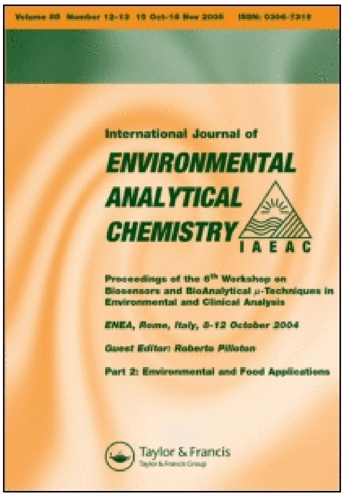

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Sampling and Analysis of Sulfur Dioxide and Particulate Sulfate in Air Using Impregnated Filters

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A simple procedure for simultaneous sampling, but separate analysis of SO_2 and SO_4^{2-} is described in this paper. Both species are collected on one and the same impregnated filter. Using tetrachloromercurate solution for impregnation, sulfur dioxide is effectively absorbed and stabilized as sulfite, but can easily be separated from the co-collected sulfate by a microdiffusion step. By this means both species can be determined in one sample by isotope dilution analysis (IDA).

Because the humidity of the impregnated filter has a distinct influence on the collection efficiency for SO_2, it is recommended to use the proposed technique for short-term sampling.

KEY WORDS: Air sampling, sulfur dioxide, sulfate, impregnated filters, microdiffusion, isotope dilution analysis.

INTRODUCTION

For the collection of atmospheric sulfur dioxide and sulfate several sampling procedures are in use. A widespread sampling train includes an aerosol (membrane) pre-filter placed ahead of a wash-bottle containing an absorber solution.[1–3] During the past years the use of impregnated filters instead of absorber solutions was recommended by several authors.[4–10] It has been observed, however, by several laboratories[3,11–16] that air filtration may lead to sampling artifacts due to interaction of SO_2 with the aerosol filter and (or) the dust collected on it.

In order to avoid such problems alternative procedures have been developed: Applying a diffusion separator (denuder), SO_2 can be extracted from the air prior to filtration.[17] An alternative approach would be the collection of sulfate and sulfur dioxide on one and the same filter, impregnated with a trapping and protecting agent for SO_2. In this case, however, selective analytical methods have to be applied to the determination of the two species. Filters impregnated with sodium tetrachloromercurate (TCM) have been used for the collection of particulate and gaseous trace compounds and the subsequent selective determination of SO_2 by a chemiluminescence technique.[18] We have developed a simple technique which also includes an impregnated filter preconcentration step, but which makes possible the separate determination of sulfur dioxide *and* sulfate present in one sample by utilizing a microdiffusion separation of SO_2. A microdiffusion technique using disposable polypropylene micro test tubes as diffusion cells has been applied in our laboratory to the separation of hydrogen fluoride from different matrices.[19] This technique allows the investigation of large series of samples on a routine basis. We have modified this procedure in order to separate SO_2 from filter extracts containing TCM. After the diffusion step, the SO_2 collected in an alkaline receptor as well as the sulfate in the diffusion residue (filter extract) are determined by isotope dilution analysis (IDA).[20,21]

EXPERIMENTAL

Apparatus

—Microlitre pipettes; polypropylene micro test tubes, capacity 1500 μl ("Eppendorf", Netheler & Hinz GmbH, D-2000 Hamburg).
—Electric rotator (Jahnke & Kunkel, D-7813 Staufen),
—Centrifuge "Christ-Mikrohämatokrit", 1600 rpm (Heraeus-Christ GmbH, D-3360 Osterode).
—Polyvinylchloride-filterholder for filters with 37 mm in diameter (see Figure 1); active filter surface diameter 22 mm.
—Vacuum pump AL17 (Neuberger KG, D-7800 Freiburg-Munzingen).
—Mass flow meter FM 361 (Tylan Corp., Torrance, Cal., USA).
—Liquid scintillation counter SL 30 (Intertechnique GmbH, D-6500 Mainz).

