

Operation Manual for the CEH DELTA System

For sampling gaseous NH_3 , HNO_3 , HONO , SO_2 , HCl
and aerosol NH_4^+ , NO_3^- , NO_2^- , SO_4^{2-} , Cl^- , Na^+ , Ca^{2+} , Mg^{2+}

CONFIDENTIAL

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NATURAL ENVIRONMENT RESEARCH COUNCIL

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1. INTRODUCTION

1.1. DELTA System

The CEH DELTA (DEnuder for Long-Term Atmospheric sampling) system is a new low-cost diffusion denuder system that was originally developed for long-term sampling of ammonia and ammonium (Sutton *et al.*, 2001), and which has also been tested for long-term sampling of acid gases (HNO_3 , HONO , HCl , SO_2) and aerosols (NO_3^- , NO_2^- , Cl^- , SO_4^{2-}). The system is based around the concept of a single bore glass denuder for sampling trace gases (Ferm 1979). When a laminar air stream passes through the denuder coated on the inside with an acid coating such as citric acid, ammonia is captured by the acid walls (to be later extracted in the laboratory), while aerosols pass through and can be collected by aerosol filters placed downstream of the denuder. Conversely, an alkaline coating (e.g. K_2CO_3) on the denuders will collect acid gases such as HNO_3 , SO_2 and HCl . The separation of aerosol from gaseous components is achieved due to the much more rapid diffusion of gaseous species to the tube wall compared with that of particles.

The DELTA system is tuned for monthly sampling, but shorter and longer periods are also possible, depending on ambient concentrations (e.g. 1 week – 3 months). Stable sampling rates of $0.3\text{--}0.4 \text{ l min}^{-1}$ are achieved using a piston air pump (or other types of air pump in conjunction with a rotameter), with air volumes being measured by a high sensitivity dry gas meter. The low sampling rate means that short glass denuders (10 – 15 cm in length, optimum length to achieve greater than 99 % capture for the gas of interest) can be used, which allows easy exchange of samples through the post. A simple enclosure is used, which can be mounted easily in the desired location. The design of the monitoring equipment is shown in Figure 1. For sampling HNO_3 , the sampling box must be set up outdoors, sampling directly from the atmosphere, with a funnel used to shelter the air intake to avoid sucking in water.

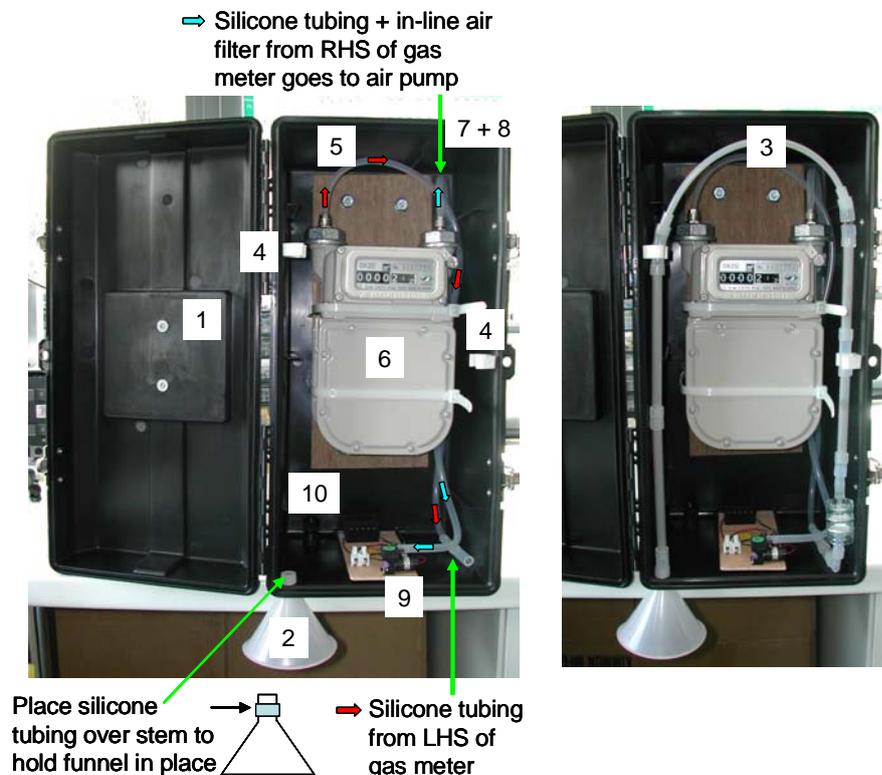


Figure 1. Front view, with door open, showing detail of components in the enclosure of the DELTA system. (The numbered components are described in the text). A sampling train for sampling full suite of reactive chemical species is shown on the RHS *in situ*. (see section 2.3).

The numbered components in Figure 1 are:

1. Durable plastic enclosure

The enclosures are set up standing on-end with the door opening frontwards to: a) allow easy access to the components, b) allow the denuder to be mounted in a vertical position (important to prevent kinking of silicone lines, but this also limits any sedimentation of larger aerosol during fog, c) provide a simple way of supporting the monitoring boxes in the field. Two holes are drilled in the base end of the box, for the electricity power lead and for the sampling inlet.

2. Sampling inlet

OUTDOOR: A plastic funnel (LDPE, 89 mm diameter) with the stem trimmed to accommodate the denuder is pushed through a hole in the base of the enclosure on the front left hand corner. A short ring of silicone tubing is placed over the stem of the funnel inside the box to prevent the funnel from dropping off.

INDOOR: A polyethylene elbow connector is connected to 5 mm I.D polyethylene tube to the outside of the cabin. Where necessary, a boom (~0.4 m long) is used to ensure the sampling inlet is kept away from the cabin. A polyethylene funnel is also attached at the inlet end. Sampling inlet may be used for sampling NH_3 and NH_4^+ , but should NOT under any circumstances be used for sampling HNO_3 , as adsorption loss of HNO_3 will incur to the inlet line.

The funnels in both cases act as rain shield for the air sampling.

3 + 4. Sampling assembly and Guide Clip

The sampling assembly is described in detail in sections 11. In use it sits alongside the left of the box (hinge side), and is kept in place using a simple plastic clip.

5. Silicone tube connection

This connects the denuder assembly to the gas meter. This should not kink (bend over and seal, preventing air flow). To ensure free flow the tube length should be carefully measured. Guying into the clip (4) also helps avoid kinking.

6. Gas meter

In the sampling enclosure, the gas meter is supported on side spars of the enclosure, and gripped in the back of the meter (simply to stabilize the meter from sliding forwards) using heavy duty velcro. The position of the large comma denotes the division between meters and tenths of meters. To ensure reliable measurements, a high sensitivity G1.6 gas meter is used.

