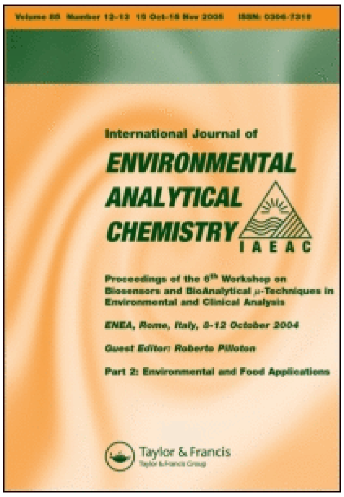

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Collection of Atmospheric Sulfur Dioxide on Impregnated Fiberglass Filters and Colorimetric Measurement†

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A specific technique for the collection and measurement of atmospheric sulfur dioxide is described in detail. Sampling is performed by aspiring polluted air through a zinc-acetate-impregnated filter. The polluted zinc acetate is extracted from the filter with a 1.0M zinc-acetate solution. The zinc sulfite formed in the solution resulting from the atmospheric SO_2 sampling is later measured colorimetrically as a red complex which is developed using a dye solution containing pyridine and sodium nitroprusside.

The study of the efficiency of the technique using different types of filters indicates that at a sampling rate of 1l/min the measuring range of a fiberglass filter is from 0.003 to 0.2 ppm when 1.0 m^3 of polluted air is sampled.

This new technique presents all the advantages of the West and Gaeke method as well as most of those of the dry collectors. Furthermore, it can also be used for the atmospheric sampling and measurement of hydrogen sulfide without interfering with the sulfur dioxide measurement. All these advantages combined with the simplicity of the technique render it particularly attractive when a given area has to be blanketed with samplers.

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The use of liquid reagents to scrub out specific pollutants from the atmosphere presents many disadvantages inherent in the transportation and manipulation of liquid-filled glassware;[1] also, the bubbling of air through the liquid reagent may cause evaporation which can subsequently introduce errors in the measurement.

In order to eliminate these disadvantages, Lodge and his co-workers[1,2] suggest the use of an impregnated filter instead of the liquid reagent to collect traces of gases in the atmosphere. As demonstrated by this group,[2] impregnated membrane filters appear to possess many of the characteristics desirable in a dry collector. These are the following: it should be stable on the shelf until used; the sample when collected should be stable until analyzed; the collector should be cheap and simple so that a given area can be blanketed with samplers; the sample should be capable of being analyzed for specific components; and the collector should have a high collection efficiency.[1]

The principles formulated by Lodge's group [1,2] and results obtained by Bourbon and Malbosc[3-5] have led to the development of a new sampling technique for atmospheric SO_2 based on a dry collector.[5,6] The sampling is effected by aspirating polluted air through a fiberglass filter impregnated with zinc acetate. After the sampling, the zinc acetate is eluted from the membrane and analyzed colorimetrically.

Four types of filters were tested in order to measure their collection efficiency, saturation concentration, and maximum concentration deviation. The data obtained were compared with similar results measured by the West and Gaeke method,[7] or by a flame photometric detector (F.P.D.). The purpose of these tests was to determine which membrane would give the best performance for the atmospheric measurement of SO_2.

IMPREGNATION OF FILTERS

Impregnation of the tested filters is carried out by immersion in a 1.0M zinc-acetate solution to which 10% (v/v) of glycerine has been added. The glycerine is used to stabilize the zinc sulfite formed by the reaction of SO_2 with the $(CH_3CO_2)_2Zn$ of the filters.[3] After a few minutes' immersion, the filters are dried in a low-temperature oven at 60°C.

AIR SAMPLING

For the atmospheric sampling, the filter under study is placed in a 47-mm Swinnex Filter Holder (Millipore No. SX0004700) and the polluted air is drawn at a definite rate in the 0.5 l to 5.0 l/min range. A constant sampling rate is usually assured by inserting a precalibrated Teflon capillary between the vacuum pump and the filter holder as shown in Figure 1. The capillaries were sporadically checked using a wet gas meter and they proved to be