Reagents, solutions, and filters

All compounds used were reagent grade (Merck, D-6100 Darmstadt).
—10^{-4} M SO_2 stock solution ($5 \cdot 10^{-5}$ M $K_2S_2O_5$). The SO_2 content of the stock was standardized by iodometric titration before each set of experiments and the solution then used to prepare SO_2 standards.
—10^{-3}, 10^{-1} and 1 M HNO_3.

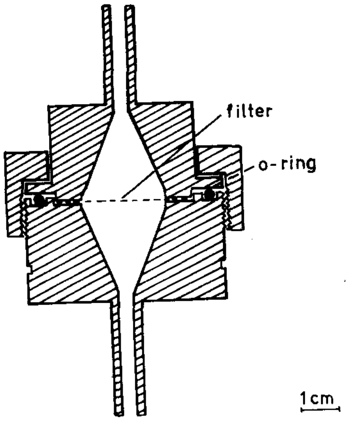

FIGURE 1. Polyvinylchloride-filterholder.

—10^{-1} and 1 M NaOH.
—10^{-1} M Na_2HgCl_4 (TCM).
—H_2O_2 solution, 30%.
—Na_2SO_4 standard solutions, each containing 0.1 mole/l of $NaNO_3$: 0.1 μgS/ml; 0.4 μgS/ml; 2.0 μgS/ml.
—Bray Scintillator[22].
—Ethanol, 98%.
—Radioreagent for IDA:
About 140 mg ($6 \cdot 10^{-4}$ moles) of freshly prepared $BaSO_4$ are dissolved in one litre of a hot (333–353 K) 0.01 M EDTA solution, which contains 0.4 moles NH_3. To 20 ml of this reagent 50 nCi (1850 Bq) of carrier free $^{35}SO_4^{2-}$ (Amersham-Buchler, D-6000 Frankfurt) are added. By this means the equimolar ratio of Ba^{2+} to SO_4^{2-} is practically not changed.
—Cellulose filters, S & S No. 2668, 37 mm in diameter (Schleicher & Schüll, D-3354 Dassel). The cellulose filters are immersed in 0.001 M HNO_3 for several hours, then rinsed with deionized-distilled water, dried at 373 K, and stored in a desiccator until used.

PROCEDURES

1. Collection of SO_2 and SO_4^{2-} on impregnated cellulose filters

An area of 22–24 mm in diameter in the center of a filter is impregnated with 200 μl of 0.1 M TCM solution by means of a microlitre pipette. The filter is placed, still wet, into the PVC-filter holder and a definite volume of air is drawn through it. During the collection the water content of the impregnated area of the filter decreases, but the filter remains moist at sampling times up to 15 min. After the sampling a disc of 26 mm in diameter is punched out of the center of each filter,[23] folded by using Teflon[R] coated forceps, and transferred into a micro test tube. In order to extract the collected sulfate as well as the sulfito mercurate together with the excess TCM, 1 ml of deionized-distilled water is added and the tube closed and rotated in an electric rotator for half an hour. After centrifugation for about 3 min, a 500-μl aliquot is taken from the filter extract for microdiffusion.

For economic analysis, series of filter samples may be pre-treated in the same manner.

2. Separation of SO_2 from the filter extracts by microdiffusion

A number of diffusion cells sufficient for the samples and standards to be analyzed is prepared by using the original Eppendorf micro test tubes.[19] The lids are cut off from the tubes to which they are attached by a plastic stem. Into the little compartment on the inner side of each lid 20 μl of 0.1 M NaOH are pipetted. The solutions are evaporated to dryness at 353 K, so that the receptor compartments now contain a small amount of NaOH (or Na_2CO_3).

