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STANISŁAW HŁAWICZKA*, PIOTR HALLALA*

FEASIBILITY OF DETERMINATION OF SUSPENDED PARTICULATE MATTER REACTIVITY BY THE INVESTIGATION OF SULPHUR DIOXIDE TRANSFORMATION TO SULPHATES

The paper deals with the type of SO_2 conversion in which sulphur compounds result from SO_2 reaction with suspended particulate matter (SPM). The method for determining the intensity of the chemisorption process is suggested. The method is based on the interpretation of the dependence between the mass of SPM (m_d) collected on filter and the concentration of sulphates (C_{SO_4}) found in the matter. The coefficients of the functions $C_{SO_4} = f(m_d)$ and $C_{SO_4}/m_d = f(m_d)$ seem to be useful in determining the affinity of SPM to SO_2.

1. INTRODUCTION

It is known that atmosphere may be regarded as a huge chemical reactor because of conversions of its pollutants. Simultaneous reactions occurring between gaseous compounds, solid and gaseous particles are also accompanied by many secondary reactions. At the same time a change in some physical parameters such as temperature, humidity, radiation and so on takes place with the conversions. The variety of physicochemical parameters make it difficult to describe simultaneously all the stages and effects of the conversions.

Sulphur oxides which basically originate from the burning of fossil fuels are the precursors of particulate sulphate formation [6]. Atmospheric sulphates, apart from the adverse health effects manifested among others in the reduction of visibility [7], have been recently considered as being the reason for acid rains damaging the aquatic and terrestrial ecosystems [1]. Although a number of models incorporating both homogeneous and heterogeneous mechanisms have been proposed for atmospheric oxidation of SO_2, the primary route for sulphate formation remains still obscure.

*Institute for Environmental Development (IKŚ), Environmental Pollution Abatement Centre, 40-832 Katowice, ul. Kossutha 6, Poland.

The total SO_2 conversion to sulphates is an extremely complex process with many interrelated and poorly characterized variables. Conversion of SO_2 which occurs according to photochemical mechanism is described satisfactorily in [6]. It seems, however, that the SO_2 conversion which occurs in the presence of suspended particulate matter is still little known. This process depends on the sorption rate of SO_2, the sizes of the particles involved, their chemical composition, and the relative humidity. Traces of metallic compounds can serve as catalysts of the conversion [2, 3].

Despite many investigations of the reactions involving SO_2, dust and other pollutants, a relatively simple method enabling to express the process in the quantitative terms have not been developed yet. Therefore the question arises what is the role of suspended particulates in the conversion of SO_2 to sulphuric acid and sulphates.

In our work we shall deal with the type of SO_2 conversion in which sulphur compounds can be formed due to the reactivity of suspended particulate matter. The method will be suggested for determining the chemisorption process intensity in order to characterize quantitatively the reactivity of suspended particulates.

2. METHODS

The term suspended particulate matter covers a wide range of minute separated particles of solids or liquids that may be emitted to the atmosphere from the combustion process, industrial operations or natural sources. In the size range below 10 μm the settling rate is negligible compared with the wind motion and air turbulence and such particles may remain in suspension for hours or days.

The particulate matter was collected for 24 h on membrane filter Synpor. During this period about 90 m^3 of air was let through the filter. The amount of collected material (m_d) was determined gravimetrically with the accuracy ± 0.001 mg under controlled temperature and humidity conditions.

Sulphates were determined in the solution obtained by their extraction with hot water. Sulphate ions were titrated spectrophotometrically with barium perchlorate according to thoronol method [4]. The accuracy of the method was about 0.4 μg of sulphates per 1 m^3 of air.

The concentration of sulphates C_{SO_4} was determined by dividing the sulphate mass found in the sample of material collected on the filter by the amount of air passed through the filter.

