



CANADA

THE MEASUREMENT OF SULPHATE IN AIR

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by

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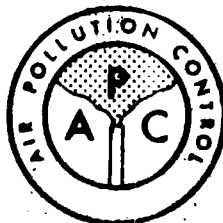
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ABSTRACT

Several workers in the literature have stated that the concentration of sulphate (SO_4) found in air is influenced by the sampling time. According to Corn and Demajo, the amount of sulphate found expressed in micrograms per cubic metre of air is less the longer the sampling time (3). This air sampling "anomaly" with respect to sulphate concentrations was confirmed by Roesler et al (4). Accepting this anomaly as fact, Lee and Wagman carried out experiments to explain it. According to them, the higher concentrations found for short sampling times were due to the oxidation of SO_2 to SO_4 at the filter surface due to catalytic action of the glass fibre sheet (5). If the concentration of "sulphate" can be four and even ten times greater for shorter sampling times (3) it is obvious that it is very important to know the true concentration, if one wishes to establish air quality standards for sulphate. As most of the sulphate data available is based on 24 hour samples, it is conceivable that this data would be used for the setting of air quality standards. If it were to be found later on that the air quality standards adopted were lower than the actual "normal" sulphate in air values, this could be most embarrassing for the legislators. The possibility of setting standards related to inaccurate background data is an ever present danger and something which should be carefully guarded against with all pollutants.

The experiments of Lee and Wagman were repeated, but the air sampling anomaly was not observed for sulphate (SO_4). Certain weaknesses of currently used turbidimetric methods for sulphate were exposed. The present paper is a translation of the paper "Le Dosage des Sulfates dans l'Air" to be published in J. Environmental Analytical Chemistry.

According to Hemeon, Amdur and Corn, zinc sulphate, ammonium sulphate and the double sulphate of zinc and ammonium were responsible for the irritating properties of fogs produced during periods of heavy atmospheric pollution (1, 2).

Corn and Demaio noticed, in the course of their work, a variation in the concentration of sulphate according to the sampling time. Fig. 1 summarizes their results. It may be observed that the concentration of sulphate, for a sampling period of 24 hours, is about 25% of that obtained after sampling for one hour. Roesler, Stevenson and Nader observed the same phenomenon (4) and Lee and Wagman attempted to explain it (5). According to the latter, the higher concentration of sulphate for short sampling times, was due to the oxidation of SO_2 to SO_4 , catalyzed by the glass fibre sheet.

If the concentration of sulphate can be four and even ten times greater according to the sampling time (3) it is obvious that it is very important to know the true concentration if one wishes to establish air quality standards for sulphate. It seemed desirable to us to repeat the experiments of Lee and Wagman (5).

METHOD OF SULPHATE ANALYSIS

A. Extraction

One carries out the extraction of sulphate by heating, just to boiling, two discs, 47 mm. in diameter, in the presence of about 5 ml. of water. This operation is repeated five times and the combined extracts, after filtration through Whatman 41, are made up to a volume of 25 ml.

It is necessary to agitate the solution thoroughly during the extraction, without at the same time mutilating the filter.

B. Measurement

Reagents

Phosphoric Acid: This solution is prepared by mixing 900 ml. of a solution 0.2N in phosphoric acid with 100 ml. of methanol. This is made up to 1000 ml. with distilled water.

Barium perchlorate: A solution saturated at room temperature.

Sulphuric Acid: A solution 0.01N, that is, containing 490 micrograms of SO_4^{--} per ml. To establish the calibration curve, prepare solutions containing, respectively, 49, 98, 196, 294 and 392 micrograms of SO_4^{--} per ml.

Blank Solution

This solution is obtained by the extraction of 20 discs 47 mm. in diameter by the method described above. These discs were cut from glass fibre filters previously washed and identical to those serving for sampling. The extraction is made with 50 ml. of distilled water, heating just to ebullition. This procedure is repeated five times and the extracts are made up to 250 ml. after filtration through Whatman 41.

Apparatus

Spectrophotometer.

Cuvettes with 50 mm. light path.

Method

Pipette into a 50 ml. conical flask a 10 ml. aliquot of the sample to which one adds successively 10 ml. of the solution of phosphoric acid and 0.5 ml. of the saturated solution of barium perchlorate. Agitate to make the solution homogeneous. Read the absorbance at 550 nm. in a cuvette with a 50 mm. light path, 5 to 20 minutes after the addition of the reagents. The reference cuvette contains distilled water (6).

