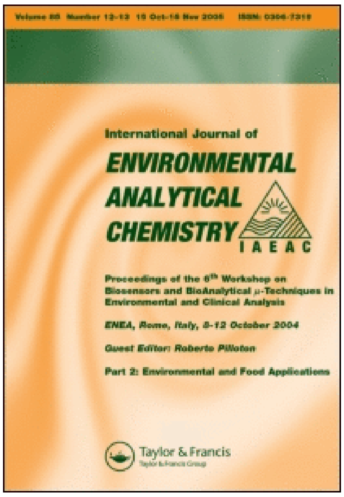

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

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To cite this Article Meixners, F. X. and Jaeschke, W. A.(1981) 'The Detection of Low Atmospheric SO_2 Concentrations with a Chemiluminescence Technique', International Journal of Environmental Analytical Chemistry, 10: 1, 51 — 67
To link to this Article: DOI: 10.1080/03067318108071531
URL: http://dx.doi.org/10.1080/03067318108071531

Intern. J. Environ. Anal. Chem., 1981, Vol. 10, pp. 51–67
0306-7319/81/1001-0051 $06.50/0

Printed in Great Britain

The Detection of Low Atmospheric SO_2 Concentrations with a Chemiluminescence Technique†

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(*Received September 5, 1980*)

A chemiluminescence effect was found during oxidation of disulfitomercurate complex in aqueous solutions with $KMnO_4$ under acid conditions. By employing a filter technique for air sampling the chemiluminescence method is applied to the detection of atmospheric sulfur dioxide. The quality of the complete procedure is demonstrated by comparative calibrations from the liquid and gas phase and comparative measurements with several other SO_2 sensitive methods. The detection limit is shown to be (10 ± 1) pptv SO_2. Some measurements of atmospheric SO_2 background concentrations are shown in order to demonstrate the potential of the whole procedure in its application to atmospheric SO_2 measurements.

KEY WORDS: Atmospheric SO_2, chemiluminescence, disulfitomercurate complex.

INTRODUCTION

Besides the recent comprehensive investigations of SO_2 as a man-made pollutant studies of SO_2 in unpolluted environments become more and more important. With increasing distance from the industrialized areas and, even more, from the continents the atmospheric SO_2 mixing ratio strongly decreases to the extreme low so-called background value which ranges between 0.01–1.0 ppbv.[1,2] Generally the SO_2 background over the oceans was explained by long range transport from the continents. But

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†Paper presented at the 10th Annual Symposium on the Analytical Chemistry of Pollutants, May 1980, Dortmund GTR.

with the discovery of organic sulfur compounds[3,4] the oxidation of these trace gases initiated by the OH radical seems to be a dominant source of atmospheric SO_2 in remote areas.[5] Due to the insufficient sensitivity none of the continuous SO_2-monitoring methods is applicable to the experimental investigations of the SO_2 background. Therefore, accumulating methods are used such as the well-established tetrachloromercurate (TCM) method.[6] By applying this method to maritime and aerological measurements the quality of the subsequent analysis performed by the rosaniline method is strongly affected by interference from other atmospheric constituents.[7] With the development of a new sensitive chemiluminescence method[8] which permits the analysis of 0.5 ng SO_2/ml in the reaction liquid the basis was created for reliable measurements of SO_2 mixing ratios in remote areas.

The reaction scheme of the chemiluminescence reaction was discussed in detail in an earlier paper.[9] The disulfitomercurate complex which is formed during the SO_2 sampling is generally stable against oxidation under neutral pH conditions. However, treating this complex with $KMmO_4$ in an acidic solution (pH 3) dissociation occurs and the free bisulfite ion is oxidized by $KMnO_4$ to a bisulfite radical, which may recombine to dithionate. This ion disproportionates into sulfate and an SO_2 molecule in an excited state which is the carrier of the chemiluminescence.

$$\begin{array}{ll}
2SO_2+Na_2[HgCl_4]+2H_2O \rightarrow & Na_2[Hg(SO_3)_2]+4HCl \\
{[Hg(SO_3)_2]^{2-}}+2H^+ & Hg^{2+}+2HSO_3^- \\
HSO_3^-+MnO_4^- & HSO_3+MnO_4^{2-} \\
2HSO_3 & S_2O_6^{2-}+2H^+ \\
S_2O_6^- & SO_4^{2-}+SO_2^* \\
SO_2^* & SO_2+h\nu
\end{array}$$

EXPERIMENTAL

The method to be described consists of separate filter sampling and subsequent analyzing by the chemiluminescence technique. Retaining the same chemical principles of absorbing and stabilizing the atmospheric SO_2 in the liquid phase as reported by West and Gaeke[6] the chemiluminescence method detects SO_2 (sulfite) traces in a solution.

Filter sampling

For the absorption and stabilization of gaseous SO_2 traces impregnated filters instead of impingers are used. This was already done by Axelrod and Hansen[10] in order to overcome the disadvantages of bubblers concerning the detection limit and the risk of contamination. The filter material (Delbag Microsorban 98, 47 mm dia.) is inserted in a teflon filterholder (see Fig. 1). Pouring 5 ml of 0.1 m TCM solution onto the filter, its surface is completely covered with a 3 mm-layer of the impregnation liquid. Then the liquid is sucked through and down into a clean sampling tube by a short operation of the pump in the sampling device (Figure 1). To be sure that the impregnation of the filter material is complete this procedure is repeated two times. The obtained 15 ml of washing solution is then analyzed by the chemiluminescence technique described below. The prerequisite for a clean filter ready for sampling is achieved when the analysis of the impregnation liquid equals the blank value of the pure TCM solution. Otherwise the washing procedure must be repeated. Air samples are now taken leading a required amount of air through the filter with a flow-rate of approximately 10 liters STP/min. Traces of atmospheric SO_2 are absorbed in the filter forming the very

