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SAMPLING AND ANALYSIS OF ATMOSPHERIC SULPHATES

The objective of the paper was to answer the question, whether fine sulphate aerosol penetrate the filter and how their concentrations measured on the filters correspond to atmospheric concentrations. The data represent the sampling point at the summit of Szrenica, 1362 m asl, and laboratory tests.

The use of cellulose filters for low-volume sampling of airborne sulphates is questionable. To obtain more reliable values for the products of SO₂ conversion in clear atmosphere, it is recommended to measure the sulphate concentrations after their passage through the filter media.

1. INTRODUCTION

Acid atmospheric aerosol and acid precipitation are the threats to the environment in the region of the Sudeten Mountains, south-western Poland. In order to understand the origin of the phenomenon and then to develop strategies to reduce the emission of toxic substances in Central Europe, an extensive research and development programme have been carried out since 1989. A preliminary determination of the characteristics of air pollution episode was made during 5-day studies, once a month, from August to December, 1988.

Episodically high levels of gaseous and particulate pollutants were found, but the primary conclusion of these investigations was that the measured concentrations of SO₂, NO_x and trace metals, as well as sulphate and ammonium aerosols did not seem to be responsible for the ecological catastrophe in the area under study. Thus, the question arose, whether the filter media were sufficiently effective to retain the fine sulphate aerosol which was likely to form in the mountains. Although a number of investigators have objected to the accuracy of the filter techniques themselves [1]–[6], this method of analysing airborne concentrations of sulphates is still receiving wide acceptance.

The primary objective of these investigations was to answer the question, whether fine sulphate aerosol penetrated the filter, and how the sulphate concentrations that have been measured on the filters corresponded with actual atmospheric concentrations.

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2. METHODS

Twenty four-hour samples of sulphur dioxide, total sulphur and sulphates in particulate matter were collected during February, May, August and December 1990, as well as February 1991, at a sampling site located at the summit of Szrenica (1362 m a.s.l), Sudeten.

Sulphur dioxide concentrations were determined [7], [8], using the modified West-Geake colorimetric technique.

For total sulphur determination, a sampling set was designed. The unit comprised a prefilter (Whatman 41 of 47 mm in diameter) for collecting the sulphate particles, as well as a bubbler with slightly acidic (pH=4.6) 0.3% solution of hydrogen peroxide for the absorption of both sulphur dioxide and the sulphate particles which have not been retained by the filters. Air flow rate was $2.4 \text{ m}^3/\text{day}$. After rinsing with deionized water, the content of sulphates in filters was analysed [9].

The concentrations of sulphates (from filter extracts and hydrogen peroxide solution) were determined by the barium-perchlorate thorin method, using automatic colorimeter [9], [10].

Since the concentrations of sulphur compounds determined by the hydrogen peroxide/sulphate method usually exceeded to a great extent the sulphur concentrations established by the West-Geake method, we decided to continue those measurements under laboratory conditions.

Measurements of daily sulphur concentrations were carried out using three sampling sets. Two of them were the same as those applied to field studies (47 mm diameter prefilter (Whatman 41) and a bubbler with slightly acidic hydrogen peroxide solution; 47 mm diameter prefilter (Whatman 41) and a bubbler with sodium tetrachloromercurate (TCM) solution). In the third sampling set, the sulphates penetrating the filter (Whatman 41) were absorbed in redistilled slightly acidic (pH = 4.6) water. The concentrations of sulphates and sulphur dioxide were determined by the barium-perchlorate thorin technique and the West-Geake method, respectively. Flow rate ($2.4 \text{ m}^3/\text{day}$) was checked with a rotameter, the total volume being measured with a wet gas meter.

3. RESULTS AND DISCUSSION

3.1. FIELD STUDIES

The variability of sulphur concentrations determined by the West-Geake method, $S(\text{SO}_2)$, and hydrogen peroxide/sulphates technique, $S(\text{total})$, is plotted in fig. 1. Thus, in terms of sulphur dioxide, sulphur concentration ranged from $1 \mu\text{g}/\text{m}^3$ to $20.0 \mu\text{g}/\text{m}^3$. In the same span of time, concentrations of sulphur compounds determined in the H_2O_2 solution, amounted to $90 \mu\text{g}/\text{m}^3$. It should be noted that measurements were performed under different meteorological conditions. Maximum concentrations of total sulphur were measured at the inflow of cold and humid maritime-polar air masses from westerly directions. It was found that even within the same air mass highly variable concentrations of different sulphur compounds were monitored. This problem was discussed in more detail elsewhere [11], [12].

