

DETERMINATION OF STRONG ACID AND SULPHATE IN PRECIPITATION1 INTRODUCTION

This document describes the sampling apparatus to be used and the procedures to be followed for the sampling and chemical analysis of precipitation in the pilot phase of the LRTAP Programme in 1972-73.

2 SAMPLING APPARATUS2.1. General description

The apparatus will normally consist of a stand with a collecting funnel and a storage container. The sampling apparatus should be constructed and positioned so as to give also the amount of precipitation, although this is normally obtained from a precipitation gage on the same site. The funnel should have a cylindrical upper section with vertical walls.

2.2. Collecting funnel

The diameter of the funnel should be between 20 and 40 cm, so that a rainfall representing more than 1/1000 of the annual precipitation will give a sufficiently large sample for chemical analysis. According to WMO<sup>1</sup> recommendations, the height of the cylindrical section should be at least equal to the diameter and the angle of the conical sections should be at least 45° from the horizontal, Fig. 1 (A).

---

<sup>1</sup> World Meteorological Organisation: Guide to Meteorological Instrument and Practices, WMO - No 8, TP 3 (4th Ed, Geneva 1971)

The material in the funnel should be polyethylene or borosilicate glass.

### 2.3. Sample\_container

The collecting bottle should be made from borosilicate glass or polyethylene. The volume should be large enough to prevent overflow. The container should be shaded against direct sunlight.

### 2.4. Guard\_ring

The stand should be equipped with a guard ring above the funnel to keep birds away from the funnel.

### 2.5. Snow\_collection\_apparatus

When the precipitation is in the form of snow, the functions of the collecting funnel and bottle may conveniently be combined by using a dustfall deposit type jar manufactured from high density polyethylene such as shown on Fig. 1 (B).

If a funnel is used, the height of the cylindrical section should be increased to at least 50 cm.

The collection apparatus should be equipped with a lid which should be used when the equipment is transferred indoors for the snow to melt. Two sets of snow collection apparatus are needed for each station.

## 3 SAMPLING

### 3.1. Sampling\_periods

Samples should be collected each day at 07.00 G.M.T.  $\pm$  2 hours. In addition, sampling at 6 h intervals should be conducted under special "alert" periods. 6 h sampling periods will be announced by the CPU (Central Project Unit) under special weather conditions, and should be made operative in each of the participating countries.

within 24 hours after receiving the message (by cable or telephone)

### 3.2. Sample collection

At the end of the sampling period, the sample is decanted into a graduated measuring cylinder for recording of the volume and a suitable aliquot is transferred to a polyethylene or borosilicate glass bottle for subsequent chemical analysis.

### 3.3 Cleaning

The funnel and the collecting bottle are then rinsed with distilled water before being put up again.

The rinsing with the distilled water should be conducted also if there has been no rainfall in the sampling period.

## 4 CHEMICAL ANALYSIS

### 4.1. Determination of sulphate

The sulphate concentration should be determined by the barium perchlorate-Thörin method, after removal of interfering cations by ion exchange. The procedure for the spectrophotometric determination has been given in LRTAP 4/71.

An automation of this procedure is possible by using a Technicon Autoanalyser or an instrument based on similar principles.

### 4.2. Determination of strong acid

The concentration of (excess) strong acids should be determined by titration using Gran's plot evaluation of the endpoint. The distributed procedure given by Brosset and Askne<sup>2</sup> or the procedure given in LRTAP 5/71 have been tested and found to give equivalent results. The latter procedure may be automated by using an analog amplifier element and a potentiometric recorder in connection with the pH-meter.

---

<sup>2</sup> C. Brosset and C. Askne: IVL report B 107, Gothenburg, Sweden, December 1971

within 24 hours after receiving the message (by cable or telephone)

### 3.2. Sample collection

At the end of the sampling period, the sample is decanted into a graduated measuring cylinder for recording of the volume and a suitable aliquot is transferred to a polyethylene or borosilicate glass bottle for subsequent chemical analysis.

### 3.3 Cleaning

The funnel and the collecting bottle are then rinsed with distilled water before being put up again.

The rinsing with the distilled water should be conducted also if there has been no rainfall in the sampling period.

## 4 CHEMICAL ANALYSIS

### 4.1. Determination of sulphate

The sulphate concentration should be determined by the barium perchlorate-Thorin method, after removal of interfering cations by ion exchange. The procedure for the spectrophotometric determination has been given in LRTAP 4/71.

An automation of this procedure is possible by using a Technicon Autoanalyser or an instrument based on similar principles.

### 4.2. Determination of strong acid

The concentration of (excess) strong acids should be determined by titration using Gran's plot evaluation of the endpoint. The distributed procedure given by Brosset and Askne<sup>2</sup> or the procedure given in LRTAP 5/71 have been tested and found to give equivalent results. The latter procedure may be automated by using an analog amplifier element and a potentiometric recorder in connection with the pH-meter.

---

<sup>2</sup> C. Brosset and C. Askne: IVL report B 107, Gothenburg, Sweden, December 1971

#### 4.3. Determination of pH

The pH of the precipitation should be determined with a first class laboratory pH-meter according to ordinary laboratory practice, using a glass electrode and with 0.05 M potassium biphthalate as primary standard, according to NSB or British Standard recommendations.

#### 4.4. Other determinations

The concentrations of sodium, magnesium or chloride should be determined in order to enable an estimation of the amount of sulphate originating from sea-spray.

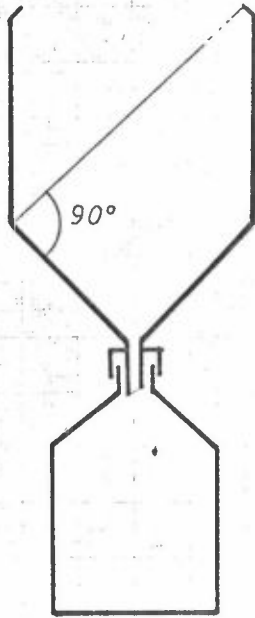
Other ions which should be determined on a voluntary basis include ammonium, nitrate, potassium and calcium.

Whenever possible, these constituents should be determined by standard laboratory methods, such as for instance atomic absorption or flame photometry for the metal cations.

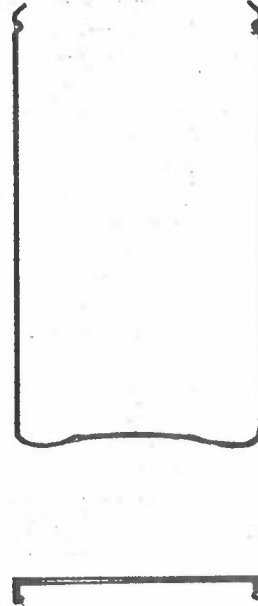
Nitrate may be determined by reduction to nitrite and coupling with the Griess-Ilosvay reagent, ammonium by the reaction with Nessler's reagent.

### 5 COLLABORATIVE TESTING

The CPU will circulate both synthetic and real precipitation samples at regular intervals in order to keep a constant check on the interlaboratory precision of the chemical determinations. In addition to this, each of the participants will be expected to send 5 x 100 ml aliquots of representative precipitation samples each month to the CPU, who will arrange for the samples to be analysed both at the CPU and at a third laboratory.



A.



B.

Proposed precipitation sampling apparatus

- A, for rain samples
- B, for snow