

PROCEDURES FOR AIRCRAFT SAMPLING AND CHEMICAL ANALYSIS1 INTRODUCTION

The procedures described below have been designed specifically for measurements of the concentrations of sulphur compounds in the free atmosphere using light aircraft. They are based on developments and practical experience by laboratories in Germany, the United Kingdom, Sweden and Norway, and are recommended for use in connection with the aircraft sampling programme of the OECD LRTAP programme.

2 SAMPLING OF AEROSOL SULPHATE AND SULPHUR DIOXIDE.2.1 Principle.

The air sample is drawn through an air intake, and a filter holder containing two filters in series. The first filter is used to collect aerosol particles, the second filter, which is impregnated with potassium hydroxide, is used to collect sulphur dioxide.*

After exposure the filters are analysed by wet chemical analysis, either by the barium perchlorate-Thorin method or by isotopic dilution analysis (IDA) after Klockow.

*Alternatively, two identical sampling equipments are used simultaneously, one with an aerosol filter and the other with an impregnated filter for collecting both aerosol particles and gaseous sulphur dioxide. With this arrangement the air passing to the aerosol sampler may be slightly heated to avoid absorption of SO₂ in a moist aerosol filter. The air passing to the impregnated filter must not be heated as this will reduce absorption efficiency for the SO₂.

X-ray fluorescence spectroscopy may be used as a non-destructive method to estimate the amount of sulphur collected on the sample filter. Because of the absorption of X-rays in the filter material, the fluorescence intensity depends critically on the distribution of sulphur with depth in the filter material. This may vary with humidity and flow rate through the filter, and will also be different for the aerosol and the impregnated filters.

It is possible to use wet analytical techniques for sulphate after the X-ray fluorescence measurements.

2.2 Air intake

The sulphate originating from anthropogenic sources have been formed in the atmosphere by oxidation of sulphur dioxide and is present as particles in the submicron size range. Strict isokinetic sampling therefore is not necessary. However, in order to avoid ram pressure, ice formation and other effects due to the disturbance of the air flow, it is suggested that the air intake should have an isokinetic nozzle.

The air intake should be covered by a lid which can be operated from the cabin.

The tube connecting the nozzle to the filter holder should be as short as possible and not exceed a length of 1,0 m. A straight or a bent air intake tube may be used (front or side intake). More important than this difference is the length of the tube. All materials will absorb and desorb SO_2 more or less. Useful materials are aluminium alloys and stainless steel which may be passivated or plastic.

Sulphur dioxide is slightly soluble in most plastic materials, (1). This solubility is too small to be of practical consequence in this connection. Polyethylene, polypropylene and teflon FEP may be used as construction materials.

Before sampling the air intake tube should be flushed for 10 minutes under sampling conditions in order to remove pollutants accumulated in the tube while the aircraft was on the ground.

For a discussion of the possibilities of the absorption of gases in the air intake tube and design criteria reference is made to Charlson (2).

Because the efficiency of the impregnated filter as a collector for sulphur dioxide depends on the relative humidity, only a small heating of the sample (less than 2°C) should occur in air intake.

2.3 Filter holder

The parts of the filter holders which are in contact with the air sample should be of an inert material, i.e. a material which does not absorb or give off sulphur dioxide or sulphur. Again, polyethylene and polypropylene are satisfactory. Silicon elastomers may be used for O-rings.

It is recommended that the exposed filter area should be circular with 22-42 mm diameter. The larger diameter will be required for leaching of the filters and determination by the Thorin method, while the smaller diameter is sufficient for the IDA method.

Because of the need for filters with low sulphate blanks, ash-free cellulose fiber filters (Whatman 40 or Schleicher and Schüll 589 2L) is used. The sulphate blank content of these filters are typically 0.02 µg/cm².

Typical flow resistance for a single filter is 0.5 atm at a linear air speed of 50 cm/s. This corresponds to sampling rates of 15 litres/min for 22 mm diameter and 40 litres/min for 42 mm diameter with two filters in series and a pressure drop of 0.5 atm. A support must be provided at the back of the filters to prevent ruptures. Drawings of filter holders are given in *Enc. 1* and *2*. A polypropylene support screen is incorporated in the Swinnex filter holder, manufactured by the Millipore Corporation.

During the sampling the filter holder will be subjected to a vacuum of 0.5 atm. Experience has shown that fibre filters leak radially when clamped between the blocks in a filter holder. In this connection it is particularly important to avoid contamination in the sampling compartment. Most of the designs have O-ring fittings to avoid leaks.

It is also important that the sampling apparatus is designed to avoid exposure of the filters to fresh air when the filters are not intentionally being exposed during the sampling operation.

2.4 Measurement of air flow and sample volume

Either a dry gas meter or a flow meter should be used to control sample volumes. Either should be calibrated for the operating conditions under actual sampling conditions. Attention must be paid to the pressure drop behind the filter if the air volume should be converted to STP and given for each sample.

2.5 Pump

Either a venturi mounted outside the aircraft or a vacuum pump may be used to provide the necessary suction. The

required output is 50 litres/min against a pressure difference of 0.4 - 0.5 atm.