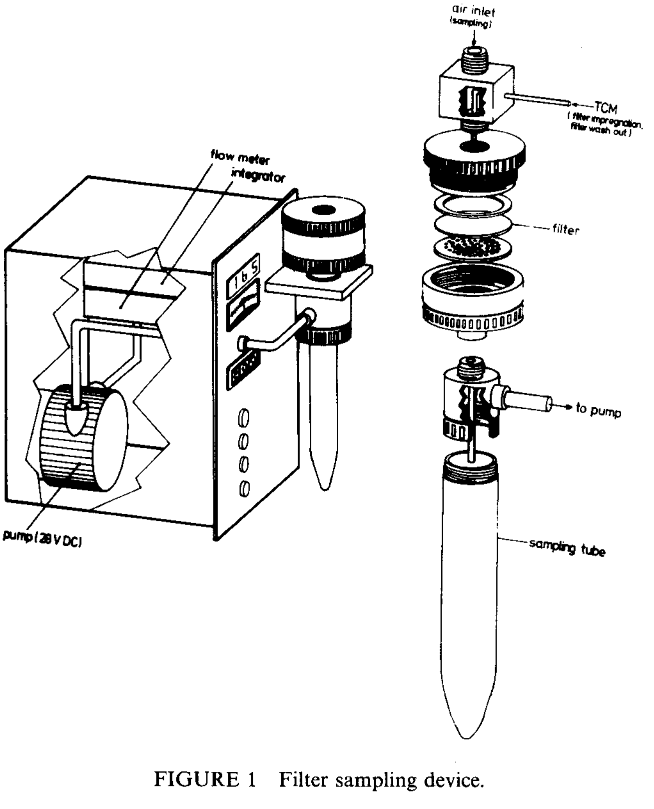

FIGURE 1 Filter sampling device.

stable disulfitomercurate complex. After sampling is completed the filter—still inserted in the filter-holder— is once again washed out 3 times with 5 ml of 0.1 m TCM solution. This 15 ml of washing solution collected in the sampling tube is immediately analyzed by the chemiluminescence technique. Experiments have shown that the washing solution of still another rinsing shows the blank. Therefore, having established the blank status of the filter it is possible to use the filter for the next sampling. The re-use of the filter material for sampling (without removing the filter out of the filterholder) can be repeated up to five times until the filter must be exchanged.

Analytical set-up and procedure

Analysis of the complexed SO_2 (disulfitomercurate) in the liquid sample is based on its oxidation to sulfate by an acid potassium permanganate solution. Figure 2 shows a scheme of the analyzing apparatus. The main part is a light proof reaction chanber with a window open to the photocathode of a photomultiplier (RCA 8575). In order to obtain a high reproducibility of the multiplier signals under laboratory and field conditions the multiplier is cooled down to a constant temperature of +5°C. The analyzing procedure starts as follows: 5 ml of the solution to be analyzed and 1 ml of a solution of 8×10^{-6} $KMnO_4$ in diluted H_2SO_4 are successively injected into the reaction chamber by automated syringes. As soon as mixing of both agents starts photons are counted for a period

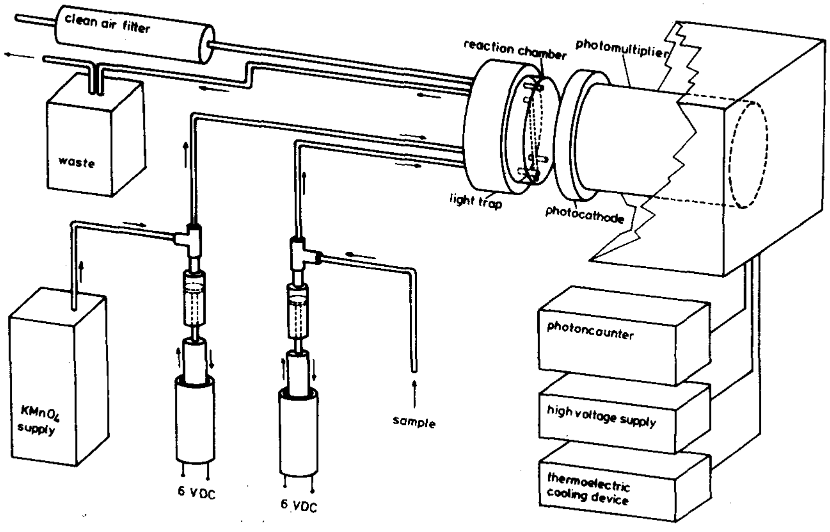

FIGURE 2 Analyzing apparatus, schematic diagram.

of 100 seconds (photocounter: Brookdeal 5Cl). The light yield is proportional to the content of complexed SO_2 present in the sample. Then the reaction chamber is emptied, whereby the incoming air has to pass through a clean-air-filter (charcoal, silicagel) to avoid the contamination of the reaction chamber.

Only 5 ml of the liquid to be analyzed are sufficient for one analysis. Because each sample consists of 15 ml the analysis procedure is applied three times on each sample. Due to the length of the tubings between syringe and reaction chamber the first analysis shows a memory effect of the previous sample and is therefore rejected. The analyses of the next two 5 ml generally have a reproducibility of better than 2%.

