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TESTING OF VARIOUS FILTER MATERIALS FOR COLLECTION AND DETERMINATION OF PARTICULATE SULPHUR IN AIR BY X-RAY FLUORESCENCE.

1. INTRODUCTION.

This is a brief summary of investigations carried out at the Norwegian Institute for Atomic Energy (IFA) by M. Bonnevie-Svendsen and A. Fǫllo, and at the Swedish Water and Air Pollution Research Laboratory (IVL) by Professor C. Brosset, Å. Åkerström and P. Grennfelt in order to compare filter materials which could be used for sampling and determination of particulate sulphur by the XRF method.

The report by M. Bonnevie-Svendsen and A. Follo[1] will be distributed separately. Some of the experimental results from the internal Nordforsk report by Brosset and Grennfelt[2] are included in Appendix. Additional information is available in references [3] and [4].

2. EXPERIMENTAL.

Two different commercial XRF spectrometers have been used for the XRF measurements:

	IFA	IVL
-Spectrometer	Siemens SRS 1	Philips PW 1540
-X-ray tube	Cr 40 kV, 40 mA	Cr 50 kV, 28 mA
-Analyser	Graphite,(002)	PET
-Pulse discriminator	0,005 keV	none
-Collimator	420 µ	480 µ
-Diaphragm	Au 12 x 14 mm	none

Parallel sampling with Millipore and Whatman 40 filters has been carried-out at Osterhausgaten in Oslo and at a rural site (Lerum) in Sweden. Equal volumes of air were sampled according to the spesifications given in LRTAP 2/72.

Sample filters have been measured both at IFA/Kjeller and at IVL/Gothenburg..

Watersoluble sulphate was determined in some of the filters from Oslo by leaching with 5 ml distilled water and subsequent ion exchange and determination by the barium perchlorate - Thorin method (LRTAP 4/71).

Impregnated filter standards prepared according to LRTAP 6/71 have been used for the comparisons, as well as standards prepared according to the method of Grennfelt et al.[3].

3. RESULTS.

3.1. Filter blanks.

The following filter qualities have been tested[1]:
Whatman Nos. 1, 40, 41 and 42, and Schleicher & Schuell quantitative paper filters. Millipore AA, Sartorius and Gelman Acropor membrane filters.

Ash-free (quantitative) filter papers were found to have the most consistently low blanks. In fact no sulphur was detected by scanning. The blank due to diffuse reflected energy was equivalent to about 0,5 µg S/cm^2. The standard deviation of this blank gives a 3σ detection limit of about 0,05 µg S/filter

Millipore cellulose ester membrane filters were also acceptable. The S content is low, but the filter blank is more variable, with detectable differences between boxes of 25 filters from the same batch of filters and even between the front and the back sides of the filters.
The other membrane filters tested were all less satisfactory. One quality contained about 8 µg S/cm^2.

3.2. Comparison between Whatman 40 and Millipore membrane filters.

Particulate matter collected on membrane filters are deposited in a layer on the surface of the filter. Because particles in the submicron range penetrate into the filter material to some extent when using fiber filters, and because the x-ray radiation is absorbed by the filter material, particulate sulphates collected on a Whatman 40 filter will give rise to a lower measured XRF intensity than the same amount of sulphate collected on a membrane filter.

The field experiments show that this factor is nearly constant [5,6].
The variations are of the same order of magnitude as the sampling errors.
It is also interesting that this ratio is also practically constant for the comparison of Whatman 40 with Whatman 1 filters[7], in spite of the fact that the porosity of Whatman 1 filters is significantly greater, which can also be deduced from the results.

3.3. Calibration.

a. The Whatman 40 filter samples are usually compared with impregnated filter standards containing known amounts of sulphate. In order to reduce some of the x-ray absorption effects, both standards and samples are measured on both sides and the sum of the intensities used for the comparison

b. Membrane filter aerosol standards may be prepared according to the method of Grennfeldt et al[3]. Comparison with the results from[2] gives a correction factor of 0,78 for the comparison of Whatman 40 filters with impregnated standards. (Calculated from[4] and the results given in Appendix, p. 6.).

c. Wet chemical analysis on 10 of the filters from Oslo gave a conversion factor of 0,63 with a standard deviation of about 10%, which is of the same order of magnitude as the spectrophotometric determination. This ratio may be systematically low because of incomplete recovery. XRF of the leached filters showed that this effect could probably make the true value about 0,68.

d. Impregnation may also be used to prepare Millipore filter standards with known sulphate contents. Comparison between parallel Whatman 40 and Millipore sampling series then yields a correction factor of 0.71.

Leaching of Millipore membrane filters gave almost identical results as the XRF method with impregnated Millipore filter standards.