After having transferred the 500-μl aliquots of the filter extracts to the micro test tubes, 50 μl of 1 M HNO_3 are added to each sample and the tubes then closed immediately with the receptor lids already prepared. All diffusion cells are rotated by an electric rotator (ca. 10 rpm) using a disc which holds the tubes in nearly horizontal positions (see Figure 2). After 3-h diffusion time, the lids are removed from the diffusion cells and trans-

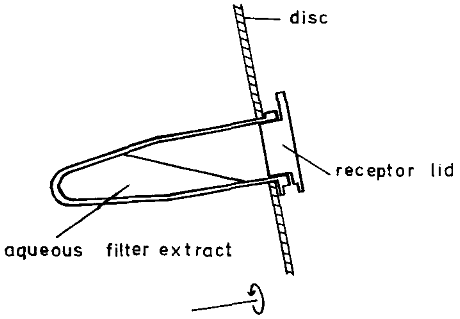

FIGURE 2. Microdiffusion cell.

ferred onto new test tubes, each of which contains already a mixture of 500 μl of H_2O, 5 μl of H_2O_2, and 20 μl of 0.1 M HNO_3. By shaking these tubes for a few seconds, the alkaline receptors are removed from the lids and neutralized, and the absorbed SO_2 is oxidized to SO_4^{2-}. The solutions obtained (solutions I) are then analyzed for sulfur by IDA.

In order to avoid systematic errors caused by incomplete separation of the SO_2 in the diffusion step, 500-μl portions of the four standard solutions in the range 0.64–6.4 μg SO_2/ml, containing the same amount of TCM as the filter extracts, are prepared from the 10^{-4} M SO_2 stock solution. These standards are subjected to the same microdiffusion and redissolution procedure as described above for the samples, and the IDA results obtained are used to prepare the calibration curve for the analysis of solutions I (determination of SO_2). It is advisable to always get two standard solutions for each concentration through the procedure.

The acidic diffusion residues, which contain all the particulate sulfate extracted from the filters are neutralized by adding 50 μl of 1 M NaOH to each of the tubes used for microdiffusion. The solutions so obtained (solutions II), with a total volume of 600 μl each, are likewise analyzed by IDA. Here the standard solutions used for calibration (0.1; 0.4; 1.0 and 2.0 μg S/ml) must contain about the same $NaNO_3$ concentration (0.1 mole/l) as the samples (0.083 moles/l). Otherwise a "salt-effect" would yield slight systematic errors.

3. Determination of SO_2 and SO_4^{2-} by IDA[20,21]

Solutions I (SO_2): The micro test tubes containing the solutions I (or the corresponding standards) are centrifuged for 30 sec in order to remove the liquid droplets from the lids. Then each solution is mixed with 100 μl of the radioreagent, equivalent to m μg of labelled sulfate sulfur with an activity A_0, and with 500 μl of ethanol. Each mixture is acidified with 30 μl of 0.1 M HNO_3 to adjust a pH of 2–3. By this means barium is demasked and barium sulfate, equivalent to the amount of barium ions present, begins to precipitate slowly. The tubes are closed again with the lids and, after standing over night, are centrifuged for 3 min. Finally the activities, A_x, of aliquots of the supernatant liquids are measured in a liquid scintillation counter.

Because the specific activity of the sulfate sulfur in the supernatant, A_x/X with X = unknown amount of sulfur, and in the precipitate, $(A_0 - A_x)/m$, must be the same, the following relationship between X and A_x can be derived:

$$X = m \cdot \frac{A_x}{A_0 - A_x} \; [\mu\text{gS}]$$

Therefore a calibration curve is obtained by plotting the ratios $A_{x,s}/(A_0 - A_{x,s})$, which have been calculated for the SO_2 standards, against the known standard concentrations. These can be expressed as [μgS] or directly as [μg SO_2].

To make results reliable the set of standards is always run together with the samples. For each series both the maximum activity A_0 and, for control, the blank activity A_b have to be determined in duplicate. A_0 can be measured with mixtures which contain 30 μl of deionized-distilled water instead of 0.1 M HNO_3, so that $Ba^{35}SO_4$ is not precipitated. A_b will be obtained when solution I is replaced by 525 μl of deionized-distilled water.

Solutions II (SO_4^{2-}): A 500-μl aliquot of each of the solutions II (or the corresponding standards) is transferred into a new micro test tube. Here each solution is mixed with 100 μl of the radioreagent and 500 μl of ethanol. The mixtures are then treated in the same manner as described above. The calibration curve is obtained by utilizing the $NaNO_3$ containing Na_2SO_4 standard solutions. Each result obtained for solutions II has to be multiplied by the factor 6/5 because the sample solutions have a volume of 600 μl.