Calibration Curve

Measure, by means of a pipette, 1 ml. of each of the standard solutions into the 50 ml. conical flasks. Add 9 ml. of the blank solution, 10 ml. of the phosphoric acid solution and 0.5 ml. of the solution of barium perchlorate. Measure the absorbance according to the method described above at the same time as the samples.

Sampling

We have adopted the methods used by Lee and Wagman to determine:

(a) Sampling at variable flow for fixed time periods. The results of experiments S-22 to S-84 were obtained on samples taken in this way.

(b) Sampling at constant flow but for variable periods of time. The samples S-99 to S-175 were taken in this way.

The seven "Hi-Vol" instruments, used for the sampling, were calibrated, before use, by means of the method recommended by the maker. Gelman A glass fibre sheet (8" x 10") was used for sampling. The filters were washed beforehand by repeated leaching with boiling distilled water.

Table I shows the results obtained by using the first method of sampling. It may be noted that the volumes vary from 727 cubic meters to a maximum volume of 1897 cubic meters. It is impossible to obtain smaller volumes with "Hi-Vol" samplers. This would be of particular interest, because the phenomenon described by Lee and Wagman becomes progressively more and more evident as the volume decreases. The use of these samplers to obtain small volumes, that is volumes smaller than 1100 cubic meters, is subject to greater errors for these small volumes. It is evident, however, that the concentration of sulphate, expressed in micrograms per

cubic meter, does not indicate in any way that there is an increase of this concentration, for volumes less than 1300 cubic meters, which is the volume below which the anomaly is observed. One should obtain, for a given day, the same concentration of sulphate, since the same parcel of air is involved.

One may conclude, from these results, that, if there is an anomaly, the method does not permit us to reveal it. It is interesting to note, in this table, that the particulate concentrations do not in any way suggest that there is an increase of sulphate with diminution of volume. In fact, it would be necessary to expect an increase in the concentration of particulate matter if there is formation of sulphate at the surface of the sheet.

Table II illustrates for us the results obtained by using the other method of sampling (S-99 to S-175) in order to obtain a 24 hour sample and another composed of samples taken for shorter periods. Once again, one observes that the concentration of sulphate is in no way greater for small volumes. It is the same for the concentration of airborne particulates.

These results are in contradiction with the phenomenon of increased sulphate concentration observed by Corn and Demaio (3) Roesler et al (4) and Lee and Wagman (5).

We have, however, reasons for doubting the explanation given by the latter authors, on the sulphate anomaly, for the following reasons:

- 1) The oxidation of SO_2^{--} , catalyzed at the surface of glass fibre sheet, can not explain the increase in the concentration of sulphate for short sampling times, when a cascade impactor is used (3).

2) The authors do not make any mention of airborne particulate matter, so that it is impossible to say whether there has been an increase in the weight of particulate matter due to the oxidation of SO_2 to SO_4 .

3) If one constructs from the results obtained by Lee and Wagman, the curve of the total quantity of sulphate as a function of volume, instead of the concentration of sulphates as a function of volume, one obtains a straight line, curve 1 of Figure 2. If there had been formation of sulphate on the sheet, the curve would normally be inflected downward for an increase in volume assuming that the formation of sulphate from SO_2 is less for large volumes. However, there is an intercept on the Y axis for a volume of zero.

It is possible to explain the sulphate anomaly in the following way. Figure 3 shows two calibration curves. The higher curve, No. 1, has been obtained in the manner described in the method of sulphate analysis, that is by employing 9 ml. of the blank solution. The lower curve, No. 2, was obtained by adding 9 ml. of water instead of the blank solution. It is seen that the two curves tend to meet for large concentrations of sulphate, because the influence exercised by the products extracted from the glass fibre, even after prior washing, tends to diminish for large concentrations. On the other hand, for low concentrations such as 50 micrograms per 20.5 ml., it is seen that absorbance has doubled or nearly so.

Curve 2 does not pass through the origin. The solubility of barium sulphate can account for this anomaly. This solubility should be about 10 micrograms per 20.5 ml. for a solution containing 0.5 micrograms per ml.