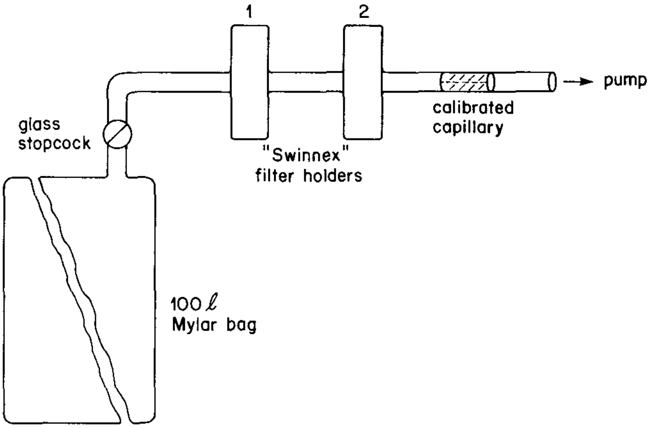
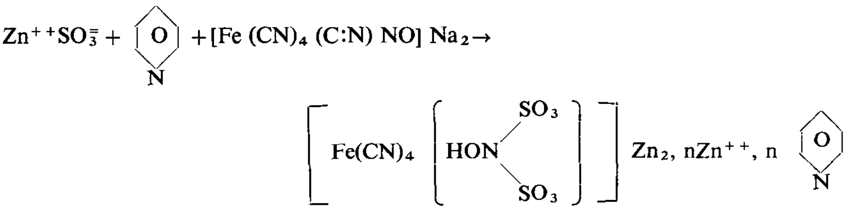


FIGURE 1 Experimental setup used for the saturation concentration measurements.

constant and accurate. The SO_2 collected on the impregnated filter reacts with the zinc acetate and is converted into zinc sulfite. The extraction or the elution of the sulfite from the filter is usually performed using 25.0 ml of a 1.0 M zinc-acetate solution. The easiest way to perform the extraction is by forcing the solution about 20 times through the membrane with two 30-ml syringes connected to the inlet and outlet of the filter holder. When the extraction is completed, a sample of 10.0 ml is taken from the resulting solution and the sulfite is titrated colorimetrically.

COLORIMETRIC REACTION

The reagent solution used to measure the SO_2 concentration colorimetrically contains the following components: sodium nitroprusside (0.50 g), water (50.0 ml), and pyridine (400 ml). To each test tube containing 10.0 ml of SO_2-polluted zinc acetate, 4.5 ml of the reagent is added. A deep-red colored complex is formed and, after half an hour's stabilization in the dark, the colorimetric reading is made at 450 nm corresponding to the λ_{max} of the complex. According to Bourbon's group,[5] the colorimetric reaction proceeds as follows:



The molecular structure of the red complex has not yet been established. Figure 2 shows calibration curves obtained with this complex. Using the equation below, the SO_2 concentration can be obtained directly from the absorbance or optical density (O.D.) reading and the calibration curves.

$$[SO_2]\ \text{mcg/m}^3 = \frac{\text{mcg/ml (curve)} \times \text{elution volume (ml)}}{\text{air sample (m}^3)}$$

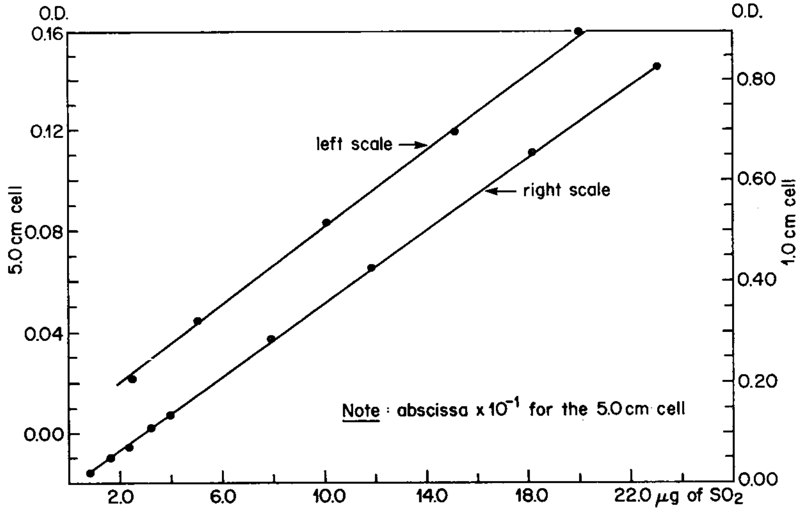


FIGURE 2 Calibration curves: absorbance or optical density (O.D.) versus the SO_2 concentration in mcg per ml of eluting solution.