7. Silicone tube connection

This connects the gas meter to the air pump. As with 5, it is important to ensure that this does not kink (bend over and seal, preventing air flow). This tube tracks the back right of the box to keep the tube out of the way.

8. In-line large particle filter

Large particles in the atmosphere are one of the main sources of wear for the air pump. Although not essential, the life of the pump between services is increased by a simple in-line air filter.

9. Air pump

The system uses small air pumps that deliver flow rates of between $0.23 - 0.4 \text{ l min}^{-1}$. At remote sites without mains power, a 6 volt or 12 volt pump which can run off batteries (solar and/or wind power) can be used. A rotameter may be required to regulate the flow between $0.23 - 0.4 \text{ l min}^{-1}$, where a pump with the desired flow rate is not available (Figure 2).

Remote locations

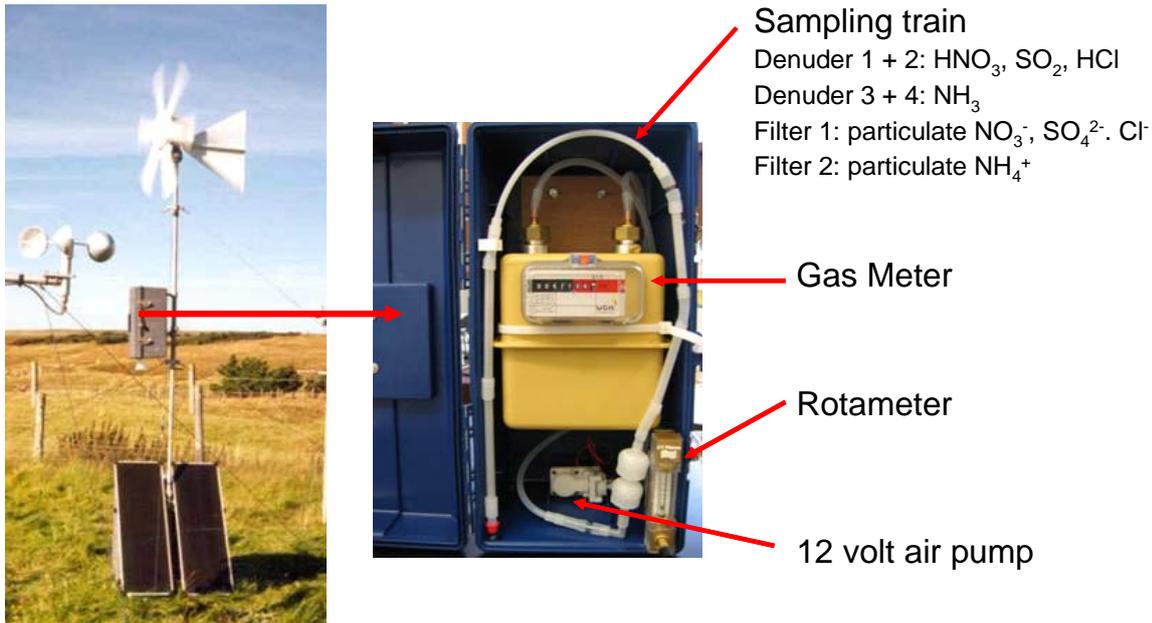


Figure 2: DELTA system with 12 volt air pump and rotameter. A full sampling train (see section 2.3) is also shown *in situ*.

10. Pump mains lead and electrical connector.

The mains electricity lead supplied with the piston pump is cut short to approximately 150 mm and connected to a durable rubberized 3 pin electrical connector, designed for joining domestic electricity extension leads.

Where the monitoring box is to be set up on a pole outside, armoured mains cable is used to link with the mains power supply. This should not exceed approximately 20 m length, purely for the purposes of practicality, although in principle much longer lengths may be used. Caution is needed to note the individual circumstances of each site and lay this cable in a safe manner. In particular, the risk of the cable being cut by grass cutting machines or being driven over by vehicles should be assessed, and where appropriate the cable set into the ground. Warning tape should be laid above such cables. A diagrammatic record of the path taken by the lead to the mains supply should be made at each site. As an additional precaution, a residual current device (30 mA earth leakage trip) should be fitted.

1.2. Installation

Since HNO_3 is 'sticky' and adsorption losses will occur to inlet lines, it is strongly recommended that the DELTA system is set up outdoors, sampling directly from the atmosphere, with a funnel used to shelter the air intake to avoid uptake of rain water. Figure 3 shows how the sampling box could be set up in the field, where the DELTA system is mounted on a pole that is securely guyed at 4 points

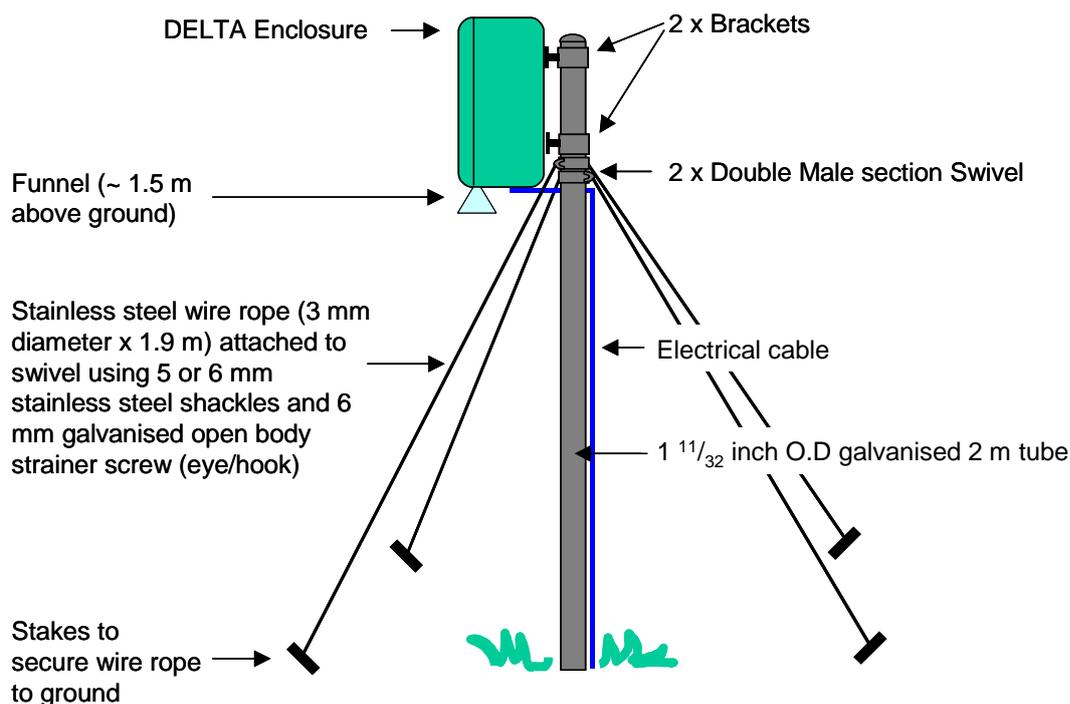


Figure 3. Mounting of the DELTA sampling enclosure for outdoor use.