The addition of an extract of the glass fibre has the effect of diminishing the solubility of barium sulphate, because of the increase in the ionic strength of the solution since the filter extract contains a high

concentration of ions. It is understandable, then, why this phenomenon is more apparent for low concentrations of sulphate. Table III allows us to see the effect of this phenomenon upon the concentration of sulphate. Column 1 gives the results obtained by using curve 1. Likewise, column 2 gives the results obtained with curve 2 after subtracting the blank. 10 ml. of the blank solution is measured in the same way as the standards of curve 2. The latter results are, on the average, 25% greater than those obtained with curve 1 for 4 hour samples, but identical with the results of 24 hour samples. As a result this can explain the anomaly observed.

Another reason for erroneous results is the presence of small glass fibres found in the filtered extract. Figure 4 illustrates some of these fibres found in the extract after filtration through Whatman No. 1, which is the filter used in the method of Jacobs (7). These can have a maximum length of 75 microns and the diameters vary from 0.3 to 1.5 microns.

Table IV demonstrates how great their influence can be upon the absorbance and as a result on the turbidimetric measurement of sulphate. Column 1 gives the reading obtained after filtration through Whatman 41 and column 2 gives the reading after filtration through millipore. It is noted that the millipore takes out the majority of these particles. At the same time it is necessary to remember that during the measurement of sulphate, the influence of these particles diminishes because of the dilution of the sample. It is observed, also, that filtration through millipore is not sufficient to eliminate all trace of absorbing material.

It would seem that the solution contains some absorbing substances. That is why it is deemed appropriate, if not necessary, to use the technique employed by Brabant et al which consists in measuring the absorbance of the solution before and after the addition of barium

salt (8). In this way, one can make a correction for the interference caused by the presence of absorbing substances in the filtrate.

CONCLUSION

The use of turbidimetric methods for the measurement of sulphate in air samples can be subject to serious errors. In order to obtain valid results it would seem necessary to carry out the filtration of the extract through millipore instead of an ordinary filter paper, to eliminate the small glass fibres as well as the tiny particles of dust which are able to go through the filter. Furthermore, it is wise to read the solution before and after the addition of barium salt in order to correct for the interference due to the colour of the solution, as described by Brabant et al (8). Lastly, it is necessary to prepare the standard curve in a medium similar to that of the samples. These various observations explain the anomaly in the sampling of sulphate. At the same time, they cannot explain the results obtained by Demaio and Corn using the cascade impactor (3). In this case, we believe that these authors have measured the airborne particulates instead of the sulphate.

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SOMMAIRE

Certains auteurs ont observé que la concentration des sulfates dans l'air urbain varie selon le volume d'air échantillonné. Selon eux, il y aurait oxydation catalytique du SO_2 en SO_4^{--} à la surface des feuilles de fibre de verre. Ce phénomène diminue au fur et à mesure que le volume prélevé augmente.

Dans le présent travail, il est démontré qu'on peut expliquer cette anomalie, d'une façon tout à fait différente interference due à la présence de substances, extraites des feuilles de fibre de verre, en même temps que les sulfates. De plus, on y étudie les principales causes d'erreurs inhérentes au dosage turbidimétrique des sulfates.

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TABLE CAPTIONS

- I Sampling at variable flow for fixed times.
- II Sampling at constant flow with varying time.
- III Effect of blank filter extracts on sulphate concentration.
- IV Effect of suspended glass fibres on absorbance readings.

TABLE I

Date 1970	Sample No.	Volume m ³	Particulates ug/m ³	Sulphate ug/m ³
Oct. 22	S-22	1777	30.5	3.59
	23	1386	26.2	5.51
	24	1101	25.6	4.27
	25	1611	26.8	3.21
	26	816	29.4	3.96
	27	918	26.3	3.82
	28	1611	25.5	3.50
			MEAN	<u>27.2</u>
Oct. 24	36	1675	65.1	8.88
	37	1372	62.5	9.13
	38	1090	66.7	12.02
	39	1312	66.6	9.98
	40	727	64.1	9.81
	41	1070	62.0	9.86
	42	1655	66.2	8.98
			MEAN	<u>64.7</u>
Oct. 31	64	1897	61.8	7.20
	65	1387	60.1	6.27
	66	1101	60.6	6.64
	67	1687	64.7	6.93
	68	755	56.0	5.80
	69	1150	59.9	5.89
	70	1611	61.0	7.44
			MEAN	<u>60.5</u>
Nov. 3	78	1091	88.1	6.10
	79	1340	83.1	5.23
	80	1305	82.8	5.42
	81	1346	84.3	5.43
	82	1428	84.3	4.66
	83	1432	86.5	6.57
	84	1713	91.5	7.42
			MEAN	<u>85.8</u>

