

DETERMINATION OF SULPHUR DIOXIDE AND OF SULPHUR ON PARTICULATES  
IN THE ATMOSPHERE

INTRODUCTION

1. The present paper gives detailed descriptions of methods to be used for sampling, chemical analysis and testing of methods. The actions to be taken by laboratories wanting to participate in the programme, are given in the last chapter.

At the expert meeting in June, it was decided that the simple OECD apparatus or similar equipment, possibly fitted for sequential sampling, should be used. The reader is referred to the OECD booklet which gives a description of this equipment. As in many countries equipment of a similar (but not identical) type is used, the essential features which should be standardized, are given in the following.

SAMPLING

2. Generally, the fundamental equipment consists of an air intake, a filter holder, a bubler, and a pump. Several of these units may be built together and controlled by a timing unit to obtain sequential sampling.

Several types of this equipment are commercially available and may be used for the present investigation provided they fulfil the requirements given below.

2.1. The pump

In most cases a membrane pump is used because of the relatively low price and constant performance. The rate of suction should be between 2 and 4 m<sup>3</sup>/24 hours. In selecting a pump, one has to make

sure that adequate capacity is obtained with the filter to be used.

The suction rate may be controlled in two different ways. A gas-meter may be placed immediately in front of the pump and the volume read off every 24 hours. Or one may use a flowmeter to control the suction rate every 24 hours. In this case the pump rate should be measured by mounting a flow meter instead of the regular air intake. The pump rate should first be measured with the exposed filter in place, then again when the new filter has been mounted. The mean value of the two readings should be used to obtain a correction for the reduction in flow rate which takes place as the filter collects more and more particles during the 24 hours exposure time. In areas outside cities or industrial areas, the volume obtained in this manner is expected to be within an error of  $\pm 5\%$ .

If a sequential sampler is used, corresponding readings must be taken for each of the collecting lines when the equipment is attended to. The operator then must turn on each pump manually to do the measurements. At this point there is a certain danger that the operator will confuse the bottles, therefore a very strict written procedure should be laid down for this operation.

The gas meter should be designed for the proper pumping capacity. Often second hand meters from gas works are used, and extrapolations have to be made to observe the low flow rate. In this case, it is essential to calibrate the meter for the proper pumping rate.

The flow meter should be a properly calibrated meter of the type with a floating ball or spindle. This instrument may remain with the operator, who may use it to control several samplers.

In discussing the accuracy of the air flow measurements, one should not forget the influence of air temperature differences at the intake and in pump or gas meter. From the gas law one may

calculate that a temperature difference of  $10^{\circ}\text{C}$  corresponds to an error of 5 % in the volume.

In some countries during winter the error may be much larger from this cause. It may then be advisable to use a couple of simple thermometers which are read off from time to time to obtain a correction factor.

For the present study, it is considered that it will be sufficient if the volume error is within  $\pm$  5 %. The laboratory responsible for the measurements should look into this problem and take appropriate action.

## 2.2. Bubler

Tests conducted in this laboratory have shown that when polyethylene is used, the measured sulphur dioxide content may increase if the absorption liquid is left in the bottle, with a suction rate of  $3,6 \text{ m}^3$  in 24 hours, the increase of the content approached asymptotically a value corresponding to  $3 \mu\text{g per m}^3$  after a few weeks. If the solution is exposed to direct sunshine the increase takes place in a few days. The reason for this behaviour is not yet quite clear. The observations made will be given in a separate note. The effect may be sufficiently suppressed if the sample is not left in the bottle for more than one week (sequential sample) and later stored in a refrigerator.

If the liquid level in the bubler is at least 60 mm above the gas inlet, no diffuser is needed. This is of some importance as a diffuser offers more resistance to the pump. The amount of liquid normally used in the bubler is 100 ml. The liquid to be used is specified in the analytical procedure. It should be checked that there are no air leaks in the bubler.

## 2.3. Filter

The filter holder is connected in front of the bubler. Different types of filter holders may be used, but the free opening of the filter should be standardized to a diameter of 25 mm.

Measurements indicate that in some filter holders the material used may absorb sulphur dioxide. It is however believed that this absorption is of little consequence when the sample is drawn over 24 hours.

A filter holder made of polyethylene in use at the Norwegian Institute for Air Research, does not absorb appreciable quantities. An other type in which rather large metal surfaces were exposed to the air, seems to be unfavourable. According to experience from corrosion experiments, metal surfaces always hold salt particles, unless they are cleaned according to special procedures. This salt will absorb moisture and form a liquid layer on the surface. When the metal surfaces are exposed to sulphur dioxide in corrosion experiments, the sulphur dioxide is readily absorbed in this liquid and oxidised to sulphuric acid.