2. SAMPLING TRAINS

2.1. Preparing coated denuders

2.1.1. Acid coated denuders for sampling NH_3

Glass denuders that are 10 cm long (1 cm OD, 0.6 mm ID) are used to achieve near 99 % capture of NH_3 . To sample atmospheric NH_3 , the glass denuder tubes are coated internally with an acid. Citric acid, phosphoric acid (H_3PO_4), phosphorous acid (H_3PO_3) or tartaric acid can all be used, but oxalic acid should be avoided because loss of the coating can occur during sampling owing to its high volatility, and the long sampling times (e.g. 1 month) used by the DELTA system. Citric acid gives a visible layer of coating on the tubes, allowing for visual inspection of the quality of coating, and is suited for use in temperate climates. Where conditions are hot and dry (e.g. Mediterranean climate), phosphorous acid (H_3PO_3) should be used instead, since this is less volatile than citric acid (Perrino 1999). However, phosphorous acid is unfortunately highly deliquescent and is therefore not recommended for conditions where humidity is greater than 70%.

Materials

- Citric acid, AnalaR grade
- Phosphorous acid, AnalaR grade
- Methanol, AnalaR grade
- Sodium Hydroxide, AnalaR grade
- Deionised water
- 10 cm long borosilicate glass tubes (10 mm o.d, 6 mm i.d)-internal walls etched with HF, or internal surface physically abraded (frosted glass appearance) to increase surface area for taking up acid coating.

Degreasing denuders before coating

Immerse a batch of clean, dry denuders in a 0.1% (m/v) sodium hydroxide solution for at least 24 hours (or until required for coating) to degrease the denuders. Before use, rinse the denuders thoroughly in tap water, followed by three rinses with deionised water. Place the denuders in a hot oven at ~100 °C to dry overnight. The dry, degreased denuders are then ready to be coated the next day or can be stored for up to a week in an airtight container.

Coating solution

- 5 % m/v citric acid in methanol

Weigh out 5 g citric acid into a 100 ml volumetric flask, dissolve in approx. 50 ml methanol and then make up to volume with methanol. This is prepared fresh on the day of use.

- 1 % m/v phosphorous acid in methanol

Weigh out 1 g phosphorous acid into a 100 ml volumetric flask, dissolve in approx. 5 ml deionised water and then make up to volume with methanol. This is prepared fresh on the day of use.

2.1.2. Alkaline coated denuders for sampling acid gases

Two carbonate coated denuders in series are used to collect HNO₃, SO₂ and HCl. The presence of ozone (O₃) is known to oxidize nitrous acid (HONO) to nitric acid (HNO₃); therefore, HNO₃ measurements may include some artefact from HONO.

Where concentration of ozone is high, calculations to adjust for this oxidation process and to provide a more accurate estimation of HONO concentrations in the atmosphere is required. Where the gas of interest is HONO, a TCM coated denuder (prepared using the coating solution: 21.7 g HgCl₂ + 11.9 g KCl in 100ml deionised water) that is selective for HONO gas can be used, followed by two carbonate coated denuders to collect HNO₃, SO₂ and HCl.

HONO is generally in low concentrations in the atmosphere, and can be assumed to be negligible. Therefore two carbonate coated denuders in series can be used to collect HNO₃, SO₂ and HCl. Glass denuders that are 14 -15 cm long are used to achieve near 99 % capture of HNO₃.

To prepare the denuders, the glass tubes are coated internally with either KOH or NaOH which converts to K₂CO₃ or Na₂CO₃ respectively by reacting with CO₂ in the atmosphere. Glycerol is also added to the coating to increase adhesion and reduce volatilisation of the coating. The method below describes the preparation of K₂CO₃ and glycerol coated denuders, which gives a visible layer of coating on the tubes. The same procedure applies for using NaOH. KOH coating is used in preference where there is an interest to measure the base cation Na⁺ in the filter pack.

Materials

- Potassium Hydroxide (KOH), AnalaR grade
- Glycerol, AnalaR grade
- Methanol, AnalaR grade
- 15 cm (or 14 cm) long borosilicate glass tubes (10 mm o.d, 6 mm i.d)-internal walls etched with HF, or internal surface physically abraded (frosted glass appearance) to increase surface area for taking up acid coating.

Degreasing denuders

Clean, dry denuders are immersed in a 1 M HNO₃ solution for at least 24 hours to clean/degrease the denuders. Before use, rinse the denuders in tap water followed by three rinses

with deionised water. Dry denuders in a hot oven at $\sim 100^{\circ}\text{C}$. They are then ready to be coated the next day or can be stored for up to a week in an airtight container.

Coating solution

The coating solution is 1% (m/v) KOH + 1 % (m/v) Glycerol in methanol (KOH converts to K_2CO_3 on reaction with CO_2 in the atmosphere). This is prepared fresh on the day of use. Weigh out 1 g KOH into a 100 ml volumetric flask, add approx. 75 ml methanol and sonicate to dissolve (takes ~ 1 hr). Make sure that the KOH is completely dissolved, before adding 1 g glycerol to the methanol solution. Mix well to dissolve and make up to volume with methanol.

2.1.3. Coating procedure

Invert the volumetric flask containing the coating solution several times to ensure that the coating solution is well mixed. Transfer the content to a 250 ml conical flask and place a small beaker over the mouth of the flask. This serves to minimise (a) evaporation of methanol, and (b) contamination from room air. Insert the denuder into a pipette filler, and using the denuder as a pipette, draw up coating solution to within 1 cm from the top. Allow the solution to remain for approx. 10 secs before dispelling the liquid in a smooth movement. Carefully wipe the outside of the denuder end that was dipped into the coating solution with a clean tissue, and quickly attach the non-dipped end of the denuder to a drying manifold (Figure 4). For a drying manifold designed to hold 8 denuders, prepare another seven denuders in the same way. The drying manifold contains silica gel to remove moisture, and a double filter pack with an acid and an alkaline impregnated paper to remove ammonia and other acid gases / aerosols. After about 5 minutes, remove the denuders one at a time in the order that they were put on the manifold and assemble them (see section 2.3). Place in sealed plastic bags and store in an airtight plastic container lined with acid-treated paper. Inspect the coated denuders after about an hour. The coating is not visible immediately, and takes a little time to develop. Reject any denuders with an imperfect coating.