Four 8" standard venturies in parallel is required to ensure a sampling rate of 40 litres/min STP when the airspeed is 120 m per hour.

Sampling time

The sampling time should be between 10 and 30 minutes.

2.6 Installations

Because of the requirements for a short connection with a minimum of sample heating, it is only possible to have an air intake in the nose of the aircraft if automatic sampling equipment is used. Such equipment is being installed in the Norwegian aircraft. Drawings of this apparatus is enclosed (Enclosure 1):

If the samples have to be changed manually, the only possibility is to have the air intake on the side of the aircraft. This may cause some concern with respect to the possibility of exhaust gases from the engines. However, these gases are usually released under the motors and behind the leading edge of the wing. For low-winged twin engine aircraft therefore, good physical separation should be possible.

An installation with intake on the side of the aircraft is *used in* the equipment developed for the UK Meteorological Research Flight (3), (Enclosure 2). The Swedish laboratory has purchased a spare luggage door on which the sampling equipment is mounted.

3 HANDLING OF SAMPLES AND CHEMICAL ANALYSIS

3.1 Preparation of filters

The sulphate blank may be reduced by washing. The improvement, however, is not substantial and it is preferable to use filters from the same batch and determine the sample blank.

Impregnated filters are prepared by adding 15 μ l per cm^2 of a 0.5 N potassium hydroxide solution. The solution should be prepared from A.R. quality potassium hydroxide not containing more than 0.1^o/oo of sulphate. The filters should be positioned horizontally during the drying operation which should take place at low temperature in SO_2 -free air. A vacuum desiccator with a suitable drying agent (CaCl_2) is recommended.

After drying the impregnated filters should be stored in an air-tight container, or in sealed filter holders. A minimum of 3 blank filters for each sampling flight should be treated exactly in the same way as the sample filters, with the exception of not being exposed to any air sample. After the flight these filters are brought back to the laboratory for analysis together with the sample filters.

3.2 Chemical analysis.

Either the isotopic dilution method or the barium perchlorate-thorin method(3) should be used for the determination of watersoluble sulphate in the sample filters.

Procedures for both these methods are enclosed (Enc. 3,4 and 5)

Analysis by the barium perchlorate - thorin method.

The exposed filters are taken out of the filter holder with tweezers, and placed in 25 ml conical flasks. 5 or 10 ml of distilled water and a small amount (10 mg) of acid cation exchange resin, (Dowex 50, H⁺ form Amberlite Zeokarb 225), is added.

The solutions are agitated by swirling once or twice. After half an hour the solution is analysed by the automated spectrophotometric barium perchlorate-Thorin method, using a Technicon Autoanalyzer or similar instrument. A filter or small ion exchange column should be inserted in the sampling line to ensure that the ion exchange material is completely removed before the barium perchlorate addition.

The procedure is capable of a detection limit of ~ 1 µg SO₂ per filter, (3).

4 DIRECT RECORDING OF PARTICLE CONCENTRATIONS

Recording of pollutant concentrations is desirable in order to obtain information of the variations or fluctuations during the 10 to 30 minutes sampling periods. It is also desirable to obtain some information about the actual concentration levels during the sampling flights. This information may be used to adjust sampling height levels or to change from 30 to 10 minutes sampling periods.

Experience has shown that there is good correlation between the number of particles in the 0.3 µm size range as determined by a Royco instrument, and the concentration of particulate sulphate in the air. The same relationship is expected to hold for particle concentrations obtained from an integrating nephelometer.

The number of condensation nuclei as determined with a Gardner counter or a Rich instrument also depends to a large extent on the past history and origin of the particles. It is therefore felt that this alternative is less satisfactory, and should only be recommended as a cheap substitute for the optical counters.

4.1 Available instrumentation

There are several optical particle counters available commercially, (Royco, Climet). Most of these have channels for different size ranges. For the purpose of the minimum programme, however, only the channel reading for the smallest particle size range detected (0.3 μm) is imperative.

The Charlson integrating nephelometer is manufactured under license by MRI. However, in order to detect low ambient air concentrations, several modifications must be carried out. An instrument of this kind is currently used in the Swedish aircraft.

Condensation nuclei counters are available in many different designs. A particularly simple and inexpensive version is the Gardner instrument. However, this is influenced by the pressure which determines the degree of supersaturation. Other more sophisticated instruments are not influenced by the outside pressure.

4.2 Air intake

As for the discrete sampling equipment, strict isokinetic sampling is neither necessary nor possible. The intake should have an isokinetic nozzle and be as short as possible.

4.3 Calibration

The absolute values for the concentration of particulate sulphate (and of SO₂) is obtained from the discrete samples. Therefore only relative values are necessary, but the results will usually be expressed as number of particles per unit volume (litre or cm³).

5 OTHER OBSERVATIONS

5.1 Humidity of the outside air

A hair hygrometer is probably sufficient. Description of suitable equipment will be sent out later.

5.2 Temperature of outside air

A simple standard aircraft instrument will be satisfactory. Experience is available also with recording equipment for more detailed studies. This will probably be of interest for the meteorological evaluation.