Preparation of liquid standards

The calibration of the chemiluminescence effect needs sulfite standards. The equivalent SO_2 content of a primary standard solution of $Na_2S_2O_5$ is determined gravimetrically and by jodometric titration. The SO_2 equivalent is in the range of 10^5ng SO_2/ml. Reagents of analytical grade and deionized water are used. Then a set of standards down to 0.5 ng complexed SO_2/ml is achieved by diluting the primary standard solution with 0.1 m TCM. Hereby micropipettes (Eppendorf, SMI) are used which are calibrated gravimetrically. Although the dilution with TCM provides a sufficient stability of the complexed SO_2 fresh standard solutions are prepared each day measurements are performed.

Dynamic gas dilution system

For investigating the filter sampling efficiency a dynamic gas dilution system was constructed (Figure 3) which allowed a calibration procedure from the gas phase. Using a high volume compressor outside air is pressed through a water vapor trap, several clean-air-filters (silicagel, activated charcoal) and aerosol filters (cotton wool, Delbag) in order to achieve a SO_2, water vapor and aerosol free carrier gas. Prediluted SO_2 mixtures (0.1–4 ppm) are generated in a commercial SO_2 calibrator (Mon. Labs., model 8500) using a NBS-calibrated permeation tube. Due to the Venturi Effect of the carrier gas in the "mixing head" these SO_2 mixtures can be further diluted up to 3 orders of magnitude. Glass tubes (Schott-system) are used for the carrier gas part of the system, while teflon material and tubing are preferred for the other parts. Monitoring the permeation output of the SO_2 calibrator and the 3 flow-meters the SO_2 mixing ratio at the outlet of the system is determined with the formula given in Figure 3. With the dynamic gas dilution system and the used permeation tubes outlet mixing ratios of 0.05-30 ppbv SO_2 can be obtained.

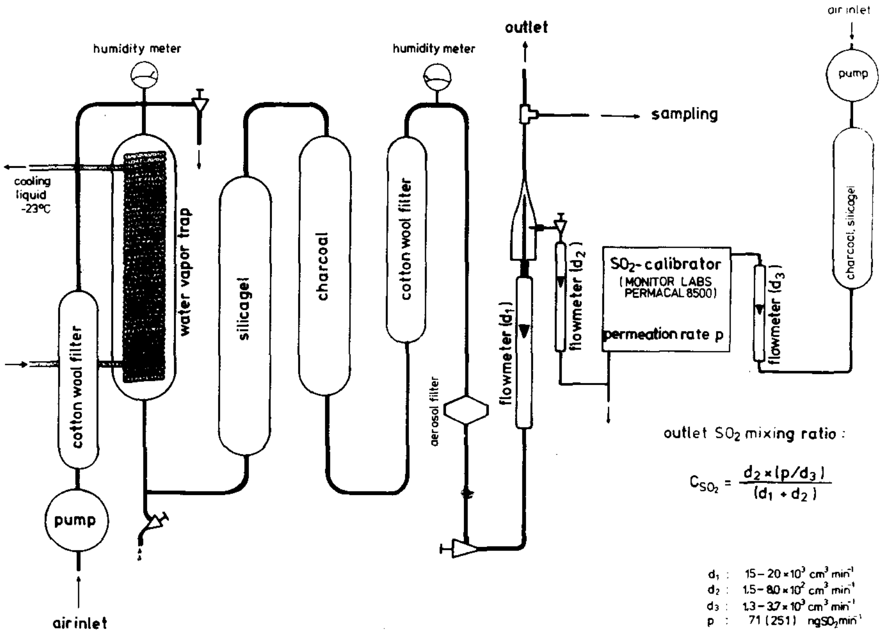

FIGURE 3 Dynamic gas dilution system for preparation of gaseous SO_2 standards.

The absence of water vapor and trace metal containing aerosol particles—but especially those containing heavy metals—in the whole system is an important condition for stable gaseous blends with extreme low SO_2 contents. Otherwise SO_2 calibration mixtures are irreproducibly affected by rapid catalytic oxidation. In addition the choice of inert material and the design of the apparatus as an open dynamic system provide that falsifications of the SO_2 blends due to absorption on the walls of the tubings are negligible.

RESULTS

Liquid phase measurements

In order to optimize the described chemiluminescence effect the influence of the pH value and the $KMnO_4$ concentration as well as the variation of technical conditions of the evaluating device on the obtained light yield were investigated.

A concentration of $8\text{–}10^{-6}$m $KMnO_4$ solution was found to cause an optimum light yield. Doubling or reducing this concentration in half shows only an insubstantial effect on the light yield while increasing the

$KMnO_4$ concentration by more than 2 orders of magnitude the chemiluminescence is greatly diminished due to the absorption of the blue $KMnO_4$.

Figure 4 shows the dependence of the relative light yield on the pH value of the $KMnO_4$ solution and on the complexed SO_2 content of the sample. Generally a maximum of the relative light yield is observed between 20–40 ng complexed SO_2/ml for all pH values. The dependence on the pH value is marked by a maximum of the relative light yield at pH 2.5. The decrease is more pronounced with higher than with lower pH values. In order to obtain a maximum of light yield even at complexed SO_2 concentrations below 20 ng/ml a pH value of 2.5 is used for the