3. RESULTS

We intended to determine the reactivity of suspended particulate with SO_2. It seemed that the contents of sulphates in the material collected on filter can be regarded as a final product of reaction of SO_2 with appropriate reactive compounds of suspended parti-

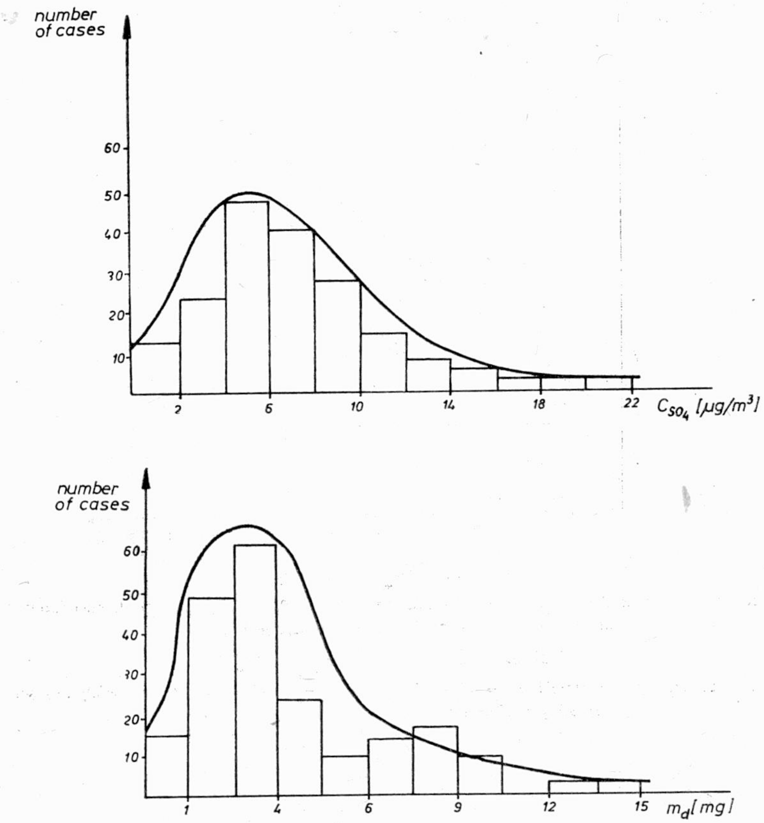

Fig. 1. The marginal distribution for C_{SO_4} and m_d (summer season)

Rys. 1. Rozkład marginalny dla C_{SO_4} i m_d (lato)

culate matter. The results presented were obtained by statistical analysis of 365 samples of the material collected on filters during 17 months (from September to December). While looking for the relationship between the mass m_d of the material collected on the filter and the concentration of sulphates C_{SO_4} found in the material — we have stated that discrete marginal distributions of C_{SO_4} and m_d have similar shapes in each period investigated (the whole year, the summer, and the heating seasons). By discrete distributions we mean the distributions obtained by counting the cases in the intervals. For example, marginal distributions for C_{SO_4} and m_d in summer are shown in fig. 1. The curves are slightly asymmetrical, but have got the same direction of the asymmetry, thus the function of regression $C_{SO_4} = f(m_d)$ is linear. This fact has been confirmed by computer-aided statistical analysis. The possibilities of nonlinear parabolic and logarithmic regressions have been also considered. The curves were tested by the method of least squares. The best curves found by this method are straight lines with the parameters shown in figs. 2 and 3.

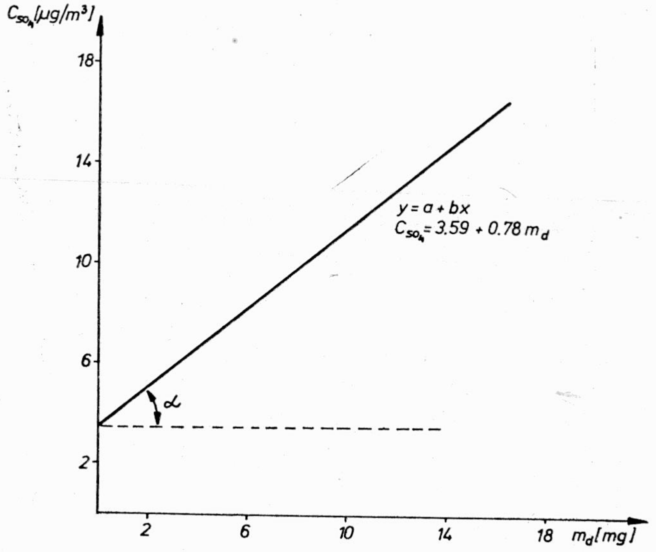

Fig. 2. C_{SO_4} versus m_d

365 observations; ranges of measured values: $m_d = 0.4–20.2$ mg, $C_{SO_4} = 0.8–25.7$ μg/m³; confidence intervals for parameters at the 95% confidence level: ±0.76 (a), ±0.12 (b)