5.3 Cloud conditions.

Cloud conditions during the sampling periods should be recorded so that the representativity of the samples can be documented. Information on the actual cloud conditions during the sampling flights are also of value for the meteorological interpretation of the results. The following informations should be given for each sampling period:

- (1) Height of base and top of cloud layers (feet).
- (2) Cloud cover in eights (1/8).
- (3) Type of clouds.

Under (3) the international meteorological abbreviations should be used to indicate to which main type the observed clouds belong. Since we are mainly interested in cloud layers below 10 000 feet, these will in most cases be either Nimbostratus (Ns), Stratocumulus (Sc), Stratus (St), Cumulus (Cu) or Cumulonimbus (Cb). Normally the pilot will be trained in making these observations.

6 VOLUNTARY PROGRAMME

There are a number of measurements which are clearly desirable, but have not been included in the minimum programme, either because the interpretation falls outside the data evaluation programme, or because no commercial instrument or well-established procedure exist for aircraft measurements.

6.1 Continuous registration of sulphur dioxide concentrations

This may be realised using either an instrument based on the coulometric principle, a flame photometer measuring the S₂ luminescence in a hydrogen flame, or a correlation spectrometer operating on the SO₂ absorption bands in the UV.

The group at the Frankfurt University has developed further the Novak cell (4), reducing the detection limit to about 4 µg/m³ and a response time of about 1 min. Instruments borrowed from Frankfurt are at the moment being used both in Norway and in the Netherlands.

The flame-photometric principle is being exploited by Baird Atomic, Inc., under a research contract with EPA. The prototype instrument is capable of detecting sub-ppb levels but certain technical problems must be solved before it can be used in an aircraft. At the moment this is being considered in connection with a possible US involvement in the aircraft sampling programme.

Use of the Barringer instrument for aircraft measurements is being tested by the Netherlands. This instrument works best under a clear blue sky, however, and it looks as if its practical use will be rather limited.

6.2 Particles

Equipment for measuring particles has been mentioned briefly in section 4, Measurement of condensation nuclei concentrations, and particle counts in different size classes will give useful information for the characterization of the aerosols and the air masses.

6.3 Other chemical constituents

Of particular interest is ammonium in the particulate phase. A sensitive and selective analytical method is available in the spectrophotometric indiphenol blue method.

Sampling of gaseous ammonia can be made using filter paper impregnated with KHSO_4 (5). Usually this concentration is fairly constant, however, in the range $2-4 \mu\text{g}/\text{m}^3$, which corresponds to the vapour pressure of ammonium nitrate.

6.4 Cloud droplets

In clouds the larger particles act as condensation nuclei, growing to droplets of up to $20-40 \mu$ in diameter. These droplets also take up gaseous sulphur dioxide which is oxidized to sulphate and bisulphate. Our experience indicates that rainout processes are fairly efficient in the removal of sulphur compounds, and within clouds the droplets may account for a very substantial amount of the sulphur oxides.

The droplets in this size range will not all reach the sampling filters, being lost by impaction to the walls, ice formation etc. Also the wetting caused by the droplets that do reach the filters may destroy the samples.

Under the conditions during which long range transport do occur, particularly over the North Sea, it is not always possible to avoid flying through clouds. It would be highly desirable to have a cloud droplet collector, which could sample quantitatively droplets above a certain critical size, for example 10 μ . The sample air volume would be defined by the area of the sampling intake (which need not be isokinetic) and the air speed, and the samples should be taken with the same frequency as the other air samples. No such sampler is currently available.

7 REFERENCES

- (1) M Benarie et Bui-The-Chuong, (1969), *Atm. Env.* 3, 475-477.
- (2) Yamada, V M and Charlson R J, (1969), *Env. Sci and Tech* 3, 483-484.
- (3) LRTAP - 4/71, "Determination of Sulphate by the Barium Perchlorate-Thorin method". Revised edition January 1974.
- (4) E Lahmann und K-E Prescher: "Automatische Schwefeldioxid- mit einem polarographisch-coulometrisch arbeitenden Gerät." *Wasser, Luft, und Betrieb*, 15(10), 366-367 (1971).
- (5) A E J Eggleton and D H Atkins: "Report of the Tees-side Investigation." AERA-R 6983. Atomic Energy Research Establishment, Harwell, Berkshire. 1972. (pp 141-145 and pp 157 -176).

ENCLOSURES.

- Enc. 1: Description of a sequentional air sampler for aircraft sampling, developed by NILU.
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- Enc. 2: A technique for measurement of sulphur dioxide and sulphate concentration from an aircraft.
By D A Johnson and D H F Atkins (The Meteorological Office Research Flight, Farnborough, and AERE, Harwell).
- Enc. 3: Determination of sulphate by substoichiometric isotopic dilution analysis.
Abstracted from a method developed by D Klockow, H Denzinger and G Rönicke.
- Enc. 4: Determination of sulphate in aerosol filters and in impregnated paper filters by the isotopic dilution analysis (IDA) method.
- Enc. 5: Spectrophotometric determination of sulphate by the barium perchlorate - thorin method.
(LRTAP- 4/71, revised version).