Because even the washed filters may still exhibit a distinct sulfate blank (see Table III), the latter has to be determined for each batch and subtracted from the sulfate contents of solutions II if necessary.The blanks are obtained by extracting discs of 26 mm diameter of the pre-purified and impregnated filters with 1 ml of deionized-distilled water and analyzing the extracts according to the IDA procedure just given.

Calculation of the total amounts of collected sulfur dioxide and sulfate, respectively: Under the experimental conditions used in the laboratory studies (40 l/h sampling flow rate, 76% r.h. of the carrier gas), about 50% of the solvent (ca. 100 μl) will be lost from the impregnated part of the filter at sampling times of about 10 min. After the extraction of the still humid filter with 1 ml of water, the total volume of the extract will consequently be ca. 1.1 ml. Because an aliquot of 500 μl is invariably taken for analysis, the results obtained for solutions I and II have to be multiplied by the factor 2.2 in order to gain the total amounts "μg SO_2/filter" or "μg S/filter" (Tables I to III).

During the field experiments summarized in Table VI the sampling times were between 60 and 240 min, so that the impregnated filters were running practically dry during the sampling. Therefore the factor 2 was used for calculation in this case.

RESULTS AND DISCUSSION

Using impregnated filters for sampling of SO_2, several parameters like thickness of the filter material, concentration of the absorbing agent, and humidity in the sampling system may influence the collection efficiency. This was demonstrated through laboratory studies employing a permeation device[24] as a sulfur dioxide reference source.

Figure 3 illustrates that only thick cellulose filters like Whatman No. 17 and Schleicher & Schüll (S & S) No. 2668 exhibit good sampling yields. The concentration of the absorber solution used for filter impregnation has an influence on the collection efficiency, when solutions with concentrations of less than 0.01 M TCM are employed (see Table I). The

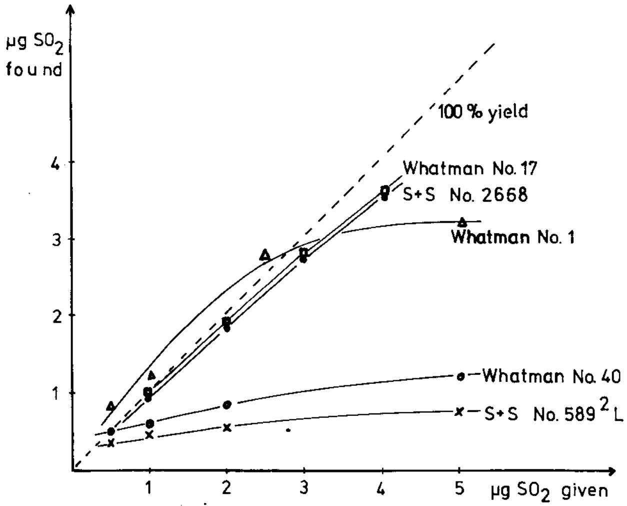

FIGURE 3. Sampling efficiency for SO_2 using different cellulose filters impregnated with 0.1 M TCM solution. SO_2 concentration in the N_2/SO_2 calibration gas: 523 ppb; sampling flow rate: 40 l/h.

TABLE I

Sampling efficiency for SO_2 as a function of the TCM concentration. Each result is the mean of two measurements. SO_2 concentration in the calibration gas: 131 ppb. R.h. of the calibration gas: 76%. Sampling flow rate: 40 l/h. All values corrected for the blank of the washed filters.

	0.1 M TCM		0.01 M TCM		0.001 M TCM	
SO_2 given [µg/filter]	SO_2 found [µg/filter]	Yield [%]	SO_2 found [µg/filter]	Yield [%]	SO_2 found [µg/filter]	Yield [%]
0.23	0.22	96	0.24	109	blank	—
0.46	0.40	87	0.44	96	blank	—
1.15	0.92	80	0.88	77	0.84	73
2.30	1.90	83	2.00	87	1.64	71

humidity of the collection media is also very important. Table II shows that only wet impregnated filters yield satisfying results. Working with dry filters even in a humid atmosphere does not prove to be efficient.