Rys. 2. Zależność C_{SO_4} od m_d

365 obserwacji; zakres zmierzonych wartości: $m_d = 0,4–20,2$ mg, $C_{SO_4} = 0,8–25,7$ μg/m³; przedziały ufności dla parametrów przy 95% poziomie ufności: ±0,76 (a), ±0,12 (b)

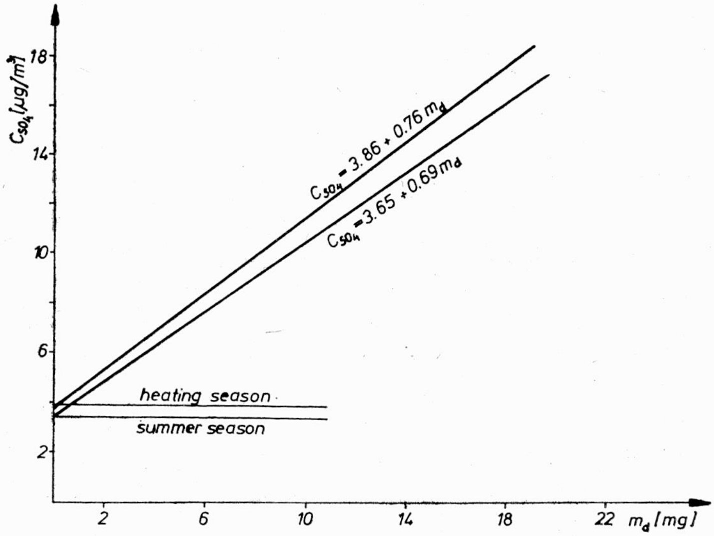

Fig. 3. C_{SO_4} versus m_d

Summer season — 142 observations, heating season — 223 observations; confidence intervals for parameters at the 95% confidence level: summer season — $a = \pm 1.18$, $b = \pm 0.16$, heating season — $a = \pm 1.01$, $b = \pm 0.25$

Rys. 3. Zależność C_{SO_4} od m_d

Lato — 142 obserwacje, okres grzewczy — 223 obserwacje; przedziały ufności dla parametrów przy 95% poziomie ufności: lato — $a = \pm 1,18$, $b = \pm 0,16$; okres grzewczy — $a = \pm 1,01$, $b = \pm 0,25$

For the whole analysed period, the summer and the heating seasons the correlation coefficients of m_d and C_{SO_4} are 0.544, 0.425, and 0.516, respectively. For the whole period the mean square of regression is 3.97, and for the summer and heating seasons the corresponding values are 3.36 and 4.30. It is of interest that sulphate concentration as the function of m_d is expressed by a straight line non-parallel to the x-axis, since the mean concentration of sulphate should not depend on the mass of material collected on filter. Figure 3 presents the dependence of m_d on the concentration of sulphate falling to summer (April–October) and heating seasons (November–March). The slopes of straight lines in figs. 2 and 3 do not differ substantially. It may be reasonable to find the correlation between the slope of the straight line and the affinity of the suspended particulate matter to SO_2. According to our opinion the slope of the straight line is closely related to the interaction between the suspended particulate matter and atmospheric sulphur dioxide. This slope can be a measure of compliance between the suspended particulate matter and reaction with SO_2. The value of the compliance is expressed by a coefficient b of the linear equation (fig. 3). Such a method for determining the reactivity of suspended particulate matter enables us to compare directly the reactivities of the matter of various origin; the higher the slope of the function $C_{SO_4} = f(m_d)$, the greater the reactivity of suspended matter to SO_2. Thus, the properties of the matter can be quantified by comparing the tangents of inclination angles (figs. 2 and 3).

