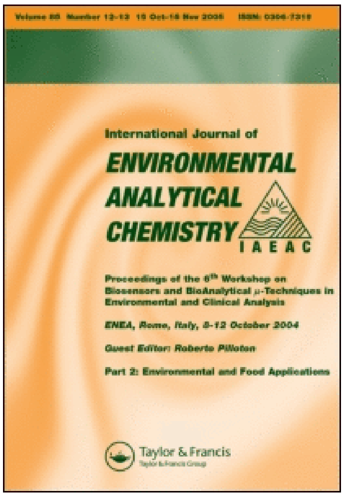

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Measurements of H_2S in the Atmosphere†

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Swamps and tidal flats are believed to be important natural sources of atmospheric H_2S, though it is very difficult to detect the low concentrations of this trace gas above the surface of these regions. In view of this problem an air sampling device has been developed for the sampling of atmospheric H_2S with chemically impregnated filters. The sulfide generated on the filter is analyzed in a washing solution employing a very sensitive fluorescence method. The quality of the method is demonstrated by comparative calibrations. The fluorescence method is calibrated in the liquid phase with standard solutions of sulfide. Furthermore the sampling and analyzing method is calibrated together by using H_2S calibration gases. The detection limit of the method is shown to be $10\,ng/m^3$ STP. Data of test-measurements in ambient air and some results of field-measurements in the lower troposphere are presented.

KEY WORDS: Hydrogen sulphide, Atmospheric trace gases, Sulfur cycle.

INTRODUCTION

The reason for developing a sensitive method for sampling and analyzing atmospheric H_2S in the ppb-range is our interest in problems concerning the atmospheric sulfur cycle. In this cycle the sulfur generally occurs in the oxidation states -2, $+4$ and $+6$. In addition to free sulfuric acid the reservoir of S^{+6} consists of sulfate particles in the atmosphere. They are released from the earth's surface to the atmosphere by sea spray or mineral dust and are removed by precipitation or as dust through dry deposition.[1] In order to describe the sulfur cycle in detail, several authors have attempted to perform a mass balance of both processes on a global scale.[2,3,4] In all cases an excess in sulfate release was reported. This excess

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must originate from the oxidation of gaseous sulfur compounds from the S^{-2} and S^{+4} states to S^{+6}. The contribution of the S^{+4} sulfur to the S^{+6} reservoir is rather well known because it is emitted by anthropogenic activity as SO_2. Its contribution of 150×10^6t SO_4/a, however, is not enough to explain the amount of the excess sulfate, which is assumed to be 270×10^6t SO_4/a.[2] Therefore it is discussed that either volcanic or biogenic activities in anoxic soils emit the amounts of sulfur gases which are necessary to balance the global sulfur budget.[5] Thus the study of these natural sources of sulfur gases was our main activity in recent years.[6]

Two main analytical problems had to be settled for this purpose:

1) Since the H_2S concentrations above the areas with anoxic soils are very low, it was necessary to develop an air sampling device in order to concentrate the atmospheric H_2S during the sampling procedure.

2) The adopted extremely sensitive analytical method had to be mobile and independent of a chemical laboratory such that it is applicable at remote areas like swamps and tidal flats or in the environment of volcanic activity.

EXPERIMENTAL

In order to accumulate the atmospheric H_2S during the sampling procedure, the air is led through impregnated filters. The chemistry of this preparation is according to a method of Natush *et al.*[7] An uncontrolled contamination during the transport of the impregnated filters is avoided since the critical steps of impregnation and washing out are performed with special devices under field conditions (Figure 1).