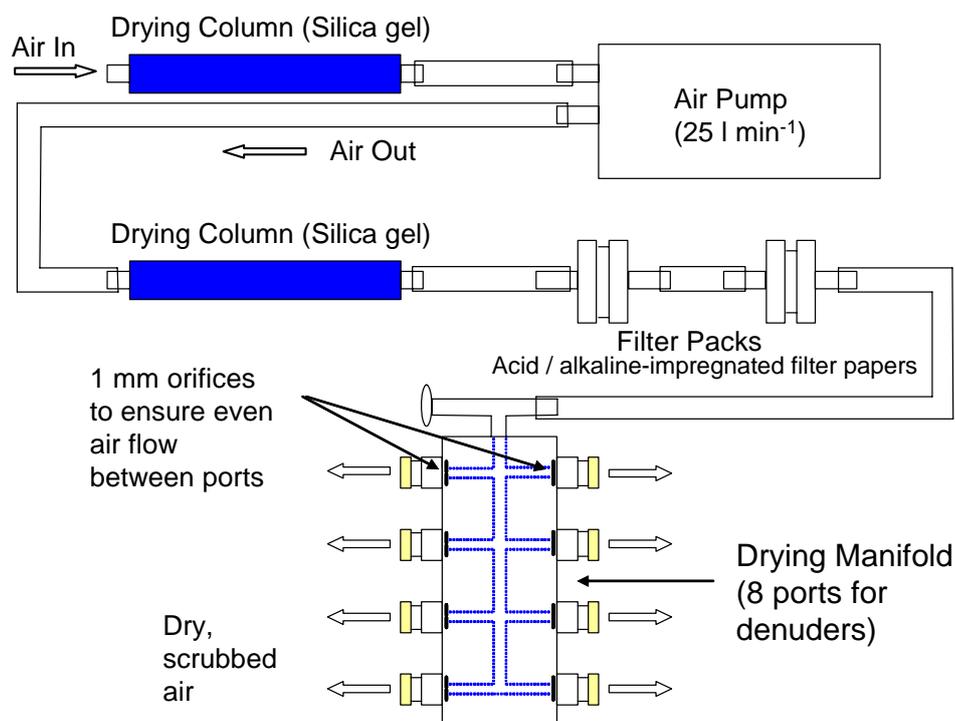


Figure 4: A drying manifold (8-port model shown) specially designed to dry individual denuders after coating.

2.1.4. *Blank denuders*

Blank denuders are prepared in exactly the same way as samples. Coated denuders are removed at regular intervals during preparation to be used as blanks. Individual denuders are capped and put in labelled gripseal bags, which in turn are stored in an airtight container lined with acid-treated paper. Tests have shown no difference between blank denuders that are stored singly or as denuder assemblies. For convenience, the blank denuders are stored singly.

2.2. Preparing Aerosol Samplers

2.2.1. *Coating Filter Paper for sampling aerosol NH_4^+*

Materials

- Citric acid, AnalaR grade
- Phosphorous acid, AnalaR grade
- Methanol, AnalaR grade
- Whatman No. 40 (or equivalent quantitative grade) Cellulose filter circles, 25 mm diameter

Impregnation solution

- *13 % m/v citric acid in methanol*

Weigh out 1.3 g citric acid into a 10 ml volumetric flask. Add ~5 ml methanol to dissolve the citric acid and then make up to volume.

- *1 % m/v phosphorous acid in methanol*

Weigh out 0.1 g phosphorous acid into a 10 ml volumetric flask, dissolve in approx. 0.5 ml deionised water and then make up to volume with methanol. This is prepared fresh on the day of use.

2.2.2. *Coating Filter Paper for sampling aerosol NO_3^- , SO_4^{2-} and Cl^-*

Materials

- Potassium Hydroxide (KOH), AnalaR grade
- Glycerol, AnalaR grade
- Methanol, AnalaR grade
- Whatman No. 40 (or equivalent quantitative grade) Cellulose filter circles, 25 mm diameter

Impregnation solution

The filter impregnation solution is 5 % (m/v) KOH and 10 % Glycerol (m/v) in methanol. Weigh out 0.5 g KOH into a 10 ml volumetric flask. Add ~7 ml methanol to the 10 ml volumetric flask to dissolve the KOH. Dissolution of the KOH may be speeded up by sonicating in an ultrasonic bath. Once KOH is completely dissolved in the methanol, add 1 g glycerol directly into the volumetric flask on a top pan balance. Then make up to volume with methanol. This is prepared fresh on the day of use.

2.2.3. *Preparation of impregnated filter papers*

Invert the volumetric flask containing the coating solution several times to ensure that the solution is well mixed. Pour some of the solution into a small 20 ml glass bottle and place a small cap over the mouth. This serves to minimise (a) evaporation of methanol, and (b) contamination from room air.

Arrange an appropriate number of filters (no more than 20 in each batch) on clean petri dishes. Working as quickly as possible, accurately dispense 60 μl aliquots of the coating solution onto the centre of each filter and place the petri dishes inside a dessicator. Evacuate the dessicator by connecting it to a vacuum pump. The impregnated filters should appear visibly dry after about 3 mins. The coated filters are now ready to be used, or they can be stored until required. For storage, it is recommended that the coated filters are stacked up and stored in a clean 47 mm petri dish. The petri dish should also be sealed with either parafilm or sealing tape, wrapped with acidified paper and then placed inside gripseal bags. This should in turn be stored in an airtight container.

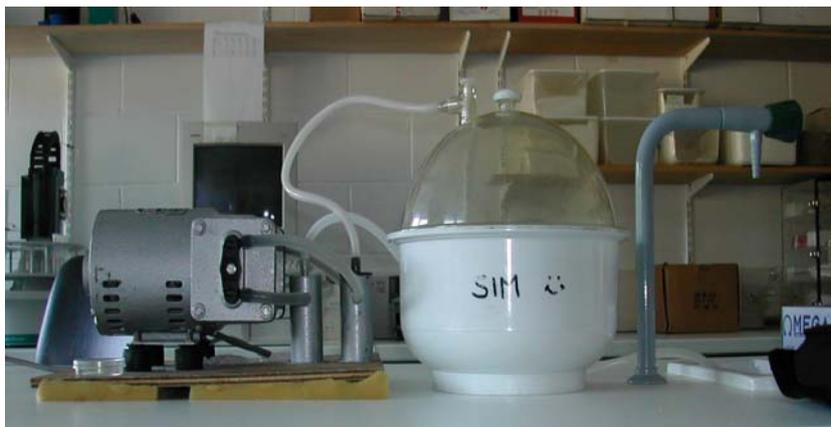


Figure 5: Preparing coated filter papers: a dessicator is attached to a vacuum pump that evacuates air, evaporating methanol off the coated filters.