As indicated by these curves, the lower limit of the technique using a 5-cm cell is of the order of 0.3 mcg of SO_2 per milliliter of eluting solution which is equivalent to about 0.003 ppm of SO_2 concentration when a volume of 1.0 m^3 of air has been sampled through the filter.

FILTER PERFORMANCE

The efficiency of the filters studied was tested in order to establish the limit of their best performance. The most interesting results are listed in Tables I and II. A mixed cellulose membrane (SSWPO4700 Millipore) and a triacetate membrane (Gelman-Ga-8 Metricel) were also tested but were soon discarded since they became deformed and friable after the drying process that follows impregnation, and this would have introduced technical difficulties. From the results described below, it will be seen how the Acropor filter (Tables I and II) also had to be discarded because it too was deformed by the drying process.

It rolls up and cannot be placed properly in the filter holder for the sampling. Furthermore, the high air flow (Table I) resistance of this membrane promotes the escape of the sampled air from around the membrane in the filter holder. These properties of the Acropor membrane explain the poor performance observed during experiments.

The saturation concentrations given in Table I correspond to the maximum weight of SO_2 collected on each filter before traces of it are detected on a filter or in a gas washing bottle placed in position 2 of the experimental setup illustrated in Figure 1. The ppm equivalent saturation concentration of 1.0 m^3 sample given in Table I would correspond to a 24-hr sampling period at an air-flow rate of 0.7 l/min. According to the Canadian maximum acceptable SO_2 concentration level (0.11 ppm on a 24-hr basis), the last three membranes listed in Table I would be satisfactory for at least a 24-hr sampling period.

Since no major chemical interference with the technique was observed,[5] the few orders of magnitude discrepancy between the observed and the stoichiometrically calculated saturation concentrations indicates that limiting collection factors are of a physical nature. Series of tests have shown that neither the relative humidity nor temperatures in the range of −40°C to 40°C alter the collection efficiency of membranes. This, together with the results of the collection efficiency as a function of the sampling rates, indicates that the limiting factors are associated with the filter's structure, its porosity and the number of gas molecular collisions with the filter.

Each collection efficiency result listed in Table II is based on at least five test runs. The experimental setup used for these tests is the one illustrated in Figure 1, without filter holder 2. Each sample studied was checked before and after the test run using an F.P.D. system (Trăcor-250H-Analyzer) or the West and Gaeke standard technique.[7] The F.P.D. system, sporadically checked against the West and Gaeke method, always showed an accuracy better than 98%. Calculation of the collection efficiency (*CE'*) is performed according to the following formula:

$$CE' = \frac{[SO_2] \text{ found on the membrane} \times 100}{[SO_2] \text{ of the sample measured with F.P.D.}}$$

According to the definition of collection efficiency given by Pate *et al.*[2] our results should be considered as the global efficiency of the technique or as its concentration measurement deviation compared with the F.P.D. system, since our *CE'* is not independent of the colorimetric concentration measurement.

Preliminary tests performed on these same filters in order to learn about their hydrogen sulfide *CE'* showed that the uncoated fiberglass filter is most efficient at a sampling rate of 1 l/min.[8] On the basis of such results and with

TABLE I

Physical properties of filters and their saturation concentration

Filter identification			Air flow rate		Saturation concentration		
			at ΔP = 700	Deviation compared with a 2.4 l/min calibrated	Stoichiometrically	Observed at 0.7 l/min on a 1.0-ppm sample	
Manufacturer	Catalogue number	Major constituent	mm of Hg[a] (l/min)	capillary (l/min)	calculated[b] mcg of SO_2	mcg of SO_2	ppm equivalence in 1 m^3 sample
Gelman	Acropor AN-450 F-2985-3	Acrilonitrile polyvinyl chloride copolymer	6	−1.4	11×10^3	~ 100	0.037
Gelman	9-730-60	Fiberglass with organic binder	30	−0.1	109×10^3	700	0.26
Gelman	9-730-64	Fiberglass	30	0.0	103×10^3	520	0.20
Millipore	AP-1004700	Paper	—	0.0	141×10^3	370	0.14

[a] From the manufacturer's catalogue.
[b] Based on the weight of zinc acetate held by each membrane.