The filter material is placed on a sieve in a teflon filter holder. 5 ml of 0.1 M nitric acid containing 2% $AgNO_3$ and 20% ethanol are sprayed on the surface of a filter by an automatic syringe. By a short operating of the air sampling pump, the liquid is sucked through filter and captured in a waste container. This procedure is repeated three times to ensure that the filter is totally soaked. During the consecutive sampling of H_2S, between 50 and 1000 l of air is passed through the filter at a rate of 600 l/h. The Ag_2S deposit produced during the sampling procedure is dissolved from the filter with a solution of 0.1 M sodium cyanide in 0.1 M sodium hydroxide while it remains in the filter holder. The wash solution, which is sprayed on the filter by a second syringe, dissolves the Ag_2S in a couple of seconds. It is sucked through the filter and collected in the clean sample tube. The procedure is repeated three times to ensure that the 15 ml of wash solution in the clean sample tube contains all the sulfide collected on the filter. Consequently this filter, which is now free of H_2S, is used for the

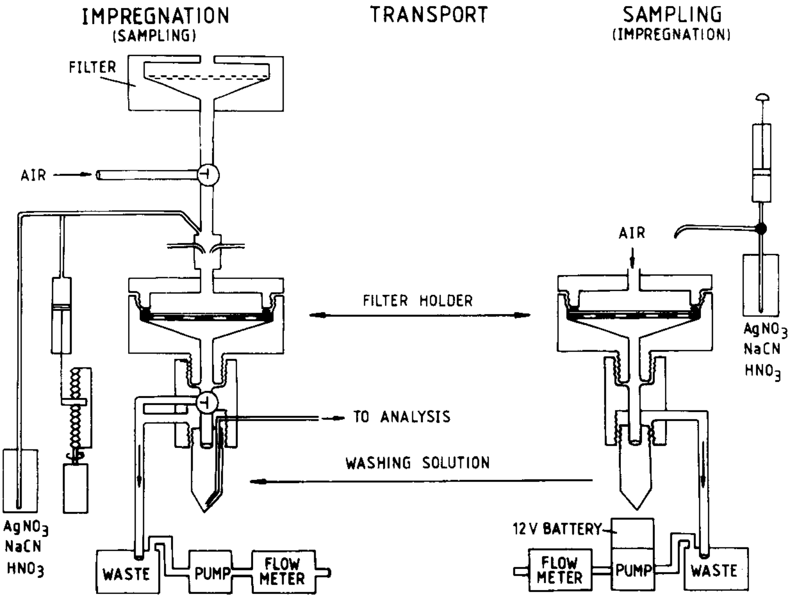

FIGURE 1 Schematic diagram of the air sampling devices. Description in the text.

next sampling of air. The filter is first treated with 5 ml 0.1 M nitric acid and then impregnated with $AgNO_3$ solution.

Since the filter material is repeatedly being used, it is possible to obtain a blank value for the filter between each measurement. If these values correspond to the blank of the analyzing method, one can be sure that the filters are clean and that the detection limit of the very sensitive analytical method can be applied to the whole detection method, which consists of sampling and analyzing.

The H_2S content of the wash solution is analyzed according to the fluorescence method of Ballschmitter,[8] which is based on the quenching effect of traces of sulfide on the fluorescence of the dye, fluorescein mercuric acetate (FMA). With the aid of additional syringes (Figure 2), 3 ml of the wash solution is transported into a mixing chamber where it is mixed with 1 ml of a 10^{-6} M FMA in 0.1 M sodium hydroxide solution. The extent to which the fluorescence of the dye is quenched by traces of sulfide is measured with a fluorescence apparatus using a flow cell.

Figure 3 shows a picture of the integrated sampling and analyzing device which works automatically and is applicable under field conditions.