2.2.4. *Assembling aerosol samplers*

Materials

- Millipore aerosol analysis monitor case, 25mm monitor type A with endcaps
- Gaskets Swinnex silicone 25mm
- Millipore Tubing adapter male Luer for 25 mm monitors

Procedure

- 1) Using a pair of clean forceps, carefully place a 25 mm diameter silicone O-ring onto the base of the Millipore aerosol filter holder, then the acid coated 24 mm filter paper, followed by another 25 mm O-ring,
- 2) Push middle section inside the base, compressing the O-ring, filter paper, O-ring stack together to form a snug fit,
- 3) Next, place a carbonate coated filter paper inside the middle section (sits on top of internal ledge inside), followed by an O-ring. Only one O-ring is required to seal this section, as the gap between the top and middle section is not as wide as the gap between the base and middle section,
- 4) Finally, push the Top section inside the middle section, compressing the filter paper and O-ring to form a gas-tight fit. The two ends of the aerosol holder can now be sealed with end caps that are supplied.

Note: The connection at the Air INLET end is short and would be difficult to get a good connection with silicone tubing alone. For this reason, a Luer adapter is inserted inside the INLET, for making secure connection to silicone tubing.

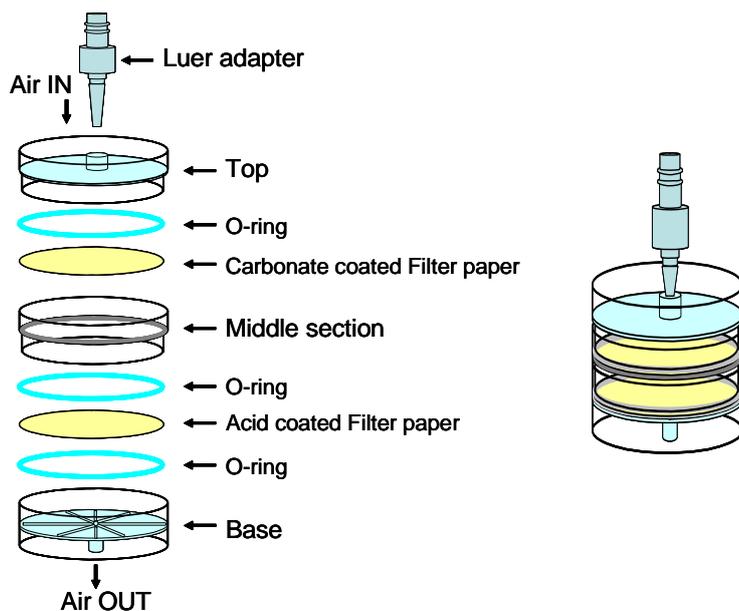


Figure 6: Exploded diagram of a 2-stage Millipore aerosol holder on LHS, showing the order in which the different components and coated filter papers are assembled. The assembled aerosol holder is shown on the RHS.

2.2.5. Blank Aerosol samplers

Blank aerosol samplers are prepared and assembled in exactly the same way as samples. The two ends of the filter pack are sealed off with the end caps provided. They are put inside labelled gripseal bags, which in turn are stored inside an airtight container lined with acid-treated paper.

2.3. Assembling sampling trains

2.3.1. Sampling train for $\text{NH}_3/\text{NH}_4^+$ only

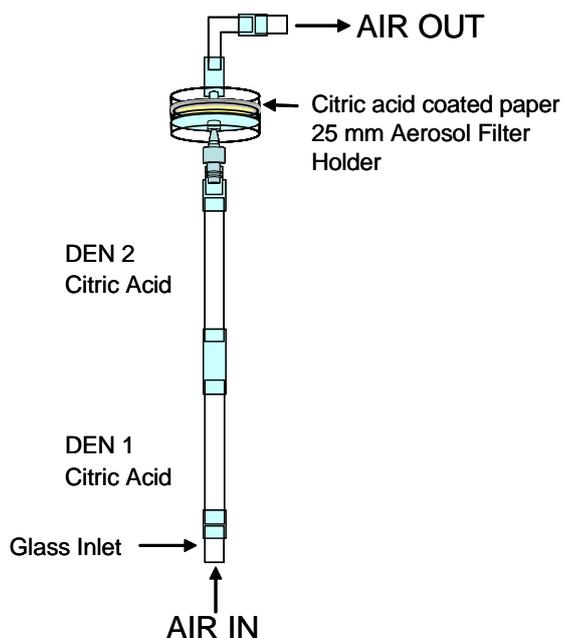


Figure 7: Double denuder and filter pack assembly for collecting gaseous ammonia and aerosol ammonium, in the DELTA system.

Gaseous NH_3 is removed from the sample air stream by denuders 1 and 2 coated with an acid such as citric acid, whilst aerosol NH_4^+ passes through and may be collected by a post-denuder filter pack on the sampling train (Figure 7). A short 2.3 cm glass inlet (not coated) at the front end serves to develop laminar flow through the denuders. For practicality in the DELTA system, an elbow connector is placed between the filter pack and a second 2.3 mm glass connector, for convenient connection to the gas meter.

2.3.2. Sampling train for full suite of reactive chemical species

The sampling train for collecting the full suite of reactive chemical species are shown in Figure 8. It consists of a short teflon inlet (2.8cm, to develop laminar flow; teflon is used because nitric acid does not stick to this material) plus two long denuders (15 cm, Denuders 1 and 2) coated with K_2CO_3 and glycerol to remove gaseous HNO_3 , SO_2 and HCl , followed by a short glass tube (2.3 cm, to develop laminar flow) plus two shorter denuders (10 cm, Denuders 3 and 4) coated with citric acid to remove gaseous NH_3 from the air stream. A 2-stage aerosol filter holder at the end of the sampling train remove aerosol NO_3^- , SO_4^{2-} , Cl^- and NH_4^+ , plus Na^+ , Ca^{2+} and Mg^{2+} from the air stream that has been stripped (or 'denuded') of gaseous components by the denuders.

Two denuders in series are used for every sample, in order to establish capture efficiency for the acid gases and for NH_3 , respectively. For practicality in the DELTA system, an elbow connector and an additional glass tube are fitted at the back end for connection to a silicone tube coming from the gas meter. The different tube sections are joined by silicone tubing, and provided with two caps for sealing before and after sampling. The sampling train may be folded over, and packed into a gripseal bag, for posting.