We assume that the reactivity coefficient of suspended particulate matter Rc_{SO_2} can be defined by the value of the tangent. This coefficient may be used to describe quantitatively the suspended particulate matter at any region.

Such a property of particulate matter has not been characterized yet. Then

$$\mathrm{tg}\alpha = Rc_{SO_2}.$$

We have also tested another function, namely

$$C_{SO_4}/m_d = f(m_d).$$

From the analysis carried out at the 95% of confidence level, we have obtained the parabolic regression curves presented in fig. 4. The obtained equations and confidence intervals reffering to each coefficient are also given in this figure.

It seems that in this figure the value of Rc_0 represented by the points of intersection of the curves with y-axis may play a similar role to that of tangents α presented in figs. 2 and 3. The obtained Rc_0 values, being of the so-called reduced value, may therefore be more versatile for the determination of investigated matter reactivity than the values Rc_{SO_2} proposed earlier. One more interesting feature of the curves presented in fig. 4 is that they have a minimum W in the range of investigated values m_d.

It is also interesting that for each curves the W values are situated near the value of 10 mg of the matter collected on filters. In this paper the sense of such behaviour of the curves will not be discussed. It seems, however, that the existence of such a minimum is not meaningless.

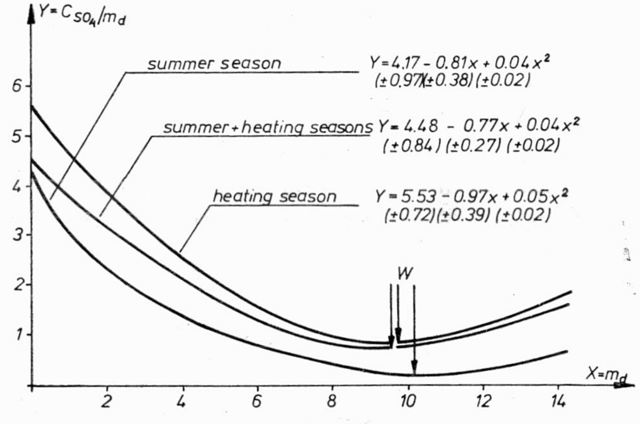

Fig. 4. C_{SO_4}/m_d versus m_d

The values of confidence intervals for equation parameters are given in parantheses, W — minimum of the curves

Rys. 4. Zależność C_{SO_4}/m_d od m_d

W nawiasach podano wartości przedziału ufności dla parametrów równań, W — minimum krzywych

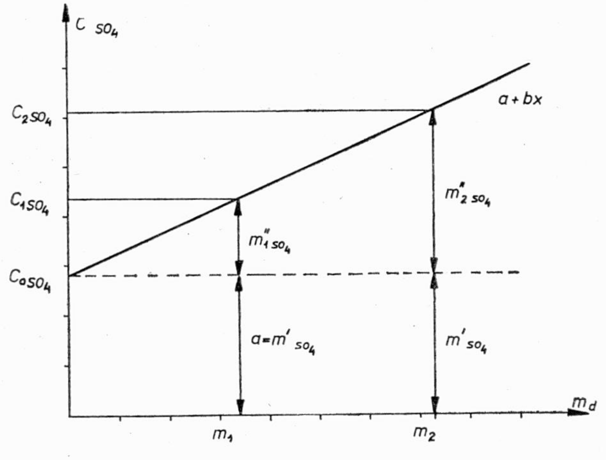

Fig. 5. The analytical aspects of interpretation of the function $C_{SO_4} = f(m_d)$

Rys. 5. Analityczne aspekty interpretacji funkcji $C_{SO_4} = f(m_d)$

Coming back to the interpretation of the curves presented in figs. 2 and 3, the function $C_{SO_4} = f(m_d)$ seems to deserve our interest also from analytical point of view. It can be seen that for $m_d = 0$ the concentration of sulphate Co_{SO_4} differs from 0 and therefore we suppose that Co_{SO_4} in fig. 5 represents the sum of sulphates, i. e. that produced in ambient air without any participation of suspended particulate matter and the native sulphate (i. e. present in plume in the moment of emission). Then

$$Co_{SO_4} = \lim_{m_d \to 0} \frac{[SO_4^{-2}]}{m_d}.$$

In other words, we think that the value Co_{SO_4} except for the native sulphate expresses the concentration of sulphate which resulted in photochemical transformation.

