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ON THE USABILITY OF FILTER PAPERS FOR THE MEASUREMENT OF AIRBORNE SULPHATE ION CONCENTRATION

The most common method for determining airborne sulphuric acid and its salts is that involving filter paper deposits. It was found that a filter paper is able to collect less than 10% of the depositing sulphate ions. The remainder, combined with atmospheric air, leave the deposit through the paper pores. More reliable values of airborne sulphate ion and sulphur dioxide concentrations were measured by making use of a sodium tetrachloromercurate solution to absorb the air pollutants of interest.

1. INTRODUCTION

Sulphur dioxide belongs to the main class of primary pollutants released into the atmosphere. This gaseous pollutant is of an unstable nature and can be altered or rendered more hazardous through interreactions which occur in the atmosphere under the influence of moisture and other environmental factors. Thus, sulphur dioxide undergoes conversion to produce sulphuric acid and sulphates. The products either occur in a liquid form (sulphuric acid) or take the form of solid particles (sulphates) and make an important part of the atmospheric aerosol. The rate of sulphur dioxide conversion in the atmosphere depends mainly on the presence of other primary pollutants, such as nitrogen oxides, ammonia and particulate matter enriched with heavy metals. The half-life of sulphur dioxide in the atmospheric air over an area with no pollution source takes quite a long time, generally amounting to ten days or so [4]. However, in a polluted area, especially when heavy metals are involved, the length of half-life for airborne sulphur dioxide is short, ranging from 1 h to about 10 min.

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Numerous authors have reported so far on the conversion of sulphur dioxide. The literature reports deal mainly with the rate and extent of conversion (i.e. the ratio $[\text{SO}_4^{-2}]/([\text{SO}_4^{-2}] + [\text{SO}_2])$). Most of the investigations were carried out in the immediate vicinity of large industrial plants (e.g. coal-fired power plants or smelters) which create favourable conditions for sulphur dioxide conversion. Some of the measurements were performed in the stack plume, while others pertained to the near-ground air layer. It was surprising to find that sulphate ion concentrations measured by the two methods were exceptionally low (tab. 1), much lower than it had been expected from the quantity of sulphur dioxide released and converted.

Table 1

Concentrations of airborne sulphur dioxide and sulphates in the vicinity of power plants
Przykłady wyników pomiarów stężenia dwutlenku siarki oraz jonów siarczanowych
w powietrzu w pobliżu elektrowni węglowych

References	SO ₂ concentration mg/m ³	SO ₄ ⁻² concentration mg/m ³	Measuring site
FORREST, NEWMAN [1]	0.655-5.102	0.039-0.078	Stack plume
	0.015-0.033	0.028-0.0406	Near-ground layer
MEAGHER, STOCKBURGER, BAILEY, HAFF [2]	0.448-1.56	0.002-0.0994	Stack plume
ZWOŹDZIAK, KMIEĆ, LISOWSKI, MATYNIAK [4]	0.089-0.1556	0.008-0.0156	Near-ground layer

The analysis of the measuring methods and results reported in the literature leads to the conclusion that the data thus obtained cannot adequately reflect the actual pollution level. In the measuring methods applied so far, air is passed through a filter paper and SO₄⁻² is determined in the matter deposited onto it. The filter paper is capable to collect solid particles of sulphate aerosols alone. Sulphuric acid mist which passes through the filter is not deposited and subject to analyses. The same holds for very fine sulphate particles which are smaller than the filter paper pores (0.3 to 0.6 μm). The atmospheric air bears large amounts of very fine sulphate grains with the particle size as small as one tenth or even one hundredth of μm, which is attested to by literature data [3]. The latter also indicate that very fine sulphate particles are predominant [3].

In the light of such information, there seems to be no doubt about the shortcomings of the measuring method applied and the inadequacy of the results obtained. Taking this into account, the authors of the paper made measurements of the total concentration of airborne sulphate ions, as well as of this part of it which corresponds to the sulphate ion portion deposited onto the filter paper.

2. EXPERIMENTAL

The measuring cycle included the sampling of aerosol, and gases (at a distance of 300 m and 3 km from the emission source) with the use of two different sampling sets. Aerosols samples were collected with a Staplex-High Volume Air Sampler which enabled a suction rate of 150 m³/h. The sampler contained round TFA-810 filter papers 10 cm in diameter and able to collect particles larger than 0.01 μ m. The other sampling set consisted of scrubbers containing sodium tetrachloromercurate (referred to as TCM solution). The solution (generally applied to sulphur dioxide absorption) was also used for the absorption of sulphuric acid mist and sulphates. A complete absorption of the above mentioned pollutants could be achieved at an air flow rate equal to, or lower than, 200 dm³/h. Both sets were working concurrently during 6 h. After the sampling procedures had been completed, analyses were made. The filter paper was washed with distilled water to measure the concentration of sulphate ions. From analyses of the TCM solution it follows that it comprised not only sulphate ion concentration but also the quantity of sulphur dioxide absorbed. All of the determinations involved spectrophotogrammetry. Analyses were carried out for 140 absorbing solutions and 140 filtrates obtained by distilled water rinsing.