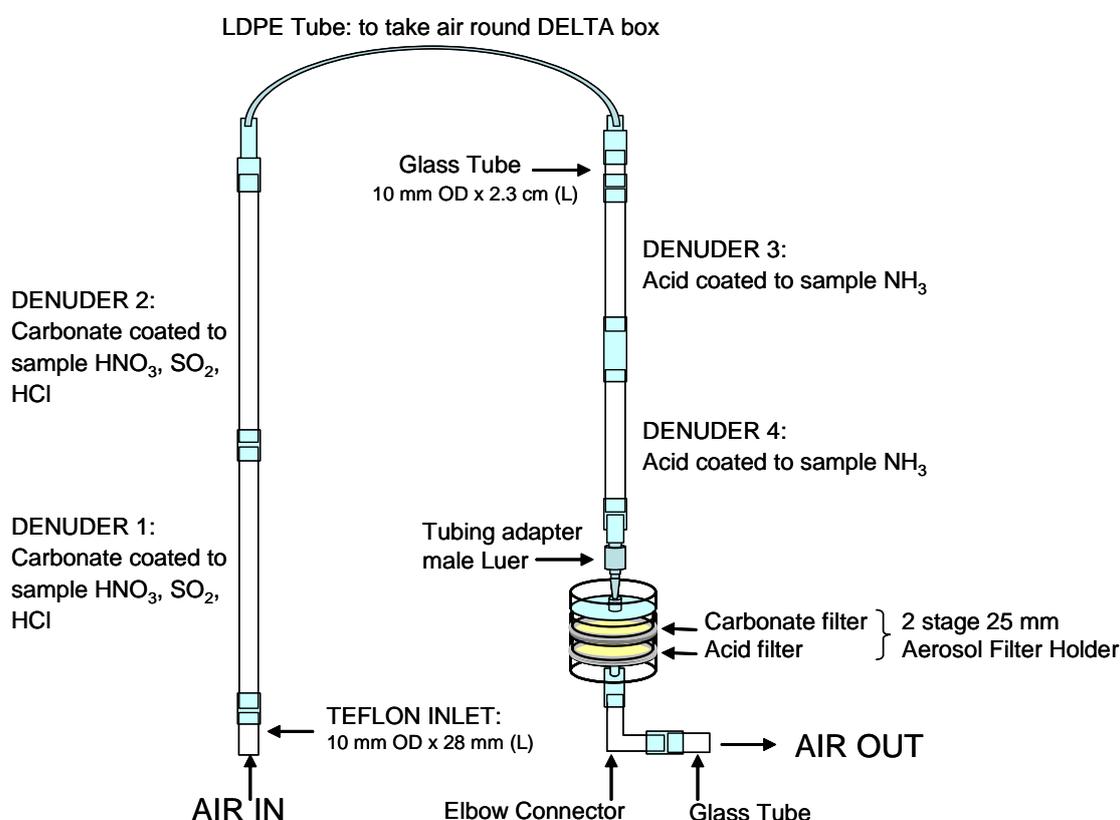


Figure 8: Full sampling train for collecting NH_3 , HNO_3 , SO_2 , HCl , and aerosol NH_4^+ , NO_3^- , SO_4^{2-} , Cl^- , plus base cations Ca^{2+} , Mg^{2+} , Na^+ .

3. EXPOSURE OF SAMPLES

3.1. Setting out sampling trains

1. Disposable gloves should be worn at all times. (This protects the samples from contamination by skin. Also avoid breathing directly on the samples).
2. Read the gas meter and mark this down on a recording card (note that the comma divides m^3 from tenths of m^3). An example record card is shown in Figure 10.
3. Remove protective caps and store the end caps in the gripseal polythene bag.
4. Connect the INLET end (2.3 cm glass inlet or 2.8 cm teflon tube) to the inlet funnel (for the outdoor box). The other end of the denuder assembly should be connected to the silicone tubing which comes from the LHS of the gas meter.
5. For systems using piston pumps: quickly oil the four points of the air pump using the oil (Tellus 37) provided (Figure 11). (The point on the piston cylinder is the most important). The points are (i) the piston cylinder, (ii) the face plate adjoining the piston, (iii) the piston junction with the rotating pin, and (iv) the main bearing.

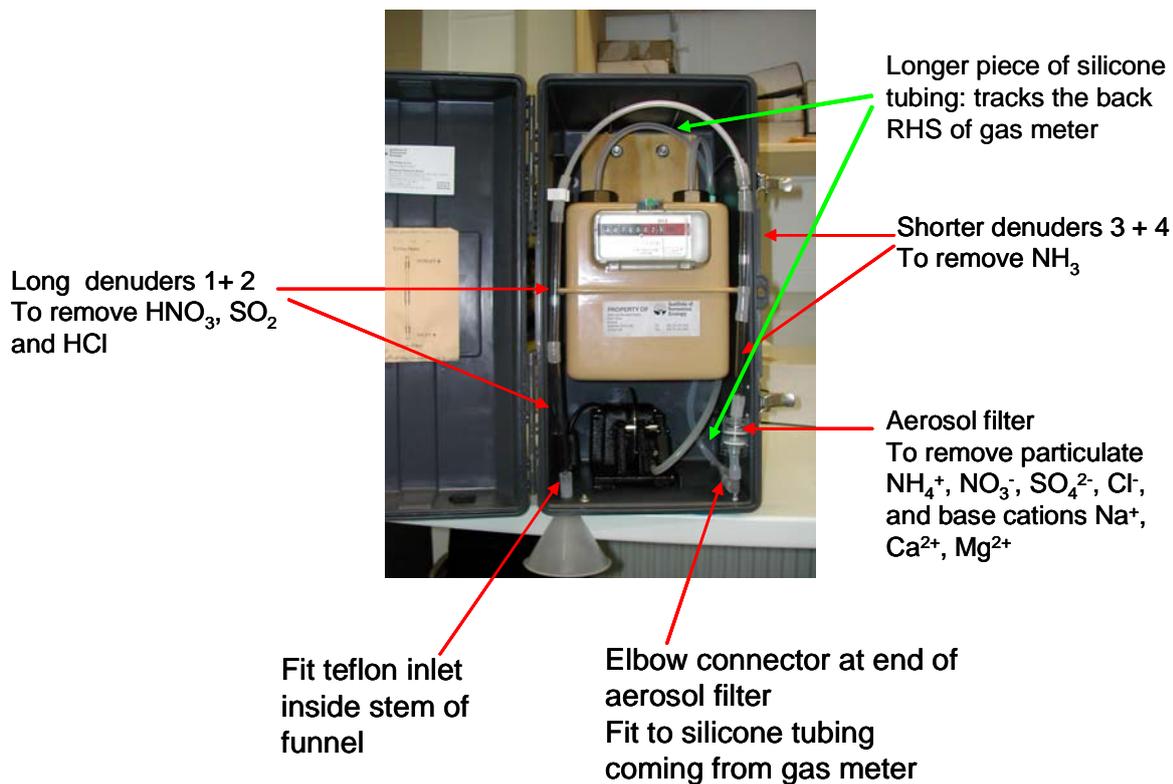


Figure 9: Diagram of Full sampling train installed in an outdoor DELTA system (using a mains powered air pump).

