

DETERMINATION OF SULPHUR DIOXIDE IN AIR AND AIRBORNE
SULPHATE IN THE PARTICULATE PHASE

1 INTRODUCTION

This document describes methods to be used for sampling, chemical analysis and collaborative testing during the pilot measuring phase of the LRTAP programme in 1972-1973.

2 SAMPLING

2.1. General

The principle of the sampling apparatus is shown in Fig. 1. It has been chosen to allow the use of existing equipment which has been used in most of the participating countries in connection with urban air pollution studies¹. The main modification of this apparatus has been the incorporation of a special air intake, which is a modified Herpertz- or LIB-sond.

The following specifications are recommended:

2.2. Air intake

An inverted funnel, 60° with lower cylindrical section, height 150 mm, diameter 75 mm.

2.3. Filter holder

The filter holder should be made from gold-plated brass or high density polyethylene. The filter holder should be designed to give an even deposition of particles over the exposed filter area. The filter holder should be maintained at a temperature higher than that of the outside air, preferably so that the relative humidity of the air inside the filter holder will not exceed 50°.

¹ Methods for measuring air pollution, OECD, Paris, 1964.

The diameter of the filter area should be chosen so as to give an air flow of 17 ± 3 liter/cm² hour. This corresponds to an effective filter diameter of 25 or 33 mm at sampling rates of 2.0 or 3.6 m³/24 h, respectively.

2.4. Filter

Whatman 40. Ashfree paper filter.

2.5. Absorption_bottle

Use a simple bubbler such as a Drechsel bottle or equivalent, made from borosilicate glass or polyethylene. The dimensions should be chosen so that the height of absorption solution will be at least 25 mm above the air inlet at the end of the sampling period. The loss of sample by aerosol droplet formation during the sampling period should be determined, and if this is more than 10 %, either the design of the bubbler should be altered or a correction factor should be given.

2.6. Absorption_solution

0.3 % H₂O₂ in de-ionized and distilled water, acidified to pH 4.5 with perchloric acid.

2.7. Tubing_and_connections

The connection between the air intake and the filter holder should be made from borosilicate ("Pyrex") glass. The length should not exceed 2 m and the diameter should be chosen to give a mean air velocity of 0.8 - 1.0 m/s. (Inner diameter 5.5 to 6.0 or 7.2 to 8.0 mm, respectively). Other tubings and connections may be polyethylene or borosilicate glass.

2.8. Pump

Normally a membrane pump will be selected because of its constant performance. The rate of suction should be either 2.0 or 3.6 m³/24h with the recommended filter and absorption solution.

2.9. Gas_meter

Either a dry gas meter or a calibrated rotameter may be used. If a rotameter is used, readings should be taken both at the

start and at the end of the sampling period. The sample air volume should be given with an accuracy of better than $\pm 10\%$. Also, the temperature of the air at the metering position should be given (to the nearest 5°C).

2.10 Sequentializer

If a sequential air sampler is being used, adequate precautions should be taken to ensure that the sample air volume is correctly given by one of the three following alternatives:

- a. taking rotameter readings with all filters and absorption bottles before and after the sample collection,
- b. recording the gas meter volume at each sample change,
- c. incorporating a device to maintain constant flow irrespective of pressure drop up to 100 cm of water and reading only the total volume on the gas meter.

3 SAMPLING PROCEDURE

Samples should be changed at 0700 G.M.T. ± 2 hours

The final volume (or weight) of absorption solution should be recorded and the samples transported and stored in the dark in polyethylene or borosilicate glass, preferably refrigerated, before the chemical analysis. The filters should be sent and stored in the filter holders or in other satisfactory containers.

4 CHEMICAL ANALYSIS

The amount of sulphur dioxide converted to sulphate in the absorption solution is determined spectrophotometrically by the barium perchlorate-Thorin method described in LRTAP 4/71 or an automated version of this procedure.