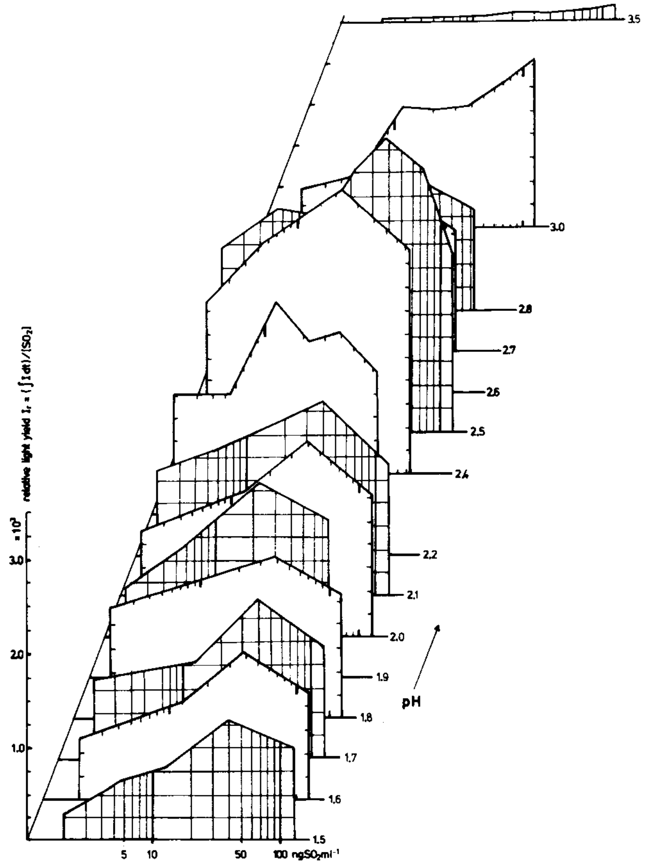

FIGURE 4 The dependence of the relative light yield on the pH value of the $KMnO_4$ solution and on the complexed SO_2 concentration of the sample (details see text).

$KMnO_4$ solution. The pH value of a diluted H_2SO_4 solution is determined with a sensitive pH meter (Orion, model 601). The $KMnO_4$ solution must be renewed every 3–4 hours in order to provide sufficient efficiency of the solution.

The detection limit of the chemiluminescence technique can best be discussed by considering Figure 5. Treating a pure 0.1 m TCM solution which does not contain any sulfite traces with 8×10^{-6} m $KMnO_4$ in the reaction chamber a certain light yield occurs. This light yield is identical

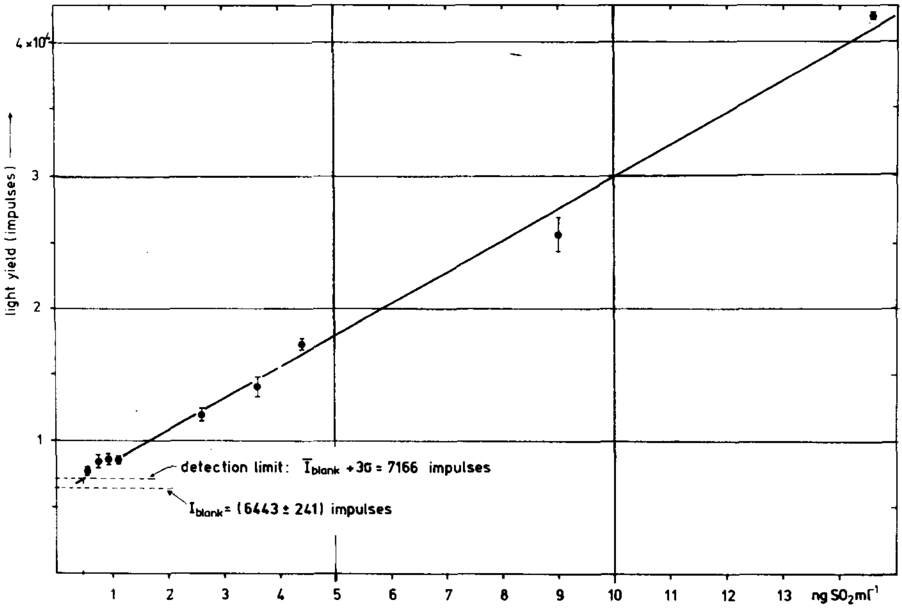

FIGURE 5 Calibration curve of the SO_2 detection method with the chemiluminescence technique.

to the blank of the method because it exceeds the dark current of the photomultiplier by more than a factor of 2. To get significant statistical results 15–30 blank values have to be measured. According to Specker and Kaiser[12] the mean of these blank values and their standard deviation define the detection limit as the mean plus 3 times the standard deviation. The calibration curve obtained by analyzing liquid standards is shown in Fig. 5. The detection limit of 7166 impulses corresponds to a complexed SO_2 concentration of 0.5 ng/ml.

The chemiluminescence method was compared with the rosaniline method by using the same sulfite standards. Generally the comparison of the two methods is difficult due to the fact that the chemiluminescence technique exceeds the rosaniline method by at least one order of magnitude concerning range and detection limits. Nevertheless, the concentration range of 10–100 ng complexed SO_2/ml was found to be overlapping. The results of the measurements were used for a regression analysis. As can be seen from Fig. 6, a significant relation exists between the two methods.

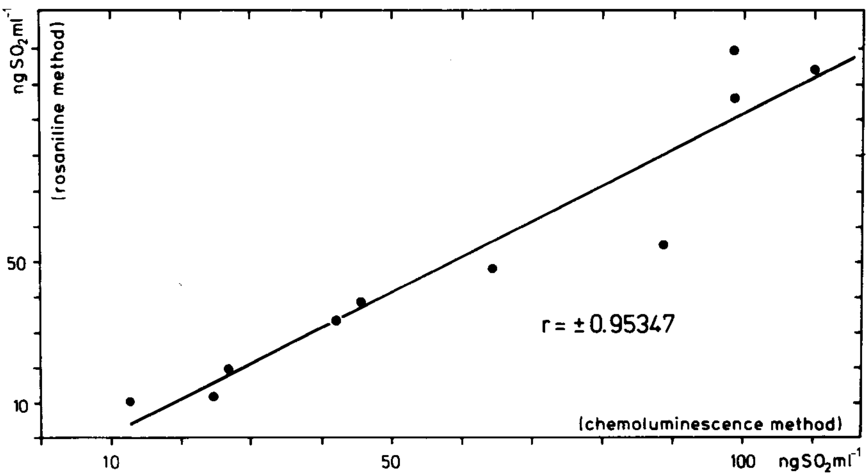

FIGURE 6 Correlation of the analytical data gained during intercomparisons of the chemiluminescence and rosaniline method.