TABLE II

Date 1970	No. of Samples	Sampling Period, hrs.	Particulates ug/m ³	Sulphate ug/m ³
Nov. 18	6	4	38.7	6.09
	1	24	36.3	6.24
Nov. 19	6	4	112.5	9.24
	1	24	113.2	9.63
Nov. 20	2	4	21.9	4.28
	1	8	25.4	4.76
	3	8	15.2	2.82
	1	24	15.7	3.04
Nov. 29	3	10	35.5	5.31
	1	30	38.7	4.23
	4	10	35.9	4.75
	1	40	36.2	4.78
	5	10	42.6	4.72
	1	50	44.1	4.59

TABLE III

SO₄⁻⁻ in Micrograms per cubic meter

Four Hour Samples	Curve 1	Curve 2
1	8.5	10.0
2	8.2	10.0
3	12.3	13.8
4	7.8	10.0
5	5.0	7.3
6	5.9	8.3
TOTAL	8.0	9.9
24 Hour sample	7.7	7.9

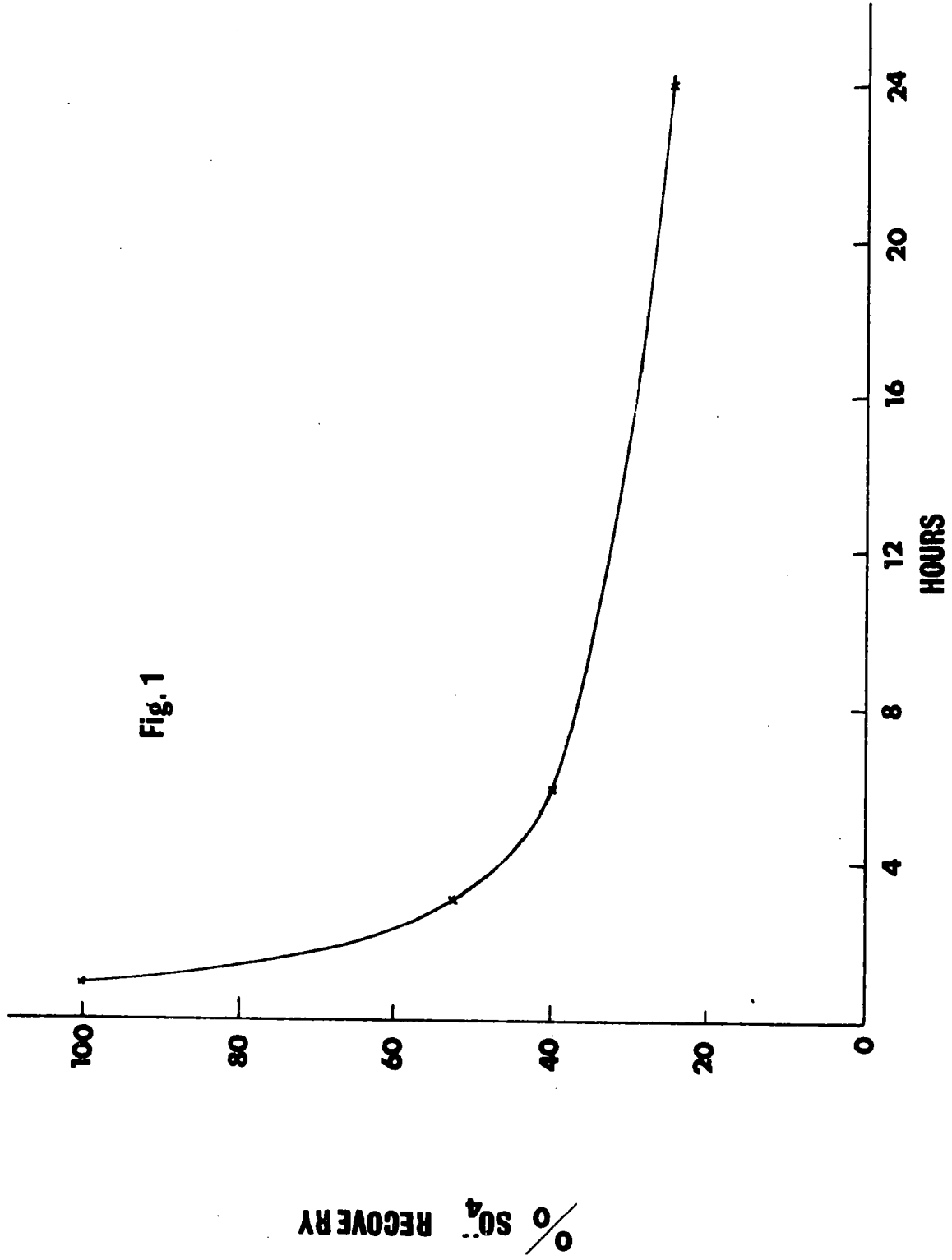
TABLE IV

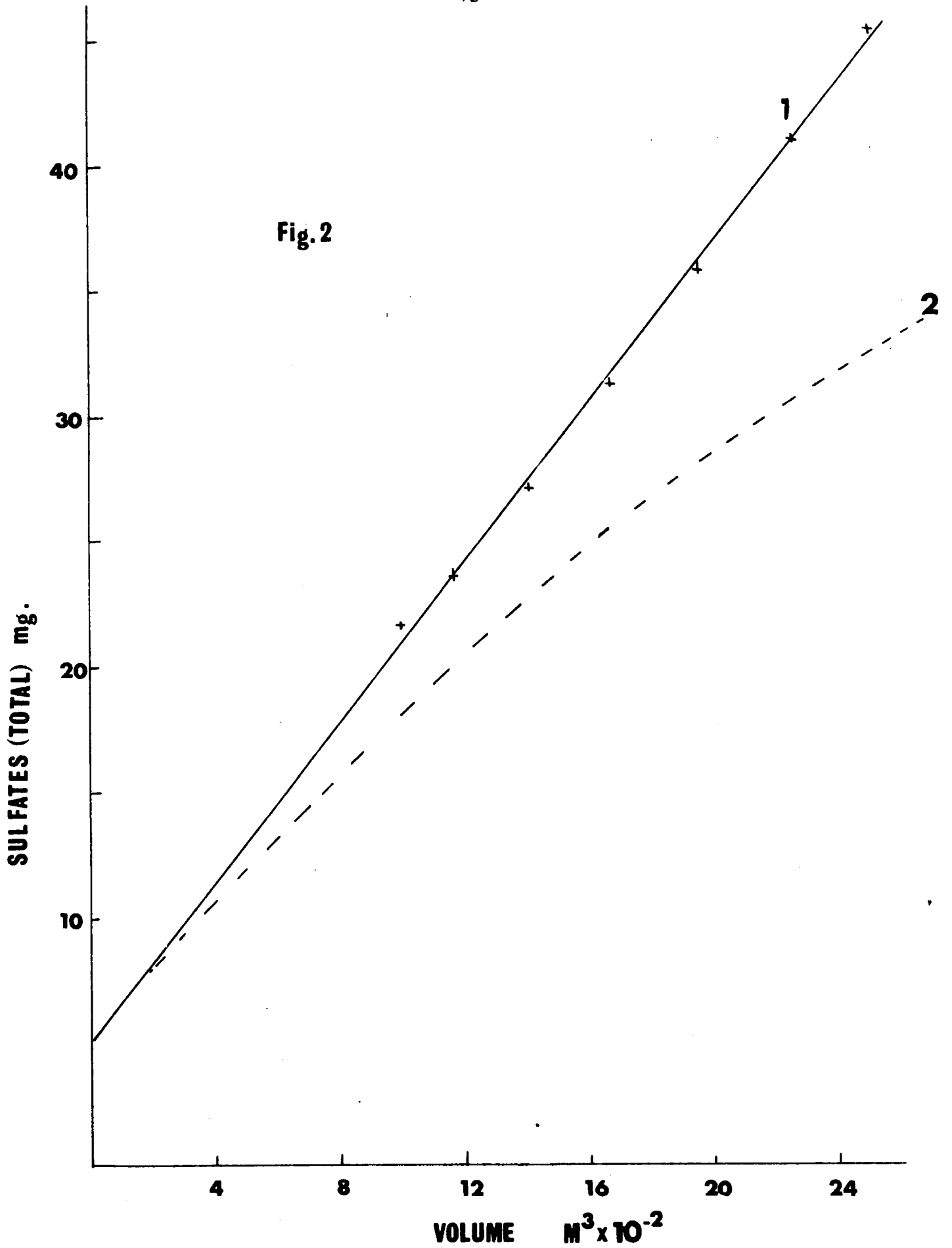
Absorbance

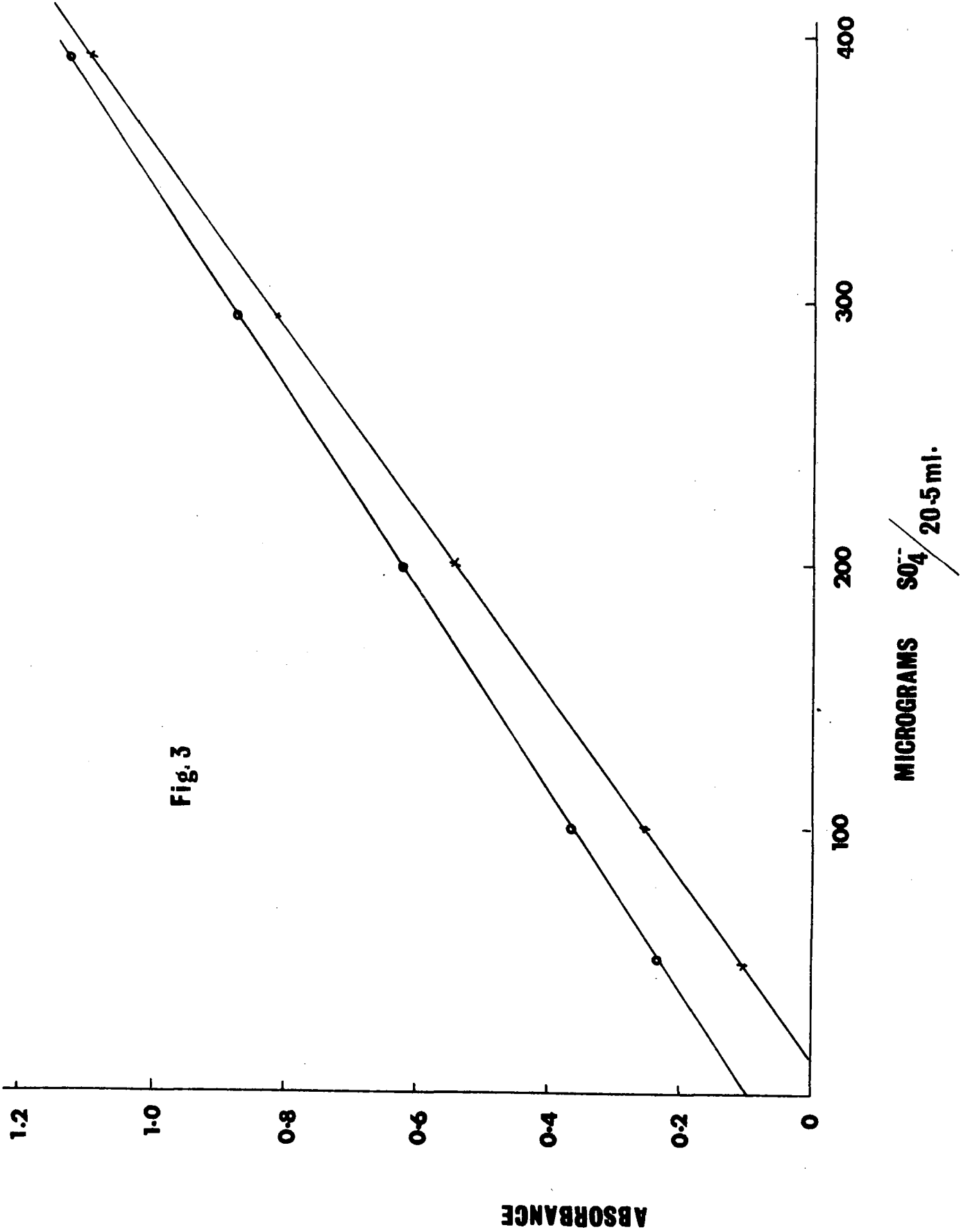
Sample	Whatman 41	Millipore
64	0.137	0.045
65	0.137	0.025
66	0.086	0.023
67	0.127	0.028
68	0.084	0.018
69	0.063	0.000
70	0.095	0.004

FIGURE CAPTIONS

- 1 Variation in sulphate concentration with sampling time (Corn and Demaio).
- 2 Reconstruction of results of Lee and Wagman.
- 3 Effect of blank extraction instrumental calibration.
- 4 Photomicrograph of glass fibres in solution (not available).







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