

8th November 1973

SAMPLING OF WATERSOLUBLE AEROSOL CONSTITUENTS.  
DETERMINATION OF NITRATE, AMMONIUM, POTASSIUM, CALCIUM,  
AND MAGNESIUM IN AEROSOL AND PRECIPITATION SAMPLES.

-----

1 INTRODUCTION

The determination of the above mentioned constituents was included in the voluntary measurement programme under the first measurement phase of the LRTAP-project. A voluntary testing of the methods has been conducted in Scandinavia under the NORDFORSK programme for testing of methods which could be applied in the OECD Programme.

A brief presentation of the arguments for an extended sampling and chemical analysis programme is given in LRTAP - 2/73, "Extension of ground sampling programme in the Second Measurement Phase".

According to the plan for the second measurement phase, aerosol and precipitation samples at selected sampling sites should be analysed for strong acid and watersoluble sulphate, ammonium, nitrate, calcium, sodium or magnesium and the aerosol sample should also be analysed for soluble iron (III) because of the effect of this ion on the titration results.

In the following details are given of technical procedures for sampling and chemical analysis, as developed and tested in the NORDFORSK programme.

No special details are given for the precipitation sampling which is supposed to be according to specifications given in LRTAP - 3/72.

## 2 SAMPLING APPARATUS

### 2.1 Alternative\_1: Separate sampling for strong acid in the particulate phase.

Reference is made to the enclosed report by Askne, Brosset and Ferm (1). A recently developed membrane filter\*, made from fluocarbon polymer, has been found which is sufficiently inert to allow determination of strong acid for air sample volumes of about 10 m<sup>3</sup>.

An additional sampler is required for the determination of the other constituents. Either a LIB aerosol sampler or a high-volume sampling apparatus should be used. The filter material should be Acropor 3000 or 5000\*\*.

### 2.2 Alternative\_2: High-volume sampling for strong acid and other watersoluble aerosol constituents.

A drawing of the high-volume sampling apparatus is given in Figure 1. This apparatus is identical with the apparatus used and tested at Råö (2). The diameter of the LIB-type sond is 400 mm and the vertical duct has an inner diameter of 92 mm.

A Becker fan-type air pump powered by a 3-phase AC motor draws approximately 125 m<sup>3</sup> of air per hour through a 142 mm diameter Acropor 5000 membrane filter. These filters have low flow resistance and good mechanical strength. The retention efficiency has been tested and found to be satisfactory at the suggested flow rate.

---

\* Fluoropore, Millipore Corp., Bedford, Mass. (USA).

\*\* Acropor, Gelman Products Inc., Ann Arbor Mich. (USA).

### Sampling

The samples should be taken on a regular 24-h sampling basis. Samples should be changed at 0700 GMT  $\pm$  1 hour as in the regular network.

Exposed Fluoropore filters are placed in airtight containers. Acropor filters are placed on filter separating discs, and folded once with the exposed surface in. The sample is then put into an airtight envelope or plastic bag for transport and storage.

Sample air volume is recorded with each filter. Either gas meters or flowmeter readings are used. The high-volume sampling apparatus has a venturi flowmeter immediately after the filter. Readings of sampling flow rate should be taken at the beginning and at the end of the sampling period. The sampling volume given should be accurate to the nearest  $\pm$  10%.

### 3 CHEMICAL ANALYSIS OF WATERSOLUBLE AEROSOL

The Acropor filters are of fairly constant weight. After conditioning the samples may therefore be weighed to give the total amount of airborne particulate matter. It is then placed in a stoppered 300 ml round flask and shaken with exactly 200 cm<sup>3</sup> bidistilled or deionised water for 30 minutes. 50 ml is transferred for the titration of strong acid. Other aliquots are taken, and if necessary diluted with distilled or deionised water (of the required purity) for determination of sulphate, ammonium, sodium or magnesium, calcium, iron, and other constituents which may be of interest.

#### 4 ANALYTICAL PROCEDURES FOR THE DETERMINATION OF INDIVIDUAL COMPONENTS

For the determination of strong acid is referred to LRTAP - 5/71 and to the enclosed IVL Report B-157, determination of sulphate should be according to LRTAP - 4/71. The recommended methods for the other constituents have been selected among proven standard methods used in water analysis. Collaboratory testing of the analysis methods have been carried out by NORDFORSK's group for water analysis.

##### 4.1 Determination of ammonium

###### 4.1.1 Principle

Ammonium is determined by the reaction with hypochlorite, phenol and nitrosylpentacyanoferrate (II) catalyst in citratebuffered alkaline solution, which gives indophenol blue. The concentration of this dye is determined spectrophotometrically by measuring the absorbance at 630 nm.

###### 4.1.2 Procedure

The enclosed procedure by Koroleff has been translated from the NORDFORSK report (3) by permission from the author and NORDFORSK (Enclosure 2).

##### 4.2 Determination of nitrate

###### 4.2.1 Principle

Nitrate is reduced to nitrite by passing alkaline ammonium chloride buffered solution through a reductor column filled with cadmium amalgam or copperized cadmium. Nitrate is reacted with sulphanilamide and N-1-naphtylethylene-diamine to give an azo dye, the concentration of which is measured by the light absorbance at 520 nm or 545 nm.

#### 4.2.2 Procedure

Two procedures are recommended, a manual procedure due to Koroleff (4), which is enclosed (Enclosure 3), and an automated procedure based on the Technicon Autoanalyzer, by Henriksen and Selmer-Olsen (5).

#### 4.3 Determination of Ca, Na and for Mg and Fe

The concentration of these elements are determined by atomic absorption spectroscopy using an air-acetylene flame. Reference is made to manuals and recommended procedures issued by instrument manufacturers.