Comparison of the concentrations of total sulphur with the concentrations of sulphur calculated basing on sulphur dioxide determination shows considerable differences be-

tween the two data sets. A paired *t*-test has revealed that they fail to be statistically similar. Therefore we hypothesize that the bubbler which contains acidic hydrogen peroxide solution is likely to include not only sulphates obtained via oxidation of sulphur dioxide, but also some other compounds containing sulphate ions. These data seem to support our suggestion that some very fine particles have not been efficiently retained by the filters.

It is a well-known fact that the sulphate aerosol is a mixture of neutral or acidic sulphates and pure acidic particles defined as SO_3 or H_2SO_4 vapour or $m\text{H}_2\text{SO}_4 \cdot n\text{H}_2\text{O}$ clusters. Owing to its partial pressure, H_2SO_4 vapour passes to the aerosol phase at ambient temperature. In secondary aerosols these particles are initially very fine [13]–[15], being therefore likely to penetrate through the filters.

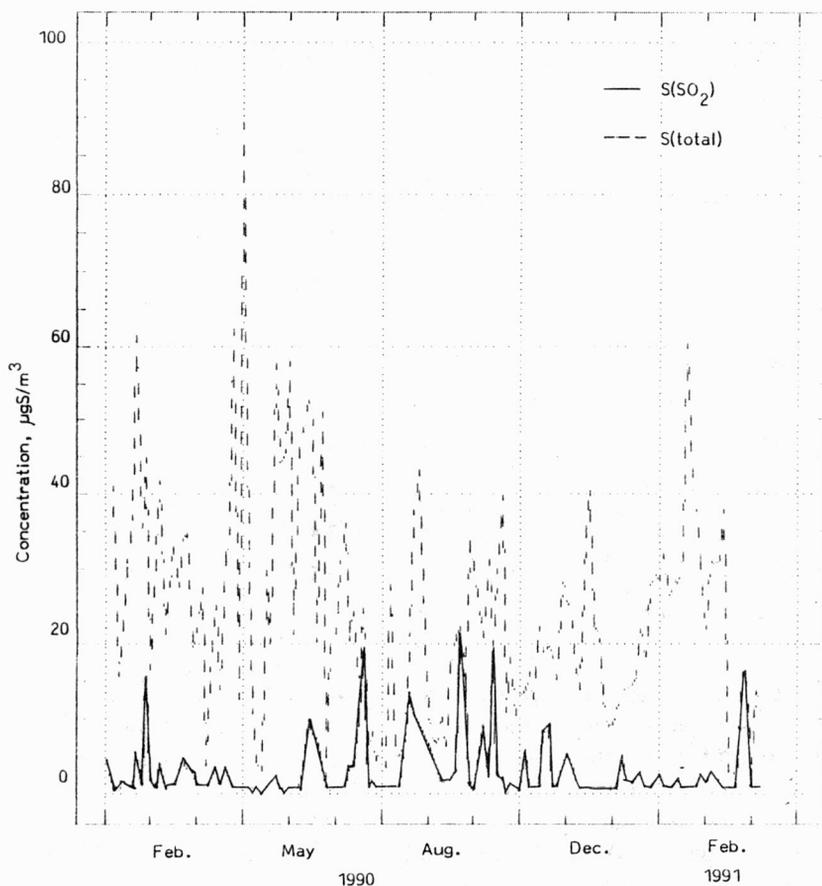


Fig. 1. Time series plot of $\text{S}(\text{SO}_2)$ and $\text{S}(\text{total})$ concentrations, summit of Szrenica, 1362 m a.s.l.

Comparison of the concentrations measured by the two methods shows that, in some instances, the values obtained due to the hydrogen peroxide method are by an order of magnitude higher. It is worth noting that ammonium and sodium ions, which are found in

the filter extract, are also identified in the absorbing solution. Thus, the filter media used in our investigations fail to retain fine particles.