Filter holders with exposed metal surfaces are therefore not favoured. If they are used, the metal surface may have to be cleaned or pretreated in some way.

Experiments show that various filter materials absorb different amounts of sulphur dioxide. Whatman Nr 1 filters absorb a measurable amount of sulphur dioxide initially (before an equilibrium is obtained after passing a few liters of polluted air), while the absorption by a Whatman Nr 41 is virtually nothing. The main difference between the two filters is the purity (Nr 41 is a double acid washed quality).

Similar experiences have been made with glass fibre filters. These filters, when untreated, absorb substantial quantities of sulphur dioxide. After an acid wash, the absorption is negligible.

Again it seems likely that salts which absorb moisture from the air are responsible for the absorption. This will be studied more closely.

The filter should have a free circular opening of 25mm diameter. A Whatman 40 is to be used in this study. The pressure drop across this filter will be equivalent to 26 cm of water at a suction rate of 2.5 l/min.

#### 2.4. Air intake

The air intake should have a conical shape provided with a lower cylindrical part. The height of the cylindrical part should be twice the diameter to suppress effects of turbulence. The air intake may be made from glass, plastic or metal. The air intake velocity should be 1,0 cm/sec, to obtain a definite cut off with respect to particle size. The specified velocity rules out particles larger than approximately 10  $\mu$ .

#### 2.5. Connections

The tubing between the air intake and the filter holder should be as short as possible and should not exceed 4 m. The material should be teflon FEP or polyethylene.

The connection between filter holder and bubbler should be very short and may be made from polyethylene tubing.

To obtain a fixed mounting for the air intake, the plastic tube may be thread inside a metal tube which is fixed to the outside wall.

#### 2.6. Operation

The sample should be collected over 24 hours, and changed at 07  $\pm$  2 h GMT. If a sequential sampler of 8 units is used, it is customary to change while bottle nr 8 is in operation. Bottle nr 8 is then left for another week in the sampler. For reasons mentioned under 2.2, this should be avoided. In practice, the easiest thing probably is to collect bottle nr 8 the following day.

### 3. CHEMICAL ANALYSIS

The chemical analysis of sulphur dioxide with the Thorin method is described in a separate paper. The sulphur on filter papers

should be determined by X-ray fluorescence. The procedure for making is described in a separate paper.

Filter paper standards for the X-ray fluorescence measurements is described in a separate paper.

To ensure comparability of results, it is very important that the methods described are meticulously followed. If a laboratory for some reason comes to the conclusion that alterations are needed, this should be reported to the CPA, while the routine analysis follows the specified method until notice is given from the CPA. Although this may result in inferior data over a period, this procedure has to be followed, otherwise the results from different laboratories will not be comparable.

#### 4. INTERCALIBRATION OF METHODS

In the following are given the procedures to be followed for standardization and comparison of results from the different laboratories.

##### 4.1. Determination of sulphur dioxide

The standard samples consist of dilute solutions of sulphuric acid in 3 % hydrogen peroxide. The essential point in making these standard solutions is the purity of the water. At this laboratory the water is produced through the following operations:

1. ion exchange
2. distillation (glass still)
3. ion exchange (in a mixed-bed cartridge reserved for this purpose)
4. filtration through a bacterial filter (Gelman Acropor)

The specific conductivity of the product should be less than  $1 \times 10^{-6} \text{ ohm}^{-1} \text{ cm}^{-1}$ .

The standard samples are kept in polyethylene bottles and will not change composition over a period of several months.

As soon as a laboratory reports positively on the attached questionnaire, five standard samples will be sent to the laboratory. For two of these standard samples, the exact content is given. For the three others, only approximate values are given.

The laboratory is asked to perform triplicate analysis of each sample and send the results expressed in  $\mu\text{g/ml SO}_2$  back to the CPA.

As a further control, the laboratory is asked to send 25 ml of sample taken during the first few weeks to the CPA. A total number of 20 samples are expected. These samples will be analysed in 2 laboratories and the results sent back to the laboratory in question. Details of this procedure will be given later.

#### 4.2. Sulphur on filters

In a separate paper a detailed description of how to prepare standard samples of sulphur for X-ray fluorescence measurements is given. The laboratory will thus be able to make its own standards. For further comparisons, standard samples provided by the CPA will be mailed to the laboratory.

During the first weeks of measurement, the samples collected by the laboratory should after measurement there be sent to the CPA which will arrange for 20 samples to be analysed at two different laboratories.