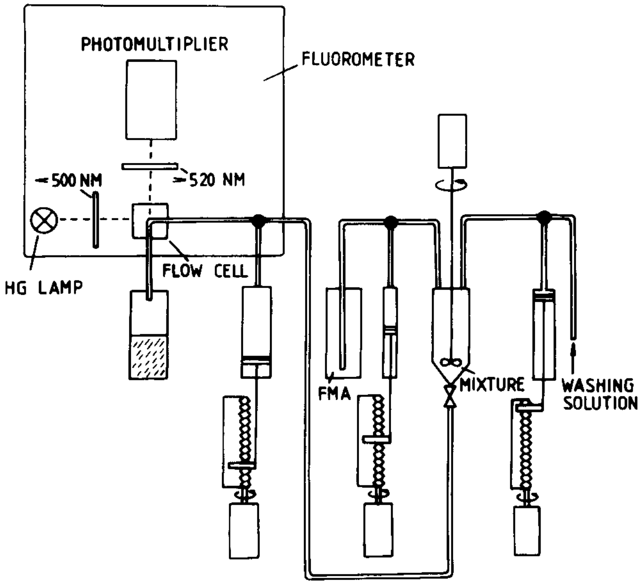

FIGURE 2 Schematic diagram of the analysis of sulfide with the fluorescence method.

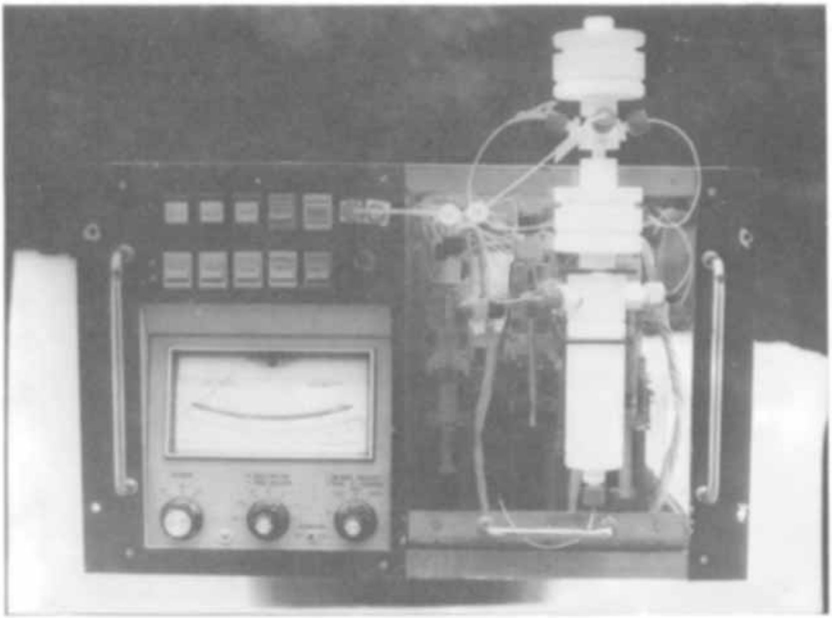

FIGURE 3 The integrated sampling and analyzing device.

In order to enhance the mobility of the sampling procedure the filter holder with the impregnated filter may be separated from the apparatus and transported to a separate sampling device (Figure 1). This instrument has its own power supply and can be installed in remote areas, like at the rims of a volcano or in swamps and tidal flats. The sampled H_2S may be transported to the analytical equipment either in the filter holder, or if it is desirable the Ag_2S is washed out at the sampling site with a mobile syringe. In this case the wash solution is transported to the analysis in the sample tubes.

RESULTS OF TEST MEASUREMENTS

At first one must consider the calibration of the method.

The fluorescence signal of the dye and the pure wash solution is set at 100% fluorescence (0% quenching) as blank.

By measuring standard samples of sulfide, the relation between the % quenching and the sulfide concentration is determined and a calibration curve is obtained (Figure 4).