REFERENCES

1 M. Bonnevie-Svendsen and A. Follo, "Work report", IFA, CH-98, Kjeller, June 1972.

2 C. Brosset and P. Grennfelt, Internal Nordforsk report, May 1972.

3 P. Grennfelt and Å. Åkerstrøm and C. Brosset (1971), Atm. Environm. 5, 1-6

4 C. Brosset and Å. Åkerstrøm, IVL Report B 113, March 1972, Gothenburg.

5 Ref.[1], p. 23 (Figure 8)

6 Ref.[2], p. 2 and Figs. 3 and 4 (Appendix, Fig. 1 and 2).

7 Ref.[3], page 2 (Appendix, page 6).

APPENDIX

Comparison of sulphur XRF intensities from parallel field samples from Lerum collected on Millipore AA, Whatman 1 and Whatman 40 filters, and calibration relative to the method described by Grennfelt et al[3].

From Brosset and Grennfelt: Internal Nordforsk report, May 1972 (Ref.[2]).

TABLE 1

Sulphur XRF intensities for different filter samples from Lerum , Sweden. Nov. - Dec. 1971.

Figures give number of counts in 20 seconds divided by the air sample volume in cubic meters.

Filters measured only on the front side.

Datum	Whatman 1 imp/m^3	Whatman 40 imp/m^3	Millipore 25 mm imp/m^3	Millipore 14 mm * imp/m^3
23/11-71	254	333	-	1112
24/11	244	395	519	915
25/11	271	322	695	602
26/11	233	270	480	842
27/11	847	1175	2053	2394
29/11	1151	1346	2048	2308
30/11	1018	1243	2313	1514
1/12	589	823	1568	1013
2/12	588	760	-	1306
3/12	721	819	1699	1354
4-5/12	238	267	1559	-
6/12	401	489	1099	1835
7/12	193	182	284	562
8/12	0	210	491	331
9/12	169	217	337	360
10/12	212	193	331	330
11/12	127	149	319	287
13/12	315	420	797	354
14/12	764	846	-	1133
15/12	595	592	-	858
16/12	627	596	-	1290
17/12	792	968	2191	1363

* Disposable 33 mm ϕ plastic filter holders masked to 14 mm dia. were used. The somewhat unsatisfactory results have been traced back to leaks in the filter holder.

TABLE 2

Sulphur XRF intensities for different filter samples from Lerum, Sweden - Nov./Dec. 1971

The figures give the number of counts in 20 seconds divided by the air sample volume in cubic meters.
Filters measured only on the front side

Datum	Whatman 1 imp/m^3	Whatman 40 imp/m^3	Millipore 25 mm imp/m^3	Millipore 14 mm imp/m^3
17/1-72	328	373	574	473
18/1	377	449	839	361
19/1	1389	1592	2753	3383
20/1	341	388	793	447
21/1	959	1214	2320	3173
22-23/1	707	833	1723	1632
24/1	1379	1474	3449	2658
25/1	1874	2294	3906	5743
26/1	2363	2840	4064	-
27/1	1439	1549	3485	4985
28/1	559	872	1679	930
29-30/1	830	957	1778	1064
31/1	1239	1803	2589	-
1/2	1523	1750		
2/2	1942	2256		
3/2	1712	2124		
4/2	-	-		
5-6/2	913	1158		
7/2	1430	1663		1023
8/2	1074	1523		3544
9/2	979	835		518
10/2	272	405	1132	1016
11/2	525	430	1321	646
12-13/2	1000	971	2217	1313
14/2	762	837	2211	2191
15/2	1045	400	905	726
16/2	584	680	1449	973
17/2	722	960	1894	1819
18/2	1236	1424	2642	2625
19-20/2	2319	2380	3999	3783

Figure 1	Comparative sulphur XRF filter measurements. Lerum, Nov./Dec. 1971 Comparison Whatman 40/Millipore AA 25 mm.	Appendix Page 3