TABLE II

Sampling of SO_2 at different humidity conditions. Sampling flow rate: 40 l/h. SO_2 concentration in the calibration gas: 523 ppb. Sampling times: 1, 2 and 4 min, respectively. All values corrected for the blank of the washed filters.

Filter impregnated with 0.1 M TCM solution	μg SO_2/filter given	N_2 carrier gas, dry		N_2 carrier gas, 76% r.h.	
		μg SO_2/filter found	% yield	μg SO_2/filter found	% yield
Whatman No. 17	1.0	0.29	29	0.24	24
dry	2.0	0.24	12	0.28	14
	4.0	0.24	6	0.26	6.5
Whatman No. 17	1.0	0.98	98	0.96	96
wet	2.0	1.68	84	1.64	82
	4.0	3.20	80	3.24	81
Schleicher & Schüll	1.0	0.24	24	0.24	24
No. 2668	2.0	0.30	15	0.40	20
dry	4.0	0.24	6	0.40	10
Schleicher & Schüll	1.0	0.98	98	0.92	92
No. 2668	2.0	1.68	84	1.60	80
wet	4.0	3.20	80	3.20	80

Variation of the sampling flow rate between 20 l/h and 120 l/h does not significantly affect the collection efficiency for SO_2.

The reproducibility of the sampling procedure, obtained by directly analyzing the extracts of the loaded filters (without microdiffusion) using IDA, is illustrated by Table III. As can be seen, the efficiency decreases with increasing amounts of SO_2 collected, this means with increasing sampling times. This effect, which needs further investigation, might be caused by changes in humidity of the impregnated part of the filter during the sampling (see above). For the time being the proposed technique can therefore be recommended only for short-term sampling employing sampling times up to about 15 min.

Controlling the SO_2 collection efficiencies over a period of several days, no systematic deviation from the measured values could be observed.

The rate of the SO_2 separation by microdiffusion is dependent on the pH, as can be seen from Figure 4. A quantitative transfer of the SO_2 to the receptor can be obtained only at a $pH \leq 1$ of the filter extract. Under these conditions separation is complete after 3-h diffusion time.

TABLE III

Reproducibility of the SO_2 sampling procedure. Sampling flow rate: 40 l/h. SO_2 concentration in the calibration gas: 131 ppb. R.h. of the calibration gas: 76%. All values corrected for the blank of the washed filters.

Added μg SO_2/filter	Sampling time [min]	Found (mean of 10 values) μg SO_2/filter	Standard dev. μg SO_2/filter	Rel. standard dev. [%]	Yield [%]
0.23	1	0.22	±0.032	±14.5	96
0.46	2	0.40	±0.034	± 9	87
1.15	5	0.94	±0.084	± 9	80
2.30	10	1.90	±0.048	± 2	83
Blank of the washed filters (26 mm diameter)		0.38 (0.19 μg S)	±0.018	± 5	

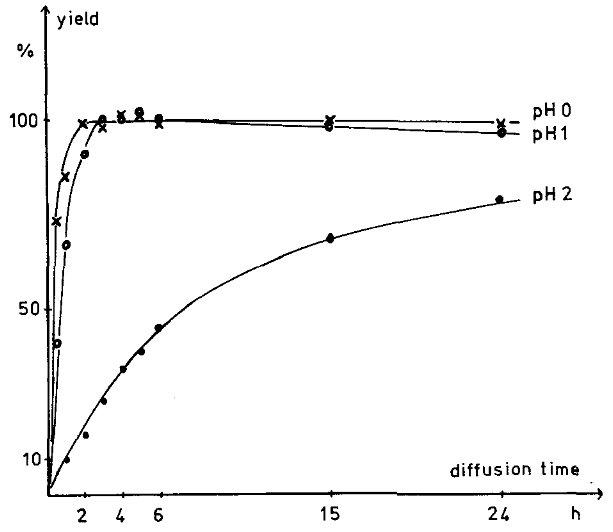

FIGURE 4. Rate of the SO_2 transfer to the receptor at different pH values. Sample volume: 500 μl; SO_2 concentration: 2.16 μg/ml (as $K_2S_2O_5$); TCM concentration: 0.01 M.