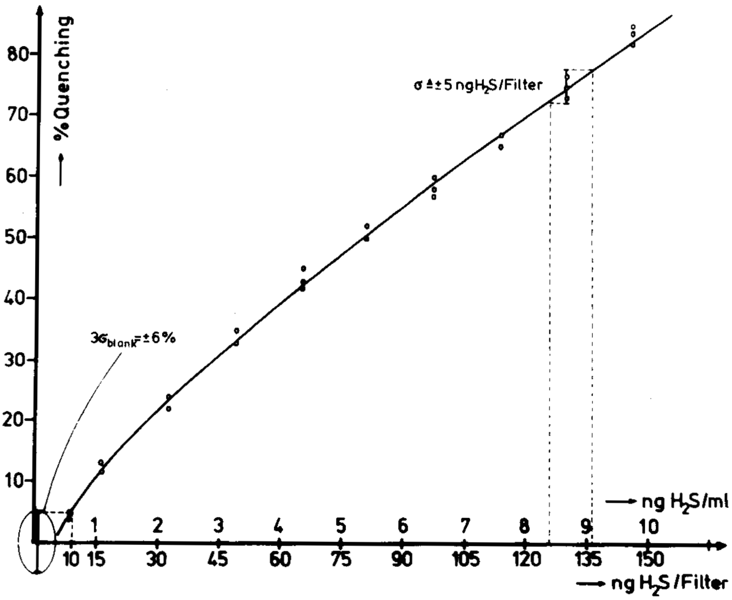

FIGURE 4 Calibration curve for the determination of traces of sulfide.

To deduce the detection limit of the method one must consider the deviation in the blank.[9] It is uncertain within the range of ±2 %. This means that a quenching above $3\sigma = 6\,\%$ is caused by traces of sulfide with a certainty of 99 %. This quenching effect of 6 % corresponds to a standard concentration of 0.7 ng H_2S/ml or since 15 ml wash solution is used to 10 ng H_2S/filter.

This means that when 1 m^3 of air is drawn through the filter, an atmospheric detection limit of 0.01 $\mu g\,H_2S/m^3$ or 6 ppt is obtained.

The reproducibility of a measured value can be determined considering the results of six parallel measurements (see Table I) which were taken in ambient air. At a mean concentration of 0.205 $\mu g\,H_2S/m^3$ a relative deviation of ±6.3 % occurred.

TABLE I

Reproducibility of the measured H_2S values

No.	Sample Volume (m^3) STP	H_2S (μg/Filter)	H_2S ($\mu g/m^3$)$^+$	ΔH_2S (%)
1	0.353	0.084	0.240	+17.1
2	0.272	0.055	0.204	− 0.5
3	0.367	0.067	0.184	−10.2
4	0.483	0.100	0.208	+ 1.5
5	0.154	0.029	0.190	− 7.3
6	0.545	0.698	0.202	− 1.5
			$\overline{H_2S} = 0.205$	$\bar{\Delta} = 6.3$

$^+$1 ppb = 1.52 g/m^3

TABLE II

Comparative Measurements with Photometrical Methods

Mo.-Blau-Imp.-M. ($\mu g/Nm^3$)	Me.-Blau-Sorp.-M. ($\mu g/Nm^3$)	Fluoreszenz-M. ($\mu g/Nm^3$)
11.580 ± 1.375	10.506 ± 0.748	9.331 ± 0.169
4.655 ± 0.546	4.048 ± 0.526	1.383 ± 1.340
8.420 ± 0.399	7.750 ± 0.483	7.266 ± 0.662

Table II shows a compilation of results which were obtained during a comparative measurement according to photometric method in which the dyes Molybdän blue or Methylen blue for the determination of H_2S were used. The test was performed during a ring measurement. It was arranged by the VDI (German association of engineers), which consented to invite about 20 participants, who are involved in H_2S measurements in industry and research.[10]

Calibration gases containing three different concentration levels were offered and the participants had to analyze the H_2S content with their various methods. The concentration given in the first and second column of the table are mean values of the results, obtained by eight and ten participants of the experiments, respectively. The results are compared with the mean values of four measurements with the fluorescence method in the last column. At higher concentrations the results are rather comparable. At the low concentration which was at the level of the detection limit of the photometrical methods, a relatively large deviation occured. This deviation may either be caused by deviations in the low H_2S concentration in the calibration gas or by an insufficient sampling efficiency of our filter method at these low concentrations. Therefore some experiments were conducted to examine the sampling efficiency of the filter method during a calibration procedure in the gas phase. A scheme of the experimental set-up according to the method of Buck *et al.*,[11] is shown in Figure 5. Several known amounts of sulfuric acid were reduced in a