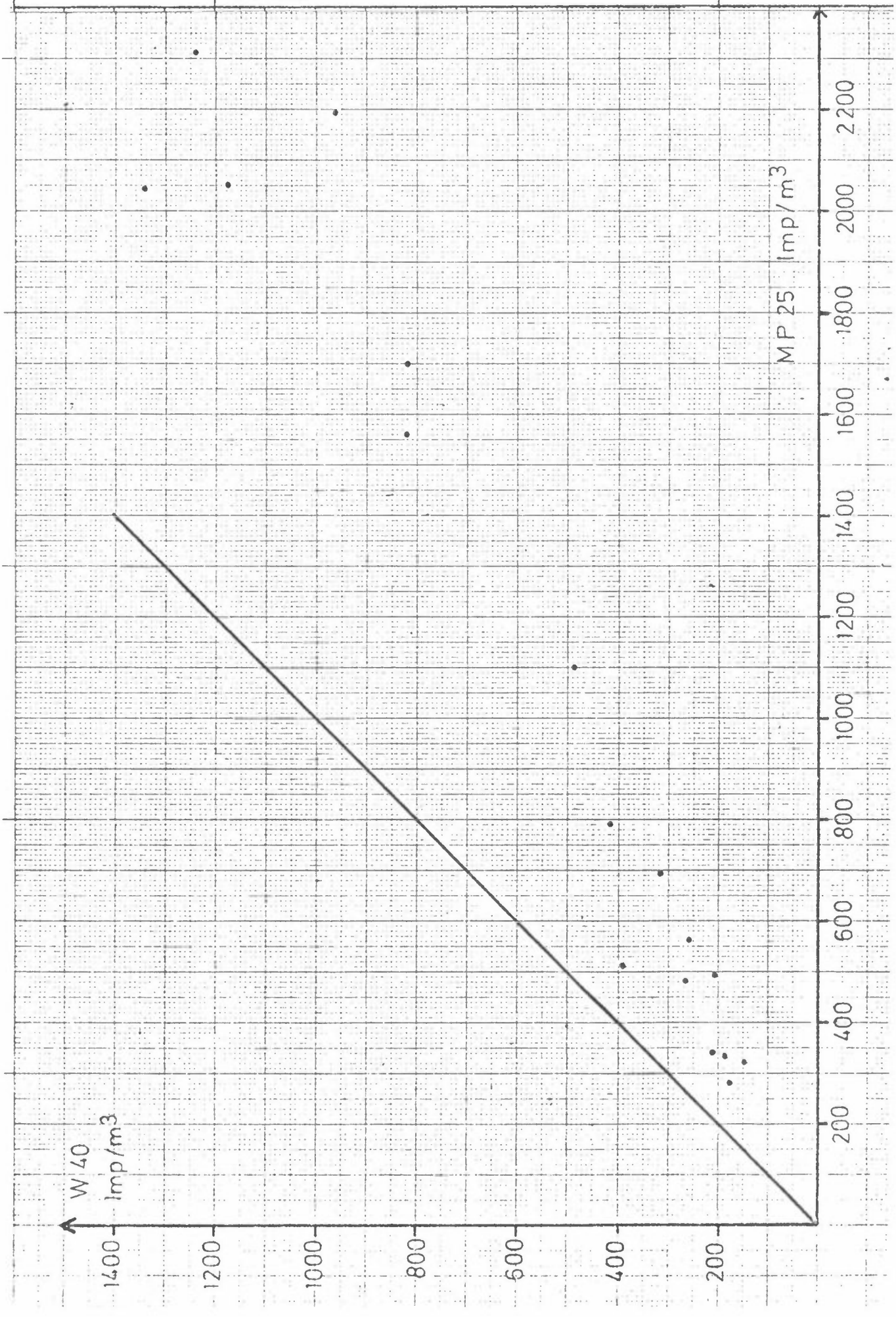

Figure 2

Comparative sulphur XRF filter measurements. Lerum, Jan. Feb. 1972

Comparison Whatman 40/Millipore AA 25 mm

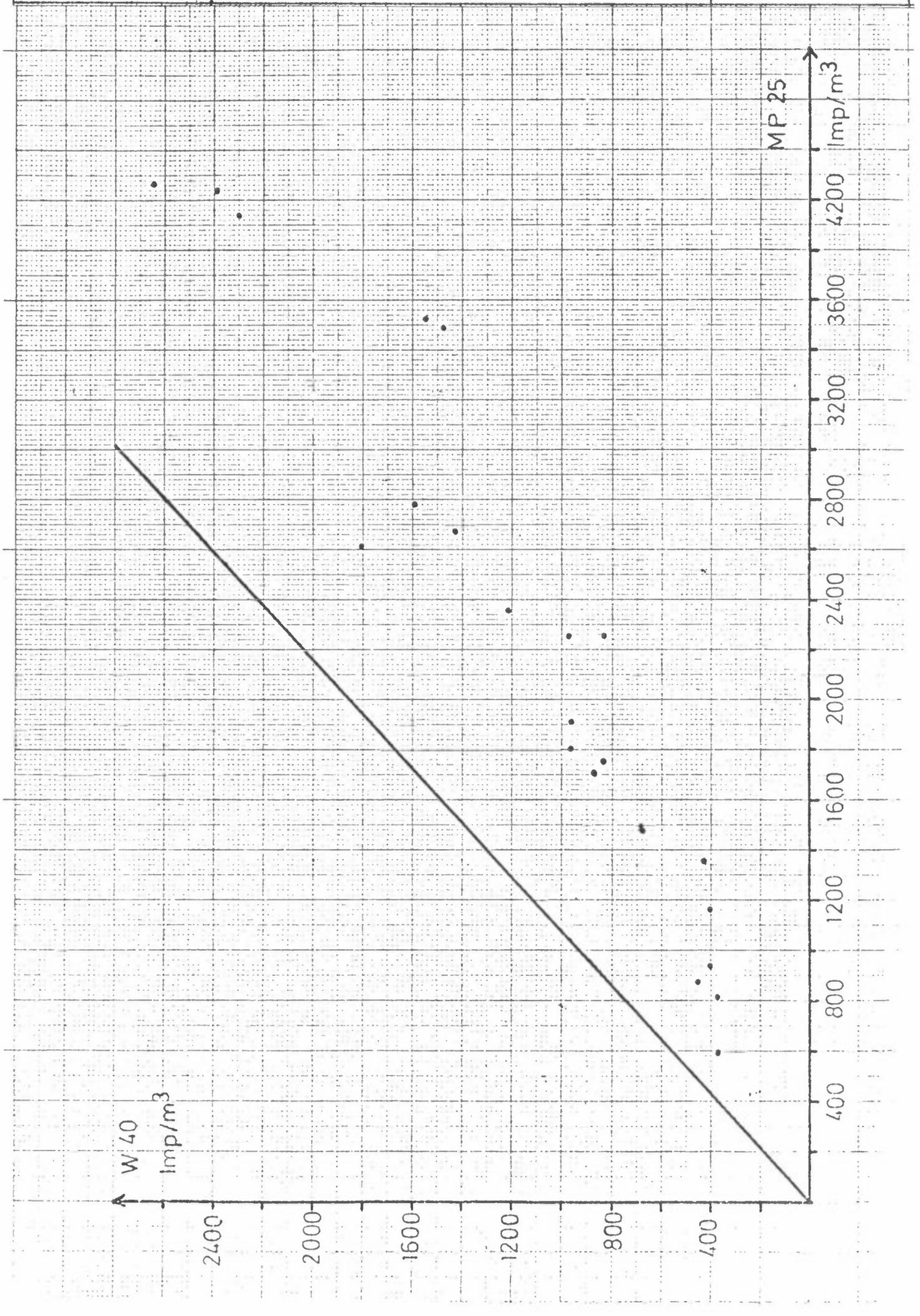

Table 3

Calculated correlation coefficients between sulphur XRF intensities from different filter qualities

	Nov./Dec.	Jan./Feb.	TOTAL
Whatman 1 - Whatman 40	0,97	0,92	0,945
Whatman 1 - Millipore 25 mm	0,95	0,92	0,935
Whatman 40- Millipore 25 mm	0,97	0,95	0,96
Millipore 14 mm-Millipore 25 mm	0,82	0,91	0,865

CALIBRATION

The following relations have been found between the measured XRF intensities (W_1 = Whatman 1, W_{40} = Whatman 40, M_{25} = Millipore 25 mm dia., M_{33} = Millipore 33 mm dia.).

$$\frac{I\ W_1}{I\ M_{25}} = 0.44 \quad (N = 21) \qquad (S = 0.08,\ 19\ \%)$$

$$\frac{I\ W_{40}}{I\ M_{25}} = 0.51 \quad (N = 22) \qquad (S = 0.10,\ 20\ \%)$$

$$\frac{I\ W_1}{I\ W_{40}} = 0.86 \quad (N = 28) \qquad (S = 0.13,\ 15\ \%)$$