The TCM concentration of the filter extract seems to have no influence on the diffusion separation of SO_2 (see Table IV). Therefore the relatively high concentration (0.1 M TCM) of the solution used for impregnation of the filters is not critical.

TABLE IV

SO_2 transfer to the receptor out of $K_2S_2O_5$ solutions of different TCM concentrations at pH 1.

SO_2 added [μg/ml]	TCM [moles/l]	SO_2 found [μg/ml]	Yield [%]
0.54	0	0.52	96
1.08	0	1.00	92
2.16	0	2.08	95
5.40	0	5.00	93
0.54	10^{-2}	0.56	103
1.08	10^{-2}	1.00	92
2.16	10^{-2}	2.16	100
5.40	10^{-2}	5.00	93
0.51	$5\cdot10^{-2}$	0.50	98
1.02	$5\cdot10^{-2}$	0.95	93
2.16	$5\cdot10^{-2}$	2.12	98
5.40	$5\cdot10^{-2}$	5.05	94

The overall reproducibility of diffusion separation and subsequent IDA is shown in Table V. Here similar statistical errors as described earlier for IDA[20,21] have been achieved.

The combined sampling of SO_2 and SO_4^{2-} and the separate determination of both species was investigated using field samples. For this purpose two filter holders were operated in parallel, the flow rate in each sampling train being adjusted by a critical orifice and measured by a mass-flow meter. Thus a comparison between the results obtained for each set of parallel samples could be made.

TABLE V

Reproducibility of diffusion separation and subsequent IDA. Volume of the $K_2S_2O_5$ "sample" solutions: 500 μl. TCM concentrations of the "sample" solutions: 0.01 M.

SO_2 added [μg/ml]	SO_2 found mean of 10 values [μg/ml]	Standard dev. [μg/ml]	Rel. standard dev. [%]	Yield [%]
0.51	0.50	±0.02	±4.5	98
1.02	0.95	±0.05	±5.3	93
2.05	1.97	±0.09	±4.7	96
5.12	4.72	±0.28	±5.9	92

After each sampling period the two filters were extracted and the extracts analyzed according to the following scheme:

Filter 1: Determination of SO_2 according to the described technique (microdiffusion separation) using IDA. Determination of SO_4^{2-} in the diffusion residue using IDA.

Filter 2: Determination of total sulfur using IDA.

In Table VI the results are listed. The sum of SO_2 and SO_4^{2-}, both separately determined by the described technique and expressed as [μg S/filter] (filter 1), is in good agreement with the total sulfur content determined by IDA as the sum of $SO_2+SO_4^{2-}$ (filter 2). It must be pointed out, however, that these mass balances illustrate the reliability of the combination of diffusion separation and IDA, but give just a rough idea of the actual SO_2 mixing ratio in the air under study. This is because the efficiencies of SO_2 collection during sampling times of more than 15 min are not yet known. The observed decrease in collection efficiency with increasing sampling time needs to be further investigated experimentally under field conditions.

TABLE VI

Determination of SO_2 and SO_4^{2-} in air samples taken at the campus of the University of Dortmund in June 1978. Sampling flow rates: filter 1 = 123 l/h, filter 2 = 112 l/h. Sampling times: 60–240 minutes. Results for filter 2 related to the sampling flow rate of filter 1. All values in the second, third and last column corrected for the blank of the washed filters.

Filter 1: microdiffusion technique + IDA			Filter 2: total sulfur (IDA)
SO_2 μg S/filter	SO_4^{2-} μg S/filter	$SO_2+SO_4^{2-}$ μg S/filter	$SO_2+SO_4^{2-}$ μg S/filter $\cdot\frac{123}{112}$
0.4	0.2	0.6	0.5
0.1	0.2	0.3	0.3
0.2	0.2	0.4	0.4
0.1	0.2	0.3	0.3
0.4	0.5	0.9	0.9
0.1	0.4	0.5	0.5
0.3	0.8	1.1	1.0
0.2	0.6	0.8	0.9
0.1	0.8	0.9	1.0
0.1	0.5	0.6	0.6

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