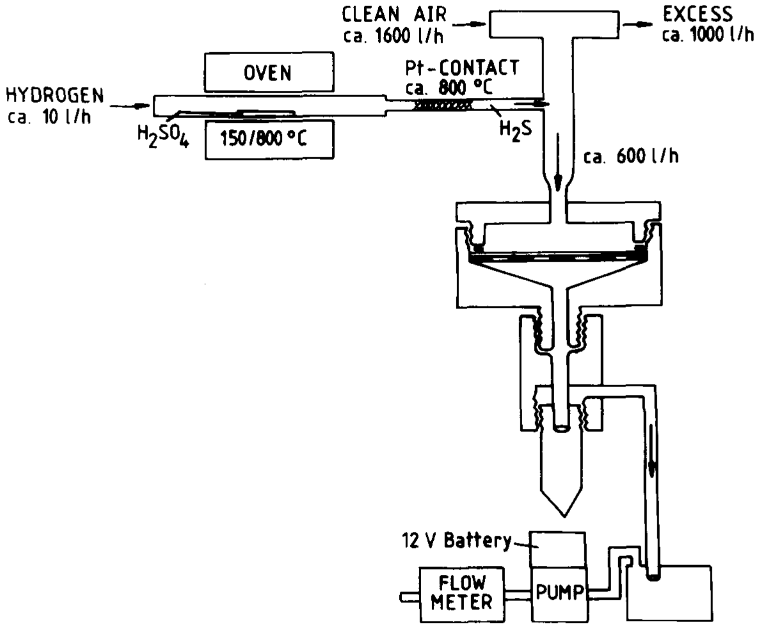

FIGURE 5 Experimental set-up for the examination of the H_2S sampling efficiency.

hydrogen stream. The so generated H_2S was diluted with clean air and collected with the filter sampling device. The result of this gas phase calibration is in good agreement with the calibration effects of standard sample in the liquid phase.

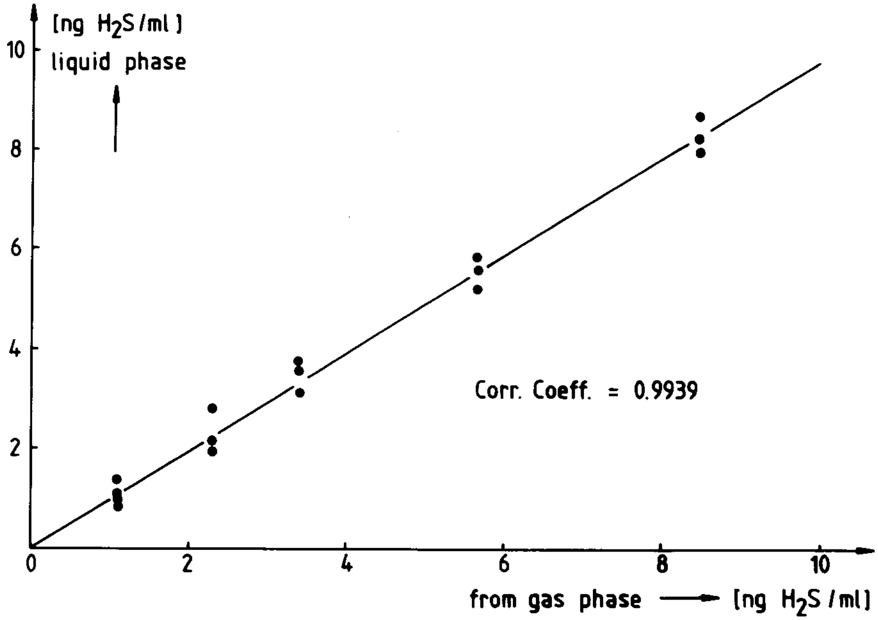

FIGURE 6 Correlation of the analysis of standard samples prepared directly in the liquid phase and of standard samples, prepared with the air sampling procedure from the gas phase.

In Figure 6 the correlation of both calibration procedures is plotted. The good correlation coefficient demonstrates, that the sampling efficiency of the filter method is sufficient, even at these low H_2S concentrations.