TABLE II

Efficiency of the technique in various sampling conditions

Filter	Collection efficiency (*CE'*) of filters								Max. conc. deviation of 25 samples of 80 l
	$[SO_2] = 1.0$ ppm				$[SO_2] = 0.02$ ppm				$[SO_2] = 0.20$ ppm
	0.83 l/min (%) ±2	1.0 l/min (%) ±2	2.0 l/min (%) ±2	5.0 l/min ±2	0.8 l/min (%) ±2	1.0 l/min ±2	2.0 l/min ±2	5.0 l/min ±2	$\frac{\Sigma\lvert[SO_2]_{filter} - [SO_2]_{F.P.D.}\rvert \times 100}{[SO_2]_{F.P.D.}}$
Acropor		> 60	> 50	> 50	—				
Organic coated fiberglass	94		87	77	—	92	93	75	
Fiberglass	97	96	92	89	96	95	93	86	4.0
Millipore absorbent pad	99	—	98	89	—	93	90	72	

a view to using the same filter for simultaneous atmospheric H_2S and SO_2 sampling,[4,5] it was decided to perform a supplementary series of 25 tests on this uncoated fiberglass filter in order to evaluate more accurately the maximum concentration deviation of the technique (on 0.2-ppm samples at a flow-rate of 1 l/min). The 4% figure in the last column of Table II is the arithmetical mean of all the absolute values of the concentration deviation measurements.

The latter results confirmed all other results of this table and also indicate that the *CE'* obtained at 0.8 l/min on 1-ppm samples would probably have been 100% if they had been calculated according to Pate's formula,[2] since they deviate from 100% by less than 4%. As mentioned above, this 4% value represents the discrepancy between this technique and the F.P.D. method.

It can be concluded that the physical limiting factors of *CE'* become important only when the *CE'* value falls below 95%. According to this, the last two filters of Table II are the most efficient in a wider flow-rate sampling range for SO_2 collection. However, since the uncoated fiberglass filter has a higher saturation concentration limit than the Millipore pad and since it has been shown by preliminary tests to be more efficient for H_2S sampling, it is considered the most interesting membrane of the group both for normal use at a flow-rate of 1 l/min and for future development.

EXTENDED USES AND FUTURE DEVELOPMENT OF THE TECHNIQUE

Taking into account that the saturation concentration of the fiberglass filter is 500 mcg of SO_2 it can be calculated that this support could be used for stack sampling at 1 l/min or less on a 100-ml sample.

Preliminary tests indicate that the coloration can be obtained directly on the filter without going through the process of elution, etc. when the filter has been impregnated with a zinc-acetate solution containing the colorimetric reagents. However, more experiments will have to be performed in order to establish the best operating conditions for obtaining an accurate colorimetric scale. As soon as this scale is established, it will be possible to adapt the technique for use with an appropriate tape sampling and measuring instrument.

DISCUSSION

As indicated previously, the measuring range of the technique using a fiberglass filter goes from 0.003 ppm to 0.20 ppm when 1 m^3 of polluted air is sampled at a flow rate of 1 l/min. This measuring range can in fact be extended if a different volume of polluted air is sampled or if appropriate path length colorimeter cells are used for the lowest concentration measurements; the use of 10-cm colorimeter cells, for example, would lower the minimum detection limit by a factor of almost two.

As indicated by Malbosc[3] and Bourbon,[4,5] similar filters impregnated with zinc acetate can also be used to sample atmospheric hydrogen sulfide which can later be colorimetrically titrated using the acidic methylene-blue technique.[9] Preliminary results[8] already indicate that the measuring range of this technique is between 0.001 ppm and 0.5 ppm of H_2S for a 100-l sample.

Previous results [3–5,8] show that impregnated filters can also be used to sample simultaneously atmospheric SO_2 and H_2S which can subsequently be selectively titrated without interference. The latter aspect and the results presented here show that this new technique not only presents all the advantages of the West and Gaeke method and most of those of dry collectors, but also makes it possible to sample and measure quantitatively and selectively, two atmospheric pollutants. All these advantages, together with its simplicity, render the technique particularly attractive when a given area has to be blanketed with samplers.

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