Gas phase measurements

When a filter technique is used for sampling atmospheric SO_2 traces the important question of sampling efficiency must be considered. Coupled with this aspect is the calibration of the whole detection system (i.e. filter sampling and chemiluminescence technique) which is only possible with gaseous SO_2 standards. Axelrod and Hansen[10] reported that the filter sampling efficiency is seriously affected by the amount of sampling volume if the relative humidity of the sampled air decreases to 10% or even less. The described dynamic gas dilution system generates SO_2 blends which are nearly perfectly dry (r.h. 5%). During investigations of filter sampling efficiency the gas phase calibration was performed with these extremely dry SO_2 blends. This was done because the filter sampling should also be applied to stratospheric measurements.[11] Furthermore, the method should be examined under the most disadvantageous conditions of ground-based measurements.

Figure 7 shows the effect of sampling volume on filter sampling efficiency. Up to 100 liters the sampling efficiency is not detectably influenced and even up to 200 liters sampling efficiency does not decrease by more than 10%. Because experience has shown that the high degree of simplicity of the filter sampling technique is an invaluable advantage under field conditions the authors did not carry out further modifications for volumes above 200 liters.

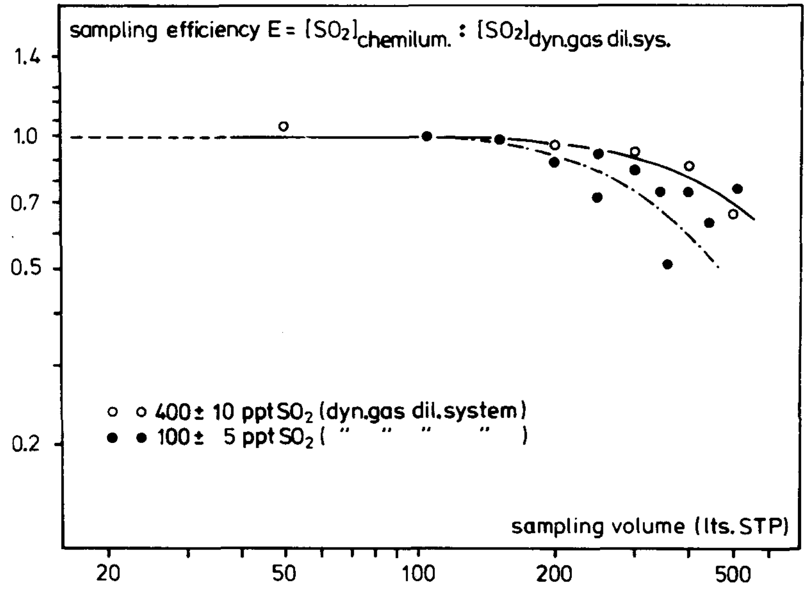

FIGURE 7 The dependence of filter sampling efficiency on the sampling volume.

Calibration of the chemiluminescence effect with gaseous SO_2 standards from the dynamic gas dilution system is possible by applying the filter sampling technique. The complexed SO_2 content of the occurring washing solutions can be calculated since the SO_2 mixing ratio, the sampling volume and the amount of washing solution are known. Then the chemiluminescence effects which correspond to the calculated concentrations are compared with the chemiluminescence effect gained in the liquid phase by analyzing standard sulfite solutions. The comparison was performed by using regression analysis (Figure 8). The excellent agreement which is observed demonstrates the equivalent quality of liquid and gas phase calibration of the chemiluminescence method.

The minimum value of the atmospheric sulfur dioxide concentration which can be detected with the whole method is determined by the

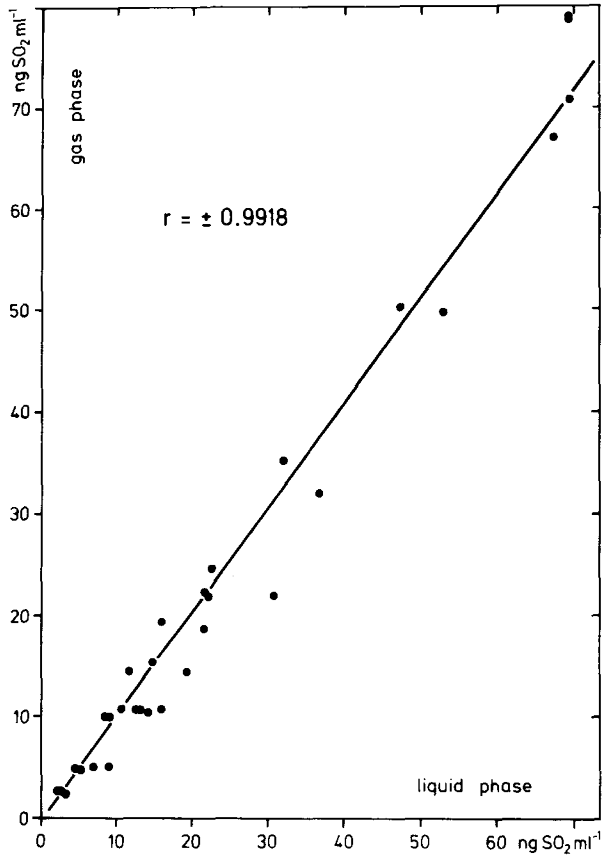

FIGURE 8 Correlation of the analytical data gained during comparison of gas phase and liquid phase calibration.

detection limit in the liquid phase, the max. sampling volume, the amount of washing solution and all observed errors during sampling and analyzing procedure. The accuracy of the gaseous SO_2 standards from the dynamic gas dilution system lies within 5–10%. The precision of the evaluation of the SO_2 content of the gaseous samples is better than 10% even in the lower ppt-range. Considering all observed and analytical errors a detection limit of (10 ± 1) pptv SO_2 is obtained.