Another problem is the interference of organic sulfur gases with the sampling efficiency or the H_2S analysis. In order to examine this problem known amounts of sulfur containing gases like methyl mercaptan, dimethylsulfide and carbondisulfide which had been available from a permeation tube were led through impregnated filters. The results of the analysis of the filters are compiled in the last column of Table III. The quenching effects are always below the 3σ blank of the analyzing method. This indicates that no interference of the organic sulfur gases with the applied sampling and analyzing method occured.

TABLE III

Data of experiments which were performed to examine a possible interference of organic sulfur compounds with the H_2S analysis

Compound	Number of Samples	Gasphase Concentration (ng/m^3)	Amount led through the Filters (ng)	Range of Quenching (%)	Mean Quenching (%)
CS_2	4	255	85.2	0–8	3.8
CS_2	4	510	170.4	1–7	4.0
CS_2	2	765	255.6	0–3	1.5
CH_3SH	4	304	101.6	1–8	4.5
CH_3SH	4	608	203.2	0–8	5.3
CH_3SH	4	913	304.8	7–7	7.0
$(CH_3)_2S$	4	335	112.0	3–8	4.5
$(CH_3)_2S$	4	671	224.0	2–6	2.8
$(CH_3)_2S$	2	1006	336.0	4–7	5.5

RESULTS OF MEASUREMENTS IN THE ATMOSPHERE

In Table IV some results of measurements in the environment of natural and anthropogenic sources are compiled. The natural sources were studied by measuring the H_2S concentration 1 m above different anoxic soils. These anoxic soils usually contain micro-organisms which are able to release H_2S to the atmosphere.[12] Measurements above the tidal flats were

TABLE IV

Mean H_2S concentrations measured in Germany in the environment of different sources

Kind of source	Sampling site	Date	Number of samples	Daytime	Mean conc. (ng/m^3)
Natural	Isle of Sylt	28.7.– 3.8.1977	21	day	0.10
Tidal Flat	Isle of Sylt	28.7.– 3.8.1977	21	night	0.35
Natural	Emsland	7.8.–16.8.1979	27	day	0.38
Swamps	Emsland	7.8.–16.8.1979	10	night	1.22
Natural	Murnauer Moos	17.3.1976	12	day	0.15
Moor	Murnauer Moos	12.5.1976	12	day	0.95
Anthropogenic	Frankfurt City	20.10.–27.10.1976	84	day	0.25
Anthropogenic	Frankfurt City	20.10.–27.10.1976	84	night	1.23
Anthropogenic	Kl. Feldberg	1.1.–31.1.1976	31	day	0.38
Anthropogenic	Kl. Feldberg	1.7.–30.7.1976	28	day	0.12

performed through the course of one week, taking the samples every two hours. Concentration maxima always occured during the night while at day time the concentrations always decreased to minimum values. The same daily variations of the H_2S concentration could be observed above swamps of the Emsland. While taking samples during one week at similar frequencies at night concentration maxima up to 2.2 $\mu g/m^3$ occured whereas at day time the values were lower in the order of one magnitude.

Besides the daily variations the natural source strength shows a variation which depends on the season. As an example two mean values of H_2S measurements are given in the table. These results were gained by taking measurements during two different days in the Murnauer Moos in spring and early summer. Samples were taken between sunrise and sunset every two hours.

The H_2S concentrations measured in the City of Frankfurt and on the Kleiner Feldberg Hill are probably caused by transport from anthropogenic sources.[13] Assuming that the source strength of the anthropogenic sources in the Rhein Main area are rather constant, measured diurnal and seasonal variations of the H_2S concentration must give a hint of the character of the atmospheric sink of H_2S. Therefore, the results of the H_2S measurements in the City of Frankfurt are shown in Figure 7 in more detail. The diagram shows that