Since the 14 mm dia. Millipore filters could not be used for calibration purposes, it was found necessary to relate the intensities to Millipore 33 mm filter standards.
Such a comparison has already been made for Millipore 33 and Whatman 1 filters (ref. 3).

It was found that:

$$\frac{I\ W_1}{I\ M_{33}} = 0.50 \quad (n = 26)$$

From this relationship and the results given above:

$$\frac{I\ W_{40}}{I\ M_{33}} = 0.58$$

Calibration by impregnation of the Whatman 40 filter and measurements of the XRF intensity on <u>one</u> side give a calibration factor of

$9.25 \cdot 10^{-3}$ µg SO_3/imp., for 20 s measuring periods

Under the same measuring conditions, the same factor for Millipore 33 mm filter standards prepared according to Grennfelt et al (Ref. 4) is:

$$3.2 \cdot 10^{-3} \ \mu g \ SO_3/imp$$

This gives

$$\frac{(I\ W_{40})\ standards}{(I\ M_{33})\ standards} = \frac{3.2}{9.25} = 0.35$$

Provided $(I\ M_{33})$ standards = $(I\ M_{33})$ samples, which will be the case if the M_{33} filter standards are representative, this gives:

$$\frac{(I\ W_{40})\ standards}{(I\ W_{40})\ samples} = 0.60$$