Interferences with other atmospheric constituents were all investigated: the results have shown that neither particles of urban aerosol nor oxidants such as NO_x and O_3 affect the analytical procedure. Detailed tests on the effect of ozone mixing ratio as high as 450 ppbv on the sampling and analyzing procedure showed no influence.[8] Any chemiluminescence effects which might occur during liquid phase reaction at wave lengths >550 nm are not detected by the used photomultiplier type.

Comparisons with other methods

As a further test of our method comparative measurements with other sensitive SO_2 methods were performed. During a general comparison experiment at a background station of the Federal Environmental Agency of Germany (UBA) in Deuselbach/W. Germany we were able to carry out simultaneous measurements of atmospheric SO_2 with a spectrometric (long path-UV-absorption)[13] and a modified conductrometric method.[14] Figure 9 shows the location and the design of the experiments. The long path UV-absorption method has determined the SO_2 mixing ratio by averaging over the indicated light path of 2.1 km between the Xenon lamp

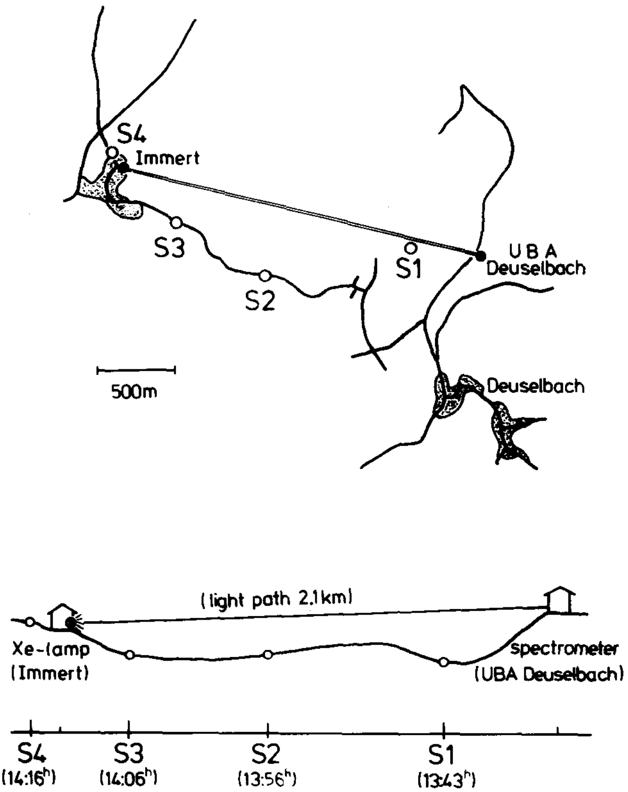

FIGURE 9 Location and experimental details of intercomparison measurements of the chemiluminescence method with long path (UV) absorption method.

(Immert) and the spectrometer (UBA Deuselbach). With a mobile equipment 4 single filter samples were taken one by one at 4 equally distant points (S1-S4) along the path. The result of the comparison between the spectrometric and chemiluminescence method is shown in Figure 10. Considering the described design of the experiment the agreement seems to be very good, except for the values near 14:07 GMT. This could be due to a local inhomogenity (farmhouse) of the horizontal SO_2 distribution.

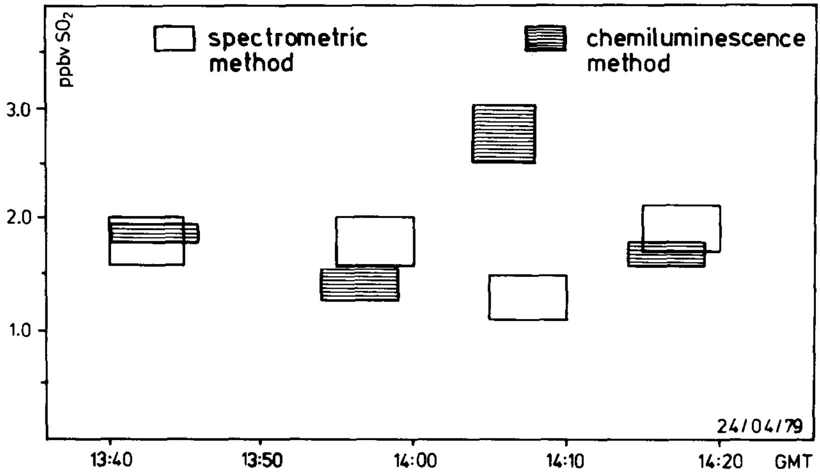

FIGURE 10 Results of the intercomparison of the chemiluminescence and long path (UV) absorption method.

The comparative measurements with the conductometric method were performed simultaneously at UBA Deuselbach (see Figure 9). In general the comparison with the conductometric method (Figure 11) shows the same trend in SO_2 mixing ratio while obvious differences occur related to the absolute amount of SO_2 mixing ratio. Using our dynamic gas dilution system for intercomparison we will clearify the origin of these discrepancies.