3.2. LABORATORY INVESTIGATIONS

The results from three samplings are listed in the table. As shown by these data, the concentrations of sulphur compounds measured in the H_2O_2 solution, $S(\text{total})$, are in every instance (except one) higher than those determined by the West-Geake method, $S(SO_2)$. As each of the two methods involves a different form of sulphuric pollutants, it is not surprising that their concentrations are not strongly correlated. But a paired t -test has revealed that the two data sets are not statistically similar.

Table
Concentrations of sulphur compounds ($\mu\text{g}/\text{m}^3$ in terms of sulphur)

S(SO_2)	S(total)	S(H_2O)	S(filter)		ΔS S(total) - S(SO_2)
			Before bubbler		
			H_2O_2	H_2O	
1.4	6.9	7.5	6.0	6.8	5.5
4.5	12.8	6.0	7.5	8.1	8.3
5.2	11.3	5.5	9.1	11.0	6.1
16.0	27.0	10.7	6.3	14.0	11.0
11.3	18.1	12.1	7.1	8.1	6.8
5.8	5.1	<0.2	8.3	8.3	0.0
1.6	8.8	12.7	5.9	4.7	7.2
5.4	15.7	11.9	5.2	3.4	10.3
8.0	12.7	13.9	3.7	5.5	4.7
4.4	20.0	9.9	5.1	5.7	15.6

The use of distilled water in the third sampling was not aimed at substantiating the ability of distilled water to absorb compounds containing sulphate ions, but rather at confirming the statement that a certain portion of fine sulphur compounds passes through the filter media. Theoretically, the concentrations of sulphate ions in distilled water are supposed to correspond to the quantity of the sulphur compounds that pass through the filter (in the form of fine particles), viz the difference in the concentrations of $S(\text{total})$ and $S(SO_2)$ is equivalent to ΔS in table. This supposition has been supported by the results of statistical analysis. A paired t -test of ΔS and $S(H_2O)$ shows that the two sets of data are statistically similar at the 95% confidence level. This finding, again, confirms that a number of compounds containing sulphate ions are not retained by the filters.

Ten subsets of measurements in the table show that the mean concentration of ΔS approached $7.6 \mu\text{g}/\text{m}^3$. The mean concentration of sulphur in the filter, $S(\text{filter})$, amoun-

ted to $6.4 \mu\text{g}/\text{m}^3$ and $7.6 \mu\text{g}/\text{m}^3$ for the samplings with H_2O_2 solution and H_2O solution, respectively. It gives a filter efficiency of 50%.

3.3. SULPHATE CONCENTRATIONS

For the purpose of this investigation, we have made a distinction between the fine sulphate aerosol ($\text{SO}_{4(\text{aer})}$) determined from ΔS and the coarse sulphate aerosol ($\text{SO}_{4(\text{filter})}$) determined from filter analysis. In most cases investigated, the sulphate concentrations were higher in fine aerosol than in coarse aerosol. The results of field studies are presented in fig.2.