3. RESULTS

In table 2 the contribution of sulphur dioxide and sulphate ions (referred to as C_{SO_2} and C_{SO_4} , respectively) is given as well as their range of concentration in the atmosphere and two methods of their determination. The column for C_{SO_4} makes a distinction between atmospheric concentration of sulphate ions calculated from the amounts deposited on to the filter paper (referred to as $C_{\text{SO}_4}^f$) and atmospheric concentrations determined from the quantity of sulphate ions absorbed in the TCM solution (referred to as $C_{\text{SO}_4}^a$). The values of the $C_{\text{SO}_4}^f/C_{\text{SO}_4}^a$ ratio (n_f) are also collected in tab. 2.

The analysis of measured data attests to alterations in the chemical composition of atmospheric air which varies from one measuring period to the other. The sulphur dioxide concentration ranged from 0.0090 to 0.6168 mg/m³; it was, as a rule, higher than the value of $C_{\text{SO}_4}^f$ (which fell between 0.0011 and 1103 mg/m³) and considerably lower than the value of $C_{\text{SO}_4}^a$ (which varied from 0.019 to 9.686 mg/m³). As may be seen, the measured values of airborne sulphate ions are notably scattered. To characterize this scattering, $n_f = C_{\text{SO}_4}^f/C_{\text{SO}_4}^a$ was calculated from the data obtained in individual measuring series, and the percentage of events with lower and higher n_f values was determined. Thus,

n_f took the following values: 0 to 0.01 at 31.65% of events; 0.01 to 0.05 at 35.2% of events; 0.05 to 0.10 at 18.7% of events (figure). The percentage of events at which n_f took a higher value (0.10 to 0.79) was 14.4.

Table 2

Some of the sulphur compound concentrations (C_{SO_2} , C_{SO_4}) and the values of n_f

Przykłady charakteryzujące stan zanieczyszczenia atmosfery związkami siarki (C_{SO_2} , C_{SO_4}) oraz skuteczność zatrzymywania jonów siarczanowych na filtrze bibułowym (n_f)

Mea- surement	C_{SO_2} mg/m ³	C_{SO_4} , mg/m ³		$n_f = \frac{C_{SO_4}^f}{C_{SO_4}^a}$
		$C_{SO_4}^f$	$C_{SO_4}^a$	
1	0.1276	0.0157	1.429	0.0111
2	0.3024	0.0373	1.333	0.0271
3	0.0489	0.0285	0.521	0.0547
4	0.1676	0.0162	0.241	0.0672
5	0.0640	0.0060	0.103	0.0582
6	0.1811	0.0141	1.322	0.0107
7	0.0954	0.0048	4.800	0.0010
8	0.0300	0.0220	0.043	0.5116
Range of concentra- tion	0.0090 – –0.6168	0.0011 – –0.1103	0.019 – –9.689	0.0007 – –0.7200

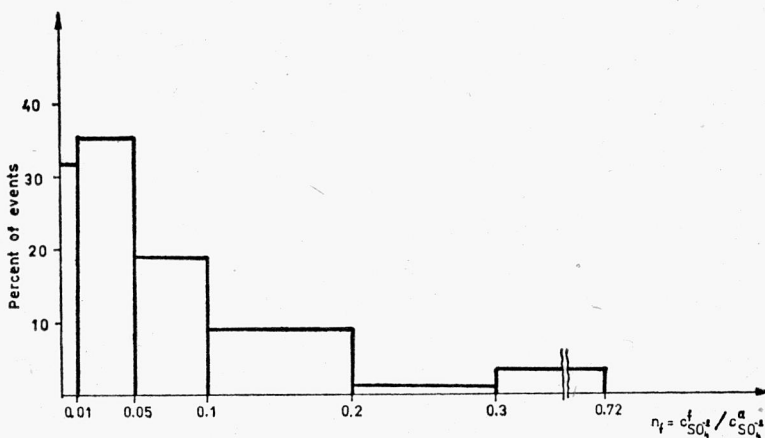


Figure. Distribution of n_f values for all samples

Rysunek. Procentowy udział przedziałów wartości n_f w całym zakresie ich zmian

4. DISCUSSION OF RESULTS.

From the investigations it follows that the deposits of sulphate ion collected on the filter paper are poor and do not exceed 10% (except a few events with an efficiency of several dozen percent). This means that over 90% of sulphate ions were able to escape through the filter paper pores. It might have been primarily the sulphuric acid mist. The partial emission of sulphate ions from the filter paper accounts for serious measuring errors, because actual concentrations of atmospheric sulphate ions are mostly ten times as high as those determined by the filter paper method. That is why the latter can neither be included in the estimates of air pollution levels nor taken into account when calculating the degree of sulphur dioxide conversion.