Application of the method

Besides the application of the chemiluminescence method to stratospheric measurements of the SO_2 distribution[11,12] investigations of the SO_2 background concentration at several remote measuring sites were performed. The locations of 3 selected sites are shown in Figure 12. Figure 13 shows the results of SO_2 mixing ratio measurements during winter

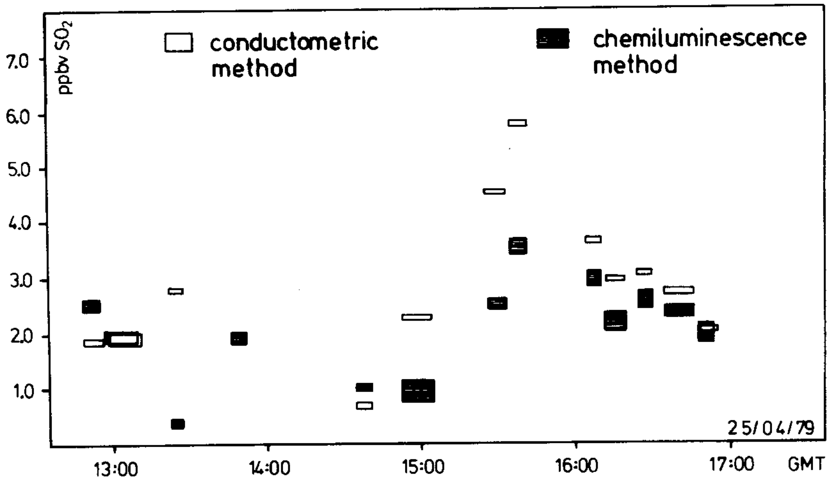

FIGURE 11 Results of the intercomparison of the chemiluminescence and conductometric method.

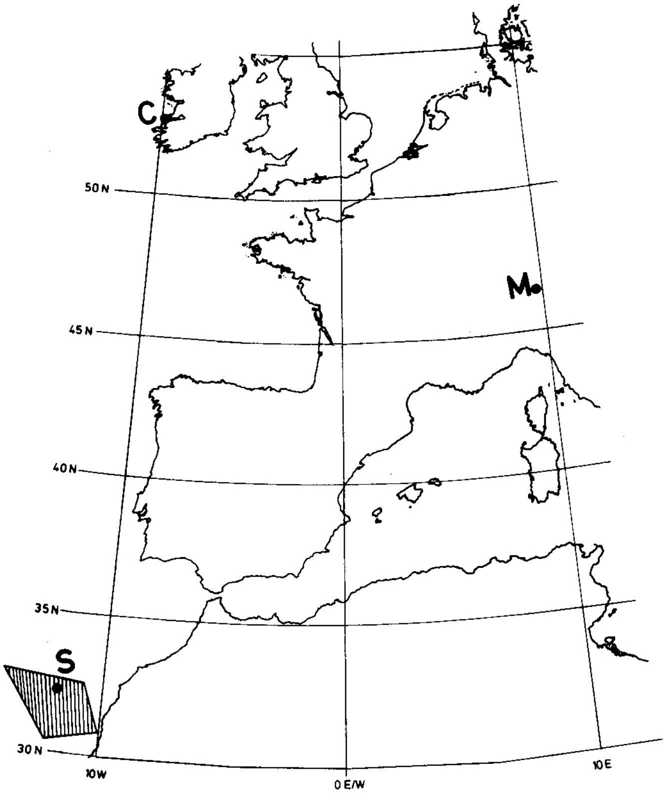

FIGURE 12 Location of three measuring sites for the investigation of SO_2 background concentrations. C—Carrigahold/Rep. of Ireland, M—St. Moritz/Switzerland, S—Cruise of German research vessel "Meteor".

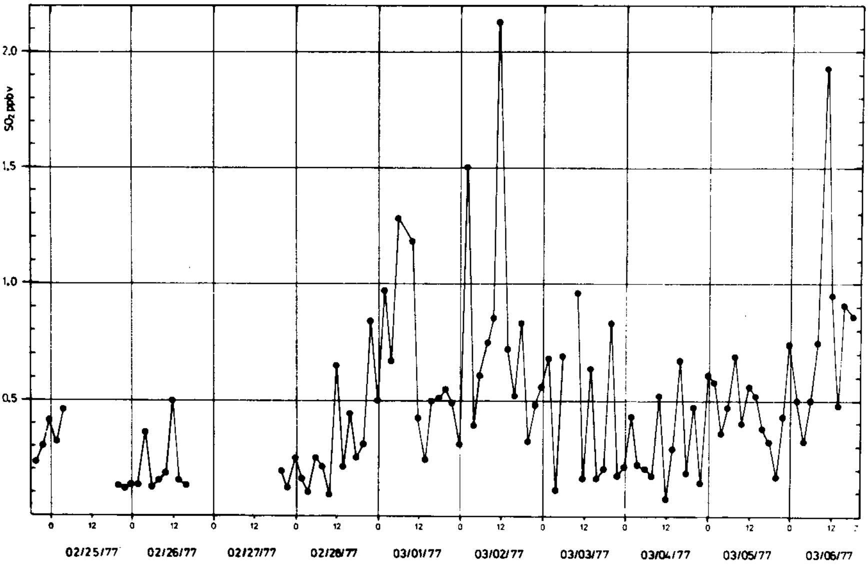

FIGURE 13 Daily variation of SO_2 mixing ratio at a measuring station near St. Moritz/Switzerland.

