta, P.K. & Dong, S. (1989): Measurement of atmospheric ammonia. *Environ. Sci. Technol* 23, 1467-1474.

Harrison, R.M. & Kitto, A.-M.N. (1990): Field intercomparison of filter pack and denuder sampling methods for reactive gaseous and particulate pollutants. *Atmospheric Environment* 24A, 2633-2640.

Harrison, R.M. & Msibi, I.M. (1994): Validation of techniques for fast response measurement of HNO<sub>3</sub> and NH<sub>3</sub> and determination of the [NH<sub>3</sub>] [HNO<sub>3</sub>] concentration product. *Atmospheric Environment* 28, 247-255.

Jacobs, A.W. (1987): O-phthalaldehyde-sulfite derivatization of primary amines for liquid chromatography-electrochemistry. *Journal of Chromatography* 392, 435-441.

Jeppesen, M.T. & Hansen, E.H. (1991): Flow-injection fluorimetric assay of nitrogen-containing substrates by on-line enzymatic generation of ammonia. *Analytica Chimica Acta* 245, 89-99.

Keuken, M.P., Wayers-Ijpelaan, A., Mols, J.J., Otjes, R.P. and Slanina, J. (1989): The determination of ammonia in ambient air by an automated thermodenuder system. *Atmospheric Environment* 23, 2177-2185.

Mennen M.G., van Elzakker B.G., van Hellemond J., Wyers G.P., Otjes R.P., Verhage A.J.L., Wouters L.W., Heffels C.J.G., Romer F.G., van den Beld L., Tetteroo J.E.H. & Hoogervorst A. (1993): A field intercomparison with five automatic ammonia monitors. RIVM-report no. 223107002.

Morrison, R. & Boyd, R.N. (1973): *Organic chemistry*, 3rd edition, New York University. Allyn and Bacon Inc., London, U.K..

Rapsomanikis S., Wake M., Kitto A.-M.N. & Harrison R.M. (1988): Analysis of atmospheric ammonia and particulate ammonium by a sensitive fluorescence method. *Environ. Sci. Technol.* 22, 948-952.

Simon, P.K., Dasgupta, P.K. & Vecera Z. (1991): Wet effluent denuder coupled liquid/ion chromatography systems. *Anal. Chem* 63, 1237-1242.

Spiller, L.L. (1989): Determination of ammonia/air diffusion coefficient using nafion lined tube. *Analytical letters* 22, 2561-2573.

Williams, E.J., Sandholm, S.T., Bradshaw, J.D., Schendel, J.S., Langford, A.O., Quinn, P.K., LeBel, P.J., Vay, S.A., Roberts, P.D., Nortons, R.B., Watkins, B.A., Buhr, M.P., Parrish, D.D., Calvert, J.G. & Fehsenfeld, F. C. (1992): An intercomparison of five ammonia measurement techniques. *Geoph. Res.* 97, 11,591-11,611

Wyers G.P., Otjes R.P. & Slanina J. (1993): A continuous-flow denuder for the measurement of ambient concentrations and surface-exchange fluxes of ammonia. *Atmospheric Environment* 27A, 2085-2090.

## National Environmental Research Institute

The National Environmental Research Institute - NERI - is a research institute of the Ministry of the Environment. Neri's tasks are primarily to do research, collect data and give advice on problems related to the environment and nature.

### Addresses:

National Environmental  
Research Institute  
Frederiksborgvej 399  
P.O. Box 358  
DK-4000 Roskilde  
Denmark

Tel: +45 46 30 12 00  
Fax: +45 46 30 11 14

*Management  
Personnel and Economy Secretariat  
Research and Development Secretariat  
Department of Emissions and Air Pollution  
Department of Environmental Ecology  
Department of Policy Analysis  
Department of Marine Ecology and  
Microbiology*

National Environmental  
Research Institute  
Vejlssøvej 25  
P.O. Box 413  
DK-8600 Silkeborg  
Denmark

Tel: +45 89 20 14 00  
Fax: +45 89 20 15 14

*Department of Freshwater Ecology  
Department of Terrestrial Ecology*

National Environmental  
Research Institute  
Grenåvej 12, Kalø  
DK-8410 Rønne  
Denmark

Tel: +45 89 20 14 00  
Fax: +45 89 20 15 14

*Department of Wildlife Ecology*

### Publications:

NERI publishes professional reports, technical instructions, reprints of scientific and professional articles, a magazine of game biology and the Annual Report.

Included in the annual report is a review of the publications from the year in question. The annual reports and an up-to-date review of the year's publications are available on application to NERI.