 Centre for Ecology & Hydrology <small>NATURAL ENVIRONMENT RESEARCH COUNCIL</small>	Please indicate if the following events have occurred over sampling period:
AMMONIA SAMPLING RECORD CARD - Denuder	Manure spreading <input type="checkbox"/>
Site Name: _____	When _____
Exposure Period: _____	Proximity _____
Operator: _____	Smell Faint <input type="checkbox"/> Strong <input type="checkbox"/> V. strong <input type="checkbox"/>
Sampling STARTS: Date (dd/mm/yy) _____ Time (24 hr, GMT) _____:_____	Fertilizer Application <input type="checkbox"/>
Gas Meter <input type="text"/> <input type="text"/> <input type="text"/> <input type="text"/> <input type="text"/> , <input type="text"/> <input type="text"/> <input type="text"/> m ³	When _____
❖ Set out denuder ☉	Proximity _____
Sampling ENDS: Date (dd/mm/yy) _____ Time (24 hr, GMT) _____:_____	Smell Faint <input type="checkbox"/> Strong <input type="checkbox"/> V. strong <input type="checkbox"/>
Gas Meter <input type="text"/> <input type="text"/> <input type="text"/> <input type="text"/> <input type="text"/> , <input type="text"/> <input type="text"/> <input type="text"/> m ³	Ploughing of field <input type="checkbox"/>
<ul style="list-style-type: none"> • Collect in denuder, capping ends with caps provided. ☉ • Oil pump with oil provided. ☉ 	When _____
Please use the reverse of this card to record any comments such as problems with the equipment or factors which may have a bearing on the results (Manure being spread, animals nearby etc.). ☉	Proximity _____
Please enclose this card with the samples in the box provided and affix the FREEPOST address label also supplied. Many thanks for your assistance with this project.	Cutting of vegetation <input type="checkbox"/>
In the event of any problems please phone Sim Tang, Mark Sutton or Linda Love. Tel: +44 (0)131 445 4343, Fax: +44(0)131 445 3943, Email: YST@ceh.ac.uk	When _____
Please send me: Oil ☉ Gloves ☉ Spare caps ☉	Proximity _____
	Burning of vegetation <input type="checkbox"/>
	When _____
	Proximity _____
	Animals grazing nearby <input type="checkbox"/>
	Sheep <input type="checkbox"/> Numbers _____ Proximity _____
	Cows <input type="checkbox"/> Numbers _____ Proximity _____
	Others _____
	Presence of insects <input type="checkbox"/>
	Where found _____
	Any other observations which may have an effect on air ammonia concentration:

Figure 10: An example record card for noting sampling information for the DELTA system

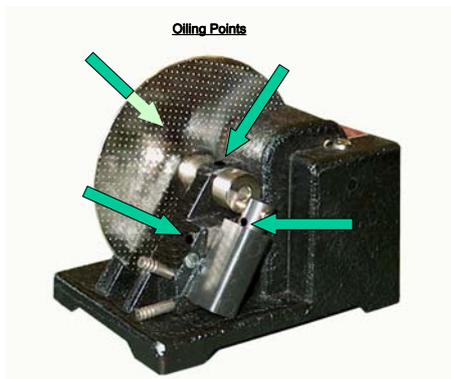


Figure 11: Oiling points on air pump

3.2. Collecting in exposed sampling trains

- 1) At the end of the sampling period, remove the denuder assembly and cap both ends using the caps which were removed at the start of the sampling period.
- 2) Fold over the double denuder and place this in the grip-seal polythene bag.
- 3) Read the gas meter and mark this down on the recording sheet. At flow rates of between 0.3 – 0.4 l min⁻¹, the volume of gas sampled in a calender month will be 12-17 m³.
- 4) The exposed sample should be stored in a clean, cool, dry place and preferably in an airtight box, lined with acid-treated paper. Arrangements should be made for the exposed sample to be returned to the laboratory for analysis as soon as possible after collection.

4. ANALYSIS

Note that disposable gloves should be worn at all times.

4.1. Extraction of denuders

- 1) Store samples at 4°C until analysis,
- 2) Label the glass tubes and aerosol samplers of the denuder assembly with a marker pen,

Denuders 1 + 2: carbonate coated

- 3) Remove the Teflon inlet, separate the denuders and cap each tube with clean caps. The teflon tube is not normally analysed (tests have shown that <1% of the total is captured in this portion), although tests should be carried out at intervals to establish that there is no loss of acid gases to the Teflon inlet.
- 4) Next, add 5 ml 0.05 % H₂O₂ solution to each denuder and replace the caps. Make sure that the caps are on snugly and invert the denuders a couple of times, checking that no leakage occurs. Place these in a test tube rack and leave to extract for approx. 30 mins. Repeat this extraction with all of the samples (including a suitable number of unexposed denuder blanks), noting the time at which the extraction process commenced.
- 5) Invert the samples again several times to ensure thorough mixing before decanting into autosampler tubes.
- 6) The carbonate coated denuders 1 and 2 are analyzed for aqueous NO₃⁻, SO₄²⁻ and Cl⁻ on an Ion Chromatography system.

Denuders 3 + 4: acid coated

- 1) Remove the aerosol sampler and the top glass tube, separate the denuders and cap the tubes with fresh, clean caps.
- 2) Next, add 3 ml deionised water to each denuder and replace the caps. Make sure that the caps are on snugly and invert the denuders a couple of times, checking that no leakage occurs. Place these in a test tube rack and leave to extract for approx. 30 min. Repeat this extraction with all of the samples (including a suitable number of unexposed denuder blanks), noting the time at which the extraction process commenced.
- 3) Invert the samples again several times to ensure thorough mixing before decanting into 3 ml autosampler tubes.
- 4) The acid coated denuders 3 and 4 may be analyzed for aqueous NH₄⁺ on the AMFIA (AMmonia Flow Injection Analysis) system (developed at ECN, Petten, NL). This analysis system is based on selective dialysis of ammonium across a membrane at high pH with subsequent analysis of conductivity. The calibration range normally used is 0 - 10 ppm, together with a number of independent standards (QCs). Other methods suitable for analysis of ammonium include Ion Chromatography and colorimetry (Indophenol blue reaction).