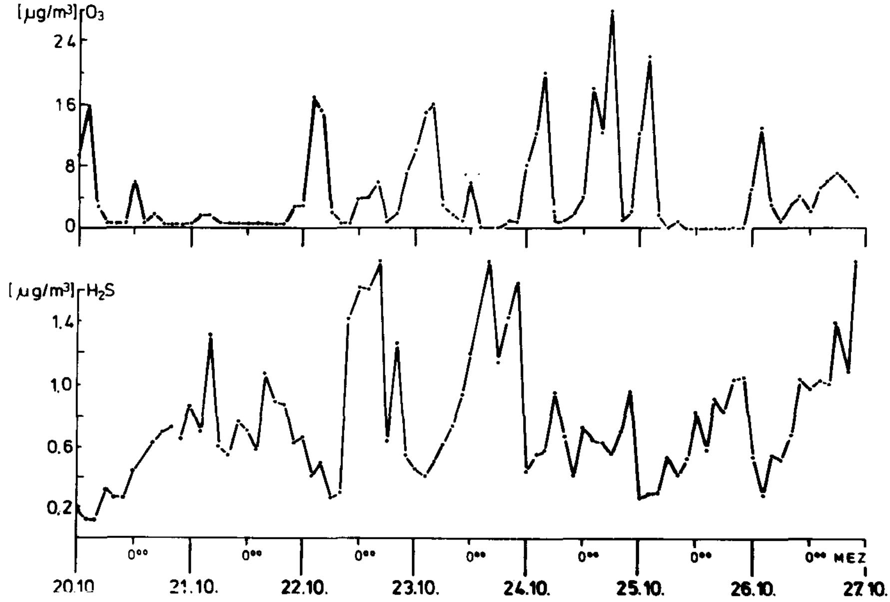

FIGURE 7 The daily variation of H_2S and O_3 concentrations measured during one week in the City of Frankfurt.

the H_2S concentration varies between 0.2 and $2\,\mu g\,H_2S/m^3$. This variation is compared with ozone concentrations which were measured simultaneously. A maximum of ozone concentration at noon time is always accompanied by a minimum of the H_2S concentration. Conversely the H_2S values increase during the night in the absence of higher ozone concentrations. The direct reaction of H_2S with ozone is too slow for the atmospheric removal of H_2S. Therefore, the OH radicals, the reaction products of ozone photolysis, must be the main oxidizing agent for H_2S in the atmosphere. In this case there must be a seasonal influence on the transport of H_2S from the Rhein Main valley to the Kleiner Feldberg Hill. Therefore, the H_2S concentration was measured every day at 12 o'clock from November 1976 till November 1977 and thereafter with some interruptions up to April 1980. In the diagram of Figure 8 mean H_2S

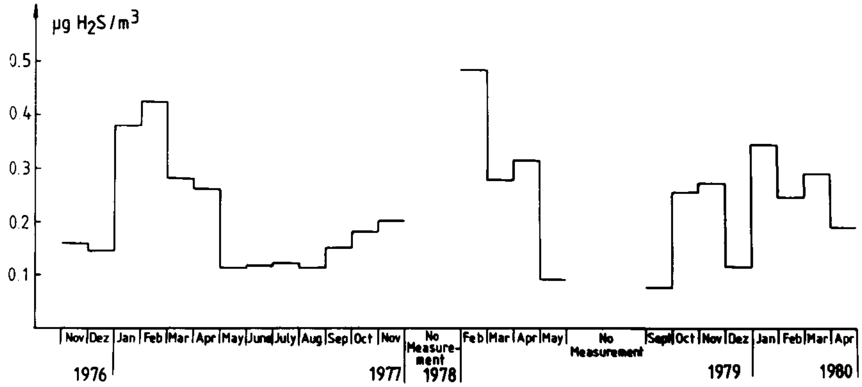

FIGURE 8 Mean values of the monthly H_2S concentration measured each day at 12 o'clock on Kleiner Feldberg hill.

values of each month are plotted against the periods of measurements. As can be seen, during the winter months higher amounts of H_2S are able to reach the measuring site at the hill than during the summer months.

