NORWEGIAN INSTITUTE FOR AIR RESEARCH

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DETERMINATION OF PARTICULATE SULPHUR COLLECTED ON WHATMAN 40 AIR FILTERS BY X-RAY FLUORESCENCE

1 PRINCIPLE

Airborne particulate sulphur species collected on Whatman 40 cellulose fiber filters are detected by the fluorescence of the sulphur K_α line at 5.372 Å using a x-ray tube with chromium anode for the excitation.

The XRF intensities from the filter samples are compared with the XRF intensities obtained from Whatman 40 filters impregnated with known amounts of sulphate in aqueous solution.

Because of the different distribution with filter depth of the sulphur in samples and standards, and because of the absorption of x-rays by the filter material, this calibration procedure gives only a relative measure of the sulfur content of the filter samples.

The advantage is the simplicity of the method which makes it well suited for inter-laboratory calibration.

2 INSTRUMENTATION

The method requires an XRF spectrometer with a chromium x-ray tube, crystal monochromator and adequate counting equipment.

An example of suitable instrumentation and measuring conditions is given below:

- Spectrometer:	Siemens, Model SRS 1
- X-ray generator:	Kristalloflex 4 (Siemens)
- X-ray tube:	AG Cr 61, 40 kV, 40 mA (Siemens)
- Analyzer crystal:	Graphite (oo2), 106, 45°
- Counter:	Proportional, propane flow 4 l/h, membrane 2 µm, 2, 720 kV
- Collimator:	420 µm
- Diaphragm:	Au, elliptical 12 x 14 mm
- Measuring channel:	Height 6V, 5V, width 5,0 V.
- Discriminator:	Differential, att. 10 x 2
- Measuring area:	25 mm dia.

In addition to this, suitable aluminium inserts should be used in the sample holder of the spectrometer, in order to obtain a reproducible geometry when measuring samples and standards filters.

3 PREPARATION OF STANDARDS

3.1. Standard solutions

About ten solutions of sodium sulphate containing known amounts of sulphate (verified by chemical analysis) in the concentration range 0,01 to 5 g/l (as SO_4).

3.2. Preparation of filter standards

Standards are prepared by printing a ring of sulphur-free, water resistant China ink with an inner diameter of 25 mm on the Whatman 40 filter paper. This circle can be drawn manually with the aid of a plastic cylinder of 25 mm diameter. In cooperation with a commercial printing company, The Norwegian Institute for Atomic Energy has obtained filters printed with rings of printing ink of diameter 25/28 mm. Then 50 µl of a standard solution is transferred to the center of the ring marked in the filter. The solutio

will be evenly distributed within the central area. The filters are then allowed to dry in the air in horizontal position, preferably suspended so that the rate of drying is the same on both sides.

4 MEASURING PROCEDURE

The measuring procedure should incorporate the following steps:

- all instrument adjustments and the electronic scalers and timing units are controlled;
- the functioning of the instrument is controlled with a sulphur reference standard in the sample holder. The monochromator wavelength control and the x-ray generator current are adjusted until a reproducible XRF intensity (counting rate) is obtained;
- the filters are placed in the sample holder and measured for 1 min each*. The number of impulse counts is recorded. The sample compartment is evacuated and the filters are rotated during the measurements;
- at least 5 blanks and 5 standards should be measured with each sample series. All filters are measured on both sides **.

5 EVALUATION

The sum of the impulse counts from the back and front of the filters minus the impulse counts from blank filters is used for the evaluation.

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* The measuring time may be reduced to 20 seconds for routine determinations.

** If the ration I_b/I_f of the x-ray fluorescence intensities from the back to the intensities from the front filter samples is low and has been found to be constant for a representative number of filters, it is permissible to measure only I_f provided I_b/I_f is determined for 10-20 representative filter samples.

A calibration graph is made up from the measurements of the filter standards, giving the sum of impulse counts from both sides of the filter standards (minus impulse counts from blanks) as a function of sulphate contents.

This calibration graph should be linear.

The calibration graph is used to determine the amount of sulphate in micrograms which in an impregnated filter standard would have given the same sum of XRF intensities as the sample filter.

This number, divided by the sample air volume,should be reported. The true air concentration of sulphate may be obtained by multiplication of this number with an experimentally determined factor which will probably be between 0,6 and 0,8.

In addition, I_B/I_F should be given for sample filters which have been measured on both sides.

REFERENCE: M: Bonnevie-Svendsen and A. Follo: Work report, IFA CH-98, Norwegian Institute for Atomic Energy, Kjeller, June 1972.