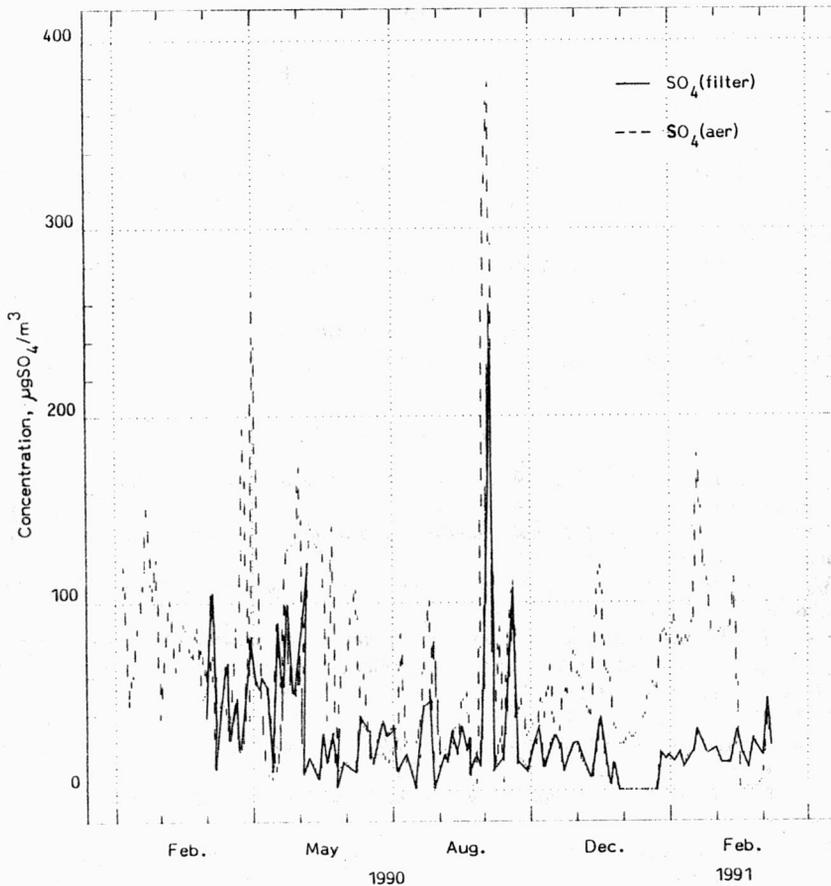


Fig. 2. Time series plot of $\text{SO}_{4(\text{aer})}$ and $\text{SO}_{4(\text{filter})}$ concentrations, summit of Szrenica, 1362 m a.s.l.

The mean concentrations of fine sulphates and coarse sulphates at the summit of Szrenica were $76.7 \mu\text{g}/\text{m}^3$ and $30.1 \mu\text{g}/\text{m}^3$, respectively. The results discussed revealed that the fine sulphates in aerosol constitute ca. 70% of the total sulphates. It proves that, making use of Whatman 41 filters alone, a considerable amount of fine sulphate aerosol is "lost".

The extent of conversion, expressed by the percentage of particle sulphur ($\text{SO}_{4(\text{aer})} + \text{SO}_{4(\text{filter})}$) in total sulphur measured in the upper parts of the mountains, was considerably greater comparing to that reported by the authors from Europe or the United States [16]–[18]. It may result from differences in the location of monitoring stations as well as the sampling technique. The measurements of sulphate concentrations based on filter analysis only caused underestimation of percentage of particle sulphur in the total sulphur measured, which ranged from 20 to 40. These values are consistent with the data reported [17], [18].

4. CONCLUSIONS

1. To obtain the reliable values of the conversion of sulphur dioxide products in the atmosphere it is recommended to measure sulphate concentration after its passage through the filter media.

2. The portion of the species containing sulphate particles, which passed through the Whatman 41 filter at the flow rate of $2.4 \text{ m}^3/\text{day}$, accounted for 70% of the total sulphate concentration in the atmosphere.

3. The high concentrations of sulphates at the summit of Szrenica and the high percentage of particle sulphur in comparison with total sulphur are the result of very rapid oxidation of sulphur dioxide to particle sulphur as the polluted air masses ascend up the mountains (more particle sulphur is present in fine particles).

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POMIAR STĘŻENIA AEROZOLU SIARCZANOWEGO W POWIETRZU ATMOSFERYCZNYM

Celem badań była odpowiedź na pytanie, czy filtry obecnie stosowane w pomiarach stężeń zanieczyszczeń siarkowych w atmosferze nadają się do skutecznego określenia ilości związków zawierających jony siarczanowe. Pomiar terenowy (w Sudetach) dowiodły, że filtry celulozowe przepuszczają znaczną ilość (do 70%) aerozoli o submikronowych cząsteczkach i dlatego wartości stopnia konwersji SO_2 oraz stopień skażenia środowiska nie są miarodajne.

ИЗМЕРЕНИЕ КОНЦЕНТРАЦИИ СУЛЬФАТНОГО АЭРОЗОЛЯ В АТМОСФЕРНОМ ВОЗДУХЕ

Целью исследований был ответ на вопрос, являются ли применяемые в настоящее время для измерений концентрации сернистых загрязнений в атмосфере фильтры пригодными для эффективного определения количества соединений, содержащих сульфатные ионы. Местные измерения (в Судетах) подтвердили, что целлюлозные фильтры пропускают значительное количество (до 70%) аэрозолей субмикронных частиц и поэтому значения степени конверсии SO_2 , а также степень заражения среды не достоверны.