CONCLUSIONS

The H_2S concentrations measured so far show that it was necessary to develop a method which has high sensitivity in the ng range. This method enabled us to study the behaviour of this gas in the atmosphere and futhermore to establish how it contributes to the sulfur cycle. The results were checked by producing sample test-measurements, which were taken not only in the analytical context but also during sampling. Only upon the basis of a great number of such secured measurements from local sources extrapolation leading to statements regarding global relationships are possible. The presented data of measured H_2S concentrations show that the natural source strength depends on the day time and on the seasonal temperature of the anoxic soil. On the other hand the atmospheric removal is dependent on the seasonal change of the zenith angle of the sun. Therefore arose the question whether the higher H_2S production in the rather warm anoxic soils of the tropics is compensated for by a higher photochemically induced oxidation of H_2S in the atmosphere of these latitudes. The mobility of the described method enabled us to perform measurements in the tropical regions of Florida. Some results are compiled in Figure 9. The rather low H_2S concentrations above these anoxic soils, which are comparable with the results presented by Slatt *et al.*,[14] show that these natural sources were perhaps overestimated in the past.

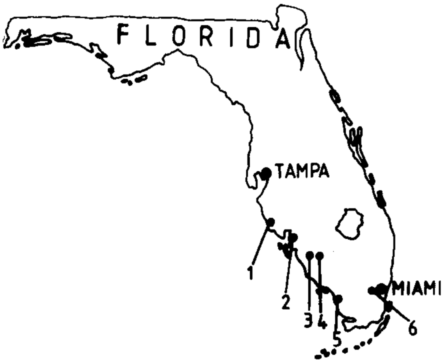

TABLE V

H_2S CONCENTRATIONS IN TROPICAL REGIONS, 1 M ABOVE GROUND				
No	Sampling site	Date	Time	conc. [$\mu g/m^3$]
1	Tidal Flat south of Sarasota	22.8.79	19:00	4.16
2	Swamp, near Fort Meyers, sweetwater	23.8.79	11:40	0.1
3	Swamp east of Naples, brackish water	23.8.79	13:15	0.33
4		23.8.79	13:30	0.21
5	Everglades Mangrove Forest	23.8.79	14:20	0.51
6	Swamp near Miami, brackish water	23.8.79	16:20	0.27

FIGURE 9 Location of sampling sites in the swamps of Florida.

Another natural source of H_2S, which in our opinion has been greatly underestimated in the past is the volcanic activity. With the new method which could be installed at the rim of craters and in aircraft we were in the position of taking measurements at various volcanic sites in Southern Italy. First results from our field research in these regions are compiled in Figure 10 showing exact locations of sampling sites. A more detailed report of these investigations,[15] which had been performed over a three year period will be published shortly.

TABLE VI

H_2S CONCENTRATIONS IN THE ENVIRONMENT OF VOLCANIC EXHALATIONS, 1 m ABOVE GROUND

VOLCANO	SAMPLING SITE	DATE	CONC. [$\mu g/m^3$]
ÄTNA	RIM W OF MAIN CRATER	19.9.77	1.08
	100 m NE OF MAIN CRATER	20.9.77	0.51
	5 km SE OF MAIN CRATER	18.9.77	0.10
	10 km E OF MAIN CRATER	18.9.77	0.14
	6 km NE OF MAIN CRATER	21.9.77	0.11
	10 km SW OF MAIN CRATER	18.9.77	NOT DETECTIBLE
	RIM S OF BOCCA NOVA	16.9.78	0.54
	RIM W OF BOCCA NOVA	14.6.79	120
	RIM NW OF BOCCA NOVA	14.6.79	540
STROMBOLI	2.5 km LEESIDE OF THE CRATER	25.9.77	0.3
	BOCCIE INSIDE OF THE CRATER	26.9.77	1.5
VULKANO	50 m LEESIDE OF THE FUMAROLE	22.9.77	13.7
	2.5 km LEESIDE OF THE FUMAROLE	23.9.77	4.0

FIGURE 10 Location of sampling sites at the volcanoes of southern Italy.

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