(25 Feb. to 6 Mar. 1977) In St. Moritz/Switzerland. Generally the SO_2 mixing ratio does not exceed 0.7 ppbv and a significant daily variation can not be seen from the results. Simultaneous anemometer records have demonstrated that the values >1.0 ppbb SO_2 are clearly correlated with wind directions from the village of St. Moritz where the winter heating period provides a certain local SO_2 source.

At Carrigaholt/Rep. of Ireland measurements were performed in order to investigate the SO_2 mixing ratio of air masses originating in maritime environments (Fig. 14). The great variations of SO_2 mixing ratio on 20 June 1979 are not yet explicable. The results for the next two days demonstrate that SO_2 mixing ratio of air masses which are not anthropogenically influenced are below 0.5 ppbv. This was strongly confirmed by the results gained on board R.V. 'Meteor" during the cruise to the Moroccan Atlantic coast (see Figure 12). Meteorological records are not indicated in Figure 15, but all samples were taken during periods in which westerly winds prevailed. The SO_2 mixing ratio tends to remain below the 0.1 ppb level. This seems to be a clear indication that the atmospheric maritime SO_2 background is well below 0.1 ppbv contrary to earlier measurements.[15]

These examples show that the new sensitive chemiluminescence method is able to provide meaningful results when applied to performing SO_2

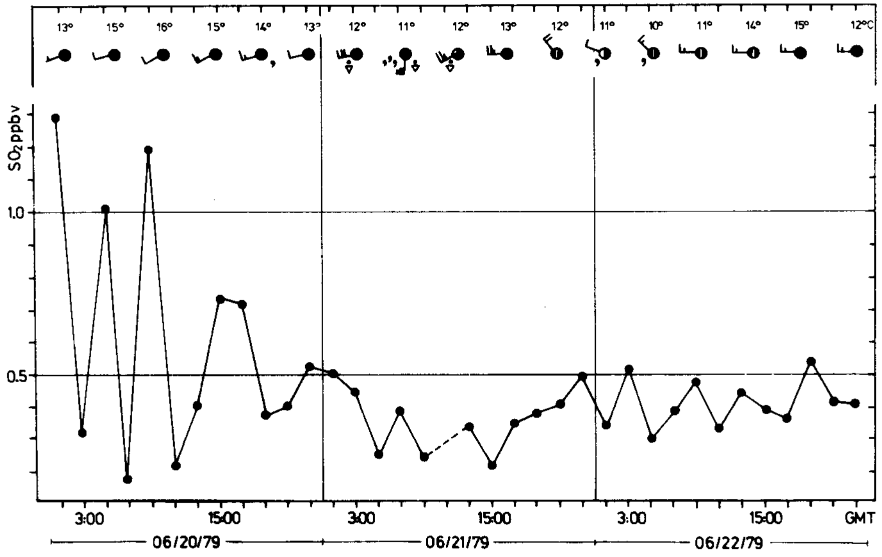

FIGURE 14 Daily variation of SO_2 mixing ratio at Carrigaholt/Rep. of Ireland.

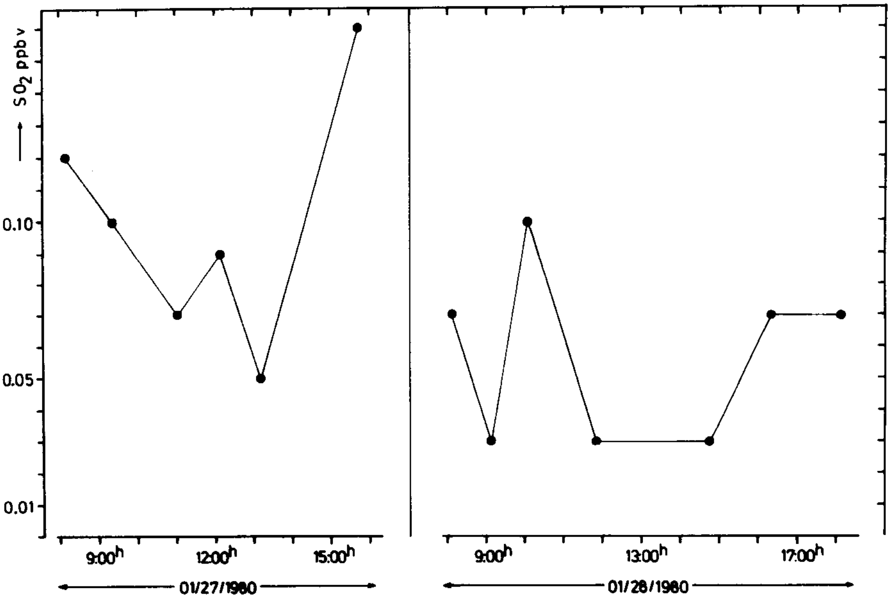

FIGURE 15 Results of on-ship measurements performed on R.V. "Meteor" at the Moroccan Atlantic coast.

background measurements. Further measurements will be carried out in the Southern Hemisphere and in the Arctic and Antarctic regions in order to obtain reliable results of SO_2 mixing ratio in these very remote areas. The knowledge of the SO_2 distribution in these regions would be a very important contribution to the understanding of the global atmospheric sulfur budget.

Acknowledgements

The authors want to acknowledge the support of Mr. W. Haunold, Mr. D. Vogler and Mr. G. Ockleman during the designing of the analyzing apparatus and during laboratory and on-ship measurements. We are grateful to Dr. U. Platt and Mr. K. J. Rumpel for permission to use unpublished data. This work was supported through "Sonderforschungsbereich 73" "Atmosphärische Spurenstoffe", German Research foundation.

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