4.2. Extraction and chemical analysis of aerosol filters

Working from the Air INLET end (top end), carefully disassemble the aerosol sampler one section at a time. Using a pair of clean forcep, remove the carbonate coated filter paper first and place in a labelled 20 ml polystyrene container. Care must be taken not to contaminate the filter paper with your fingers. Next, remove the acid coated filter paper and place in a second labelled 20 ml container.

Aerosol Filter 1: carbonate coated

- 1) The carbonate coated filters are extracted in 5 ml of 0.05 % H₂O₂. Cap the container with a clean cap, label with sample name and leave to extract for at least one hour. Repeat this extraction with all of the samples (including a suitable number of unexposed filter pack blanks), noting the time at which the extraction process commenced.
- 2) At the end of the extraction period, using a pair of clean forceps, pinch an edge of the filter paper and dunk it up and down in the extractant a few times to ensure that all the chemical species of interest are released, and that the solution is well mixed.
- 3) Filter the samples with a 0.45 um disposable filter and carefully decant the extracted solution into autosampler tubes, ensuring that there are no fibres in the solution being poured out that can cause blockage in the analytical equipment.
- 4) The filter sample extracts are analysed for NO₃⁻, SO₄²⁻, Cl⁻, Na⁺, Mg²⁺ and Ca²⁺ by IC. The base cations may also be analysed by ICP-OES where the equipment is available.

Aerosol Filter 2: acid coated

- 5) The acid coated filters are extracted in 4 ml of deionised water. Cap the container with a clean cap, label with sample name and leave to extract for at least one hour. Repeat this extraction with all of the samples (including a suitable number of unexposed filter pack blanks), noting the time at which the extraction process commenced.
- 6) At the end of the extraction period, using a pair of clean forceps, pinch an edge of the filter paper and dunk it up and down in the extractant a few times to ensure that all the chemical species of interest are released, and that the solution is well mixed.
- 7) Next, carefully decant the extracted solution into autosampler tubes, ensuring that there are no fibres in the solution being poured out that can cause blockage in the analytical equipment.
- 8) The filter sample extracts are analysed for NH₄⁺ on the AMFIA system, by IC or colorimetry (indophenol blue reaction).

The amount of a trace gas collected (Q) on a denuder due to air sampling is given by:

$$Q = (c_e - c_b) * v \quad (1)$$

Where c_e is the liquid concentration of an exposed sample, c_b is the liquid concentration of a blank sample and v is the liquid volume of the extraction solution.

The air concentrations (χ_a) of the trace gas is then determined as:

$$\chi_a = Q/V \quad (2)$$

where V is the volume of air sampled, which is found directly from the gas meter readings, and is typically 15 m³ per month.

The use of two denuders in series allow for the determination of capture efficiency, by comparing the amounts of the trace gas in both. An infinite series correction factor, based on the capture efficiency, is applied to account for any trace gas not captured by the two denuders. The corrected air concentration ($\chi_{a(\text{corrected gas})}$) is then determined as:

$$(\chi_{a(\text{corrected ammonia})}) = \chi_{a(\text{Denuder 1})} * [1/(1-(\chi_{a(\text{Denuder 2})} / \chi_{a(\text{Denuder 1})}))] \quad (3)$$

At a typical capture efficiency of 90 % in the first denuder, the correction represents 1 % of the corrected air concentration. At 80 %, 75 % and 70 % capture, the correction amounts to 6 %, 11 % and 17 % of the total, respectively. Below 60 % capture efficiency, the correction amounts to

greater than 50 % and should not be applied. The air concentration of the trace gas is then determined as:

$$\chi_a = \chi_a (\text{Denuder 1}) + \chi_a (\text{Denuder 2}) \quad (4)$$

4.4. Calculation of aerosol concentrations

- The air concentration (χ_a) of an aerosol species (for example NH_4^+) from filter pack sampling is determined according to equations 1 and 2 described in section 4.3.

The calculated air concentrations (χ_a) of the aerosol species (e.g. NH_4^+) is also corrected for ammonium which is due to incomplete capture of gaseous NH_3 by the double denuder. The corrected air concentrations ($\chi_{a (\text{corrected ammonium})}$) of NH_4^+ is then determined as:

$$\chi_{a (\text{corrected ammonium})} = \chi_{a (\text{NH}_4^+)} - [(\chi_{a (\text{corrected ammonia})} - (\chi_{a (\text{Denuder 1})} + \chi_{a (\text{Denuder 2})})] \quad (5)$$

Loss of NH_3 due to volatilisation of NH_4^+ from the filter paper has been investigated, by adding a third citric acid coated denuder after the filter pack, and was found to be negligible

The carbonate coated filter paper has also been analysed for NH_4^+ , to check for potential loss of NH_4^+ to the first filter, and was found to be negligible.

4.5. Quality assurance of results

The performance of the denuder system is assessed according to the following tests:

1. Denuder capture efficiency

Over 75% of the total amount of a trace gas in the two denuders should be captured in the first denuder. Values less than this indicates poor capture efficiency in the first denuder, due to an imperfectly coated acid film or some other problems. Below 75 % capture efficiency, the quality of the data becomes less certain, and is subject to a correction factor, as described in section 4.3.

2. Average air sampling rate

The average air sampling rate for denuders must be $> 0.22 \text{ l min}^{-1}$. The air pumps used are relatively stable, at $0.25 - 0.4 \text{ l min}^{-1}$. Low measured flow rates indicate that the pump may need oiling, or servicing, that an extended power cut has occurred or that there is a leak in the system.

5. CLEANING PROCEDURES

5.1. Glass components

1. Soak in approx. 1 % Decon (or equivalent lab detergent) solution for at least an hour,
2. Rinse several times with tap water,
3. Rinse 3 times with deionised water,
4. Shake off as much of the water as possible,
5. Dry in oven at up to $100 \text{ }^\circ\text{C}$,
6. Remove all components as soon as they are dry. Never leave them sitting around in the ovens longer than necessary, to minimise contamination,
7. Put on clean gloves and carefully put away the components in clean airtight storage containers or gripseal bags.

5.2. Plastic components

1. Remove all labels, and disassemble all components before washing,
2. Soak in approx. 1 % Decon (or equivalent lab detergent) solution for at least an hour,
3. Rinse several times with tap water,
4. Rinse 3 times with deionised water,
5. Shake off as much of the water as possible,
6. Dry in oven at 40-50°C,
7. Remove all components as soon as they are dry. Never leave them sitting around in the ovens longer than necessary, to minimise contamination,
8. Put on clean gloves and carefully put away the components in clean airtight storage containers or gripseal bags.

6. REFERENCES

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