#### 4.4 Determination of K and Al (voluntary)

For the determination of potassium by atomic absorption or flame emission a red-sensitive photomultiplier must be used ( $\lambda = 766,5 \text{ nm}$ ) and cesium nitrate of the required purity should be added to suppress ionization. In addition to iron (III), the concentration of watersoluble Al (III) ions may be of importance for the strong acid titration (1). The determination should be carried out by atomic absorption spectroscopy using a nitrous oxide-acetylene flame.

#### REFERENCES

- |     |                                     |  |
|-----|-------------------------------------|--|
| (1) | C Askne, C Brosset and M. Ferm      | Determination of the proton-donating property of airborne particles.<br>IVL Report B 157<br>Swedish Air and Water Pollution Research Laboratory, Gothenburg, 1973. |
| (2) | K Andreasson, C Brosset and B Steen | Investigation of Long Distance Transported Air-borne Particulate Matter during the December Episode 1972.  |

IVL Report 154  
Swedish Air and Water Pollution  
Research Laboratory, Gothen-  
burg, March 1973.

- (3) Ingvar Dahl (ed) Interkalibrering av indofenol-  
metoden för bestämning av am-  
moniakk.  
NORDFORSK, Miljøvårdssekretari-  
atet 1973:1.
- (4) Idem Interkalibrering av metoder för  
bestämning av nitrat og total-  
nitrogen.  
NORDFORSK, Miljøvårdssekretari-  
atet 1973:3.
- (5) A R Selmer-Olsen and Automatic methods for Deter-  
A Henriksen mining Nitrate and Nitrite  
in Water and Soil Extracts.  
Analyst, 95, 514-518 (1970).

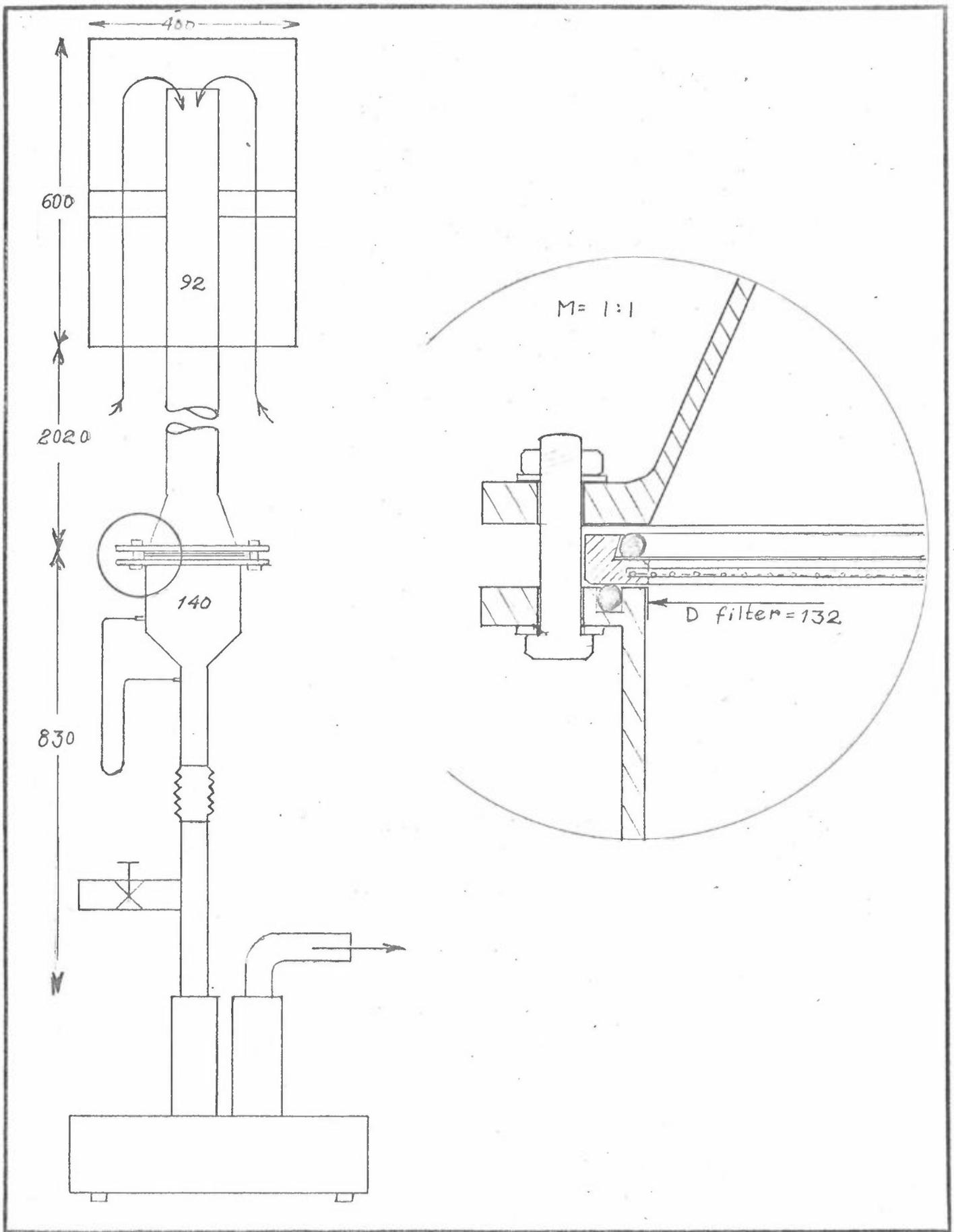


Figure 1: High-volume aerosol sampling apparatus.  
 Scale 1:1. Construction material  
 aluminium alloy. 57 S.