The amount of sulphate collected on the filter is determined by the X-ray fluorescence of the sulphur K_{α} -line, using impregnated filters as reference standards. The recommended

procedure for this determination is given in LRTAP-4/72. enclosed.

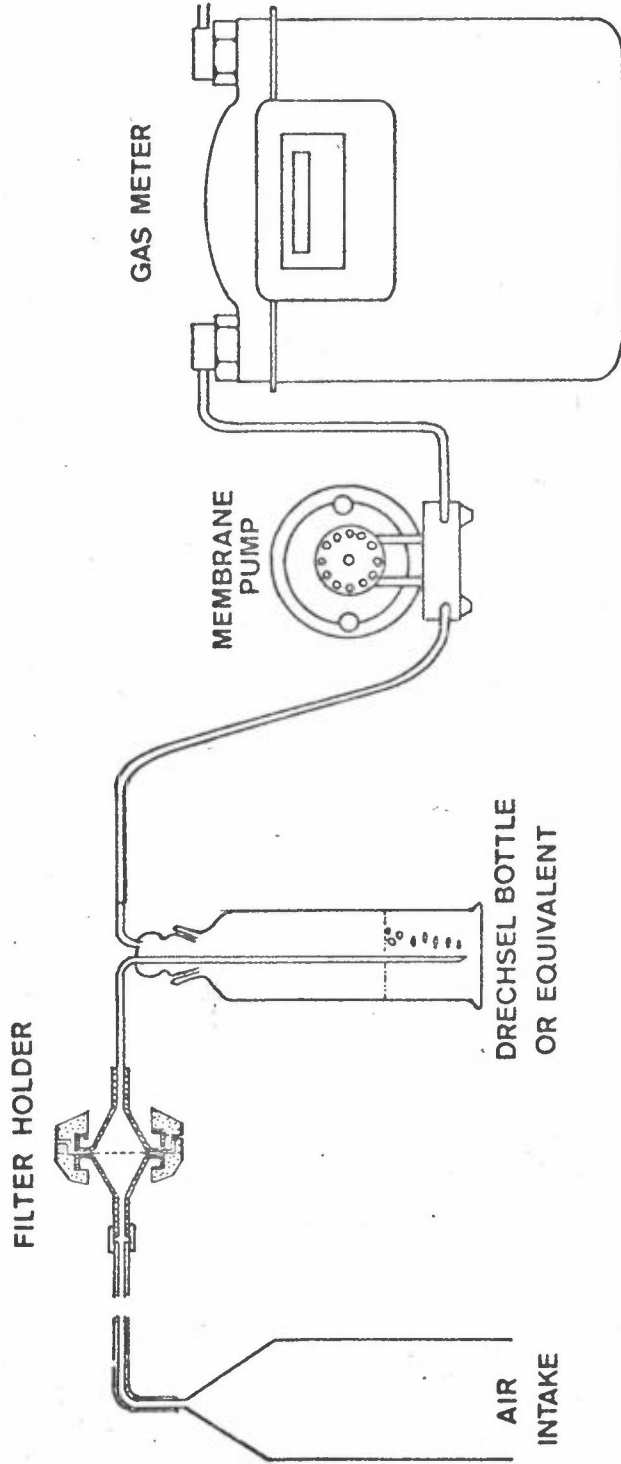
The results are expressed as μg sulphur dioxide (SO_2) and μg sulphate (SO_4) per sample and per cubic metre.

5 COLLABORATIVE TESTING OF METHODS

The CPU will circulate synthetic standards and analyzed samples at regular intervals in order to keep a constant check on the interlaboratory precision of the proposed methods for chemical analysis.

In addition to this, each of the participants are asked to send 5 representative 20 ml sample solution aliquots and 5 analyzed filters to the CPU every month.

The CPU will then arrange for the samples to be analysed both at the CPU and at a third participating laboratory.



Simple air sampling equipment

Figure 1