A complete absorption of sulphate ions from the atmosphere was found to occur in the TCM solution, which is conventionally used for the absorption of sulphur dioxide. The substitution of this solution for the filter paper has the following advantages: 1) the data obtained in this way are reliable, as they reflect the actual quantity of sulphuric acid and its salts occurring in the gaseous phase; 2) it is possible to perform concurrent measurements of atmospheric sulphur dioxide concentration, a quantity required for calculating the extent of conversion.

The method proposed in this paper may be of utility not only in determining the air pollution level, but also in investigating the process of sulphur dioxide conversion.

5. CONCLUSIONS

1. Atmospheric sulphate ion concentrations measured by the filter paper method are far below the actual values. The quantity of sulphate ions deposited on the filter paper generally falls below 10%. The remainder passes through the filter pores along with the atmospheric air.

2. Sulphate ion and sulphur dioxide concentrations measured by absorption in a sodium tetrachloromercurate solution seem to be reliable.

3. To calculate the extent of sulphur dioxide conversion in the atmosphere it is advisable to make use of the sulphate ions and sulphur dioxide concentration values determined in the same absorbing solution. The filter paper method is insufficient to yield reliable data.

REFERENCES

- [1] FORREST J., NEWMAN L., *Atm. Envir.*, 9 (1975), p. 959.
- [2] MEAGHER J. F., STOCKBURGER L., BAILEY E. M., HAFF O., *Atm. Envir.*, 12 (1978), p. 2197.

- [3] *Siarka w biosferze (Sulphur in the biosphere)*, (in Polish), PWRiL, Warszawa 1980.
- [4] ZWOŹDZIAK J., KMIEĆ G., LISOWSKI A., MATYNIAK Z., Report of the Institute of Environment Protection Engineering, Technical University of Wrocław, No. 26 (1982), (in Polish).
- [5] ZWOŹDZIAK J., KMIEĆ G., LISOWSKI A., MATYNIAK Z., Report of the Institute of Environment Protection Engineering, Technical University of Wrocław, No. 47 (1982), (in Polish).

ANALIZA PRZYDATNOŚCI FILTRÓW BIBUŁOWYCH DO POMIARU STĘŻENIA JONÓW SIARCZANOWYCH W POWIETRZU ATMOSFERYCZNYM

Dotychczas do poboru prób powietrza atmosferycznego zanieczyszczonego kwasem siarkowym i jego solami stosowano często filtry bibułowe. Stwierdzono, że zatrzymują one mniej niż 10% jonów siarczanowych, gdyż pozostałe ~90% przechodzi z powietrzem przez pory bibuły. Wiarygodne wyniki stężeń jonów siarczanowych oraz dwutlenku siarki można otrzymać stosując roztwór czterochlorortęcianu sodu, który absorbuje wymienione zanieczyszczenia.

ÜBER DIE NACHTEILE DES FILTRIERPAPIERVERFAHRENS ZUR BESTIMMUNG DES SULFATIONENGEHALTES IN DER LUFT

Es wird festgestellt, daß die bisherigen Meßwerte des Schwefeldioxid- und Sulfationengehalts in der Luft mit bedenklichen Fehlern belastet sind. Im Filtrierpapierverfahren werden weniger als zehn Prozent der ablagernden Sulfationen angehalten. Der Rest entgeht durch die Poren zusammen mit der entlaufenden Luft. Mehr Wahrhaftigkeit scheinen jene Meßwerte zu haben, die im Natriumtetrachloromercuratverfahren bestimmt werden.

АНАЛИЗ ПРИГОДНОСТИ БУМАЖНЫХ ФИЛЬТРОВ ДЛЯ ИЗМЕРЕНИЯ КОНЦЕНТРАЦИИ СУЛЬФАТНЫХ ИОНОВ В АТМОСФЕРНОМ ВОЗДУХЕ

До настоящего времени для отбора проб атмосферного воздуха, загрязнённого серной кислотой и его солями, часто применялись бумажные фильтры. Отмечено, что они задерживают меньше, чем 10% сульфатных ионов, так как остальные около 90% переходят с воздухом сквозь поры фильтровальной бумаги. Достоверные результаты концентраций сульфатных ионов, а также двуокиси серы можно получить, применяя раствор тетрахлорртутата натрия, который абсорбирует отмеченные загрязнения.