In our investigations we have found the mean value of Co_{SO_4} equal to 3.59 μg/m³. It is represented in fig. 2 by the intersection with the y-axis. For summer and heating seasons these concentrations are 3.65 and 3.86, respectively (fig. 3). The values m''_{1SO_4} for $m_d = m_1$ or m''_{2SO_4} for $m_d = m_2$, i.e. in general m'' values in fig. 4, represent the contents of sulphate in the particulate matter collected on filter which originated due to reactivity of some compounds present in the suspended particulate matter. Therefore we associate this fraction of sulphate with the reactivity of suspended particulate matter expressed by coefficients Rc_{SO_4} and Rc_0.

4. DISCUSSION

The paper deals with problems of sulphate dioxide transformation in the atmosphere. The first one is the reactivity of suspended particulate matter with SO_2. The second one is the interpretation of $C_{SO_4} = f(m_d)$ function which suggests various origin of sulphate determined in particulate matter on filter. As far as the second problem is concerned we would like only to express our view-point based on general interpretation of the function presented in fig. 4.

It is also possible that these two kinds of sulphates play various roles in the nature. It seems probable that the sulphate denoted in fig. 4 by m' contribute to acid rain. We shall not make any attempt to explain here our hypothesis because the topic is very broad and it needs further investigations. It is, moreover, interesting from analytical point of view. It seems advisable to develop an analytical method which would allow us to distinguish sulphates of different origin in the matter collected on filters.

Coming back to the proposed method for determination of the reactivity of the suspended particulate matter to SO_2, we consider that coefficients Rc_{SO_4} and Rc_0 can be very useful in environmental investigations. These coefficients comprise total reactivity of suspended particulate matter, understood as the sum of sorptive properties, chemical affinities to SO_2 as well as catalytic properties for transformation of SO_2.

The rate of SO_2 transformation to sulphate ranges from one to a few percent per hour [5]. We assume that coefficients Rc characterize a particle suspended in ambient air the size of which is below 10 μg.

The settlement velocity of such substances is very low due to natural motion of the air. Therefore they can remain suspended in the air for many days. We assume that such a period of time suffices for the sorption of SO_2 by the suspended matter to reach the equilibrium state. Under such assumption it is possible to neglect the time in all considerations referring to the interpretation of Rc_{SO_2} and Rc_0 coefficients.

Sorption properties strongly depend on physical properties of suspended matter, such as porosity and refinement. Since at the same time chemical affinity of the matter to SO_2 depends on mineral composition and catalytic properties on the cations included in suspended particulates, it seems that *Rc* may characterize suspended particulate matter of various regions in the versatile way. What is of a particular interest is that *Rc* coefficients combine both physical and chemical properties. As yet we have not had any factor of that kind which could associate these two groups of properties of the matter.

It is difficult to predict actual applications of coefficients *Rc*, but there is no doubt that they may be useful in a quantitative approach to some problems in environmental engineering. They can be used also when some processes in atmosphere are to be evaluated, especially in order to determine contamination of soil, water, plants, and other surfaces by air pollutants. It seems also that *Rc* should be taken into account in the equations which describe the process of air pollutants diffusion.

Since interaction between SO_2 and suspended matter is regarded as being typical, it seems that Rc_{SO_2} and Rc_0 can be assumed as the universal coefficients which can generally characterize the interaction of suspended particulate matter with other gaseous pollutants of ambient air.

It should be emphasized that appart from the data presented, our paper contains some controversial ideas which we hope that being properly presented by us will be well understood. The verification of pertinence of proposed method is possible by analysing the data from other regions. Such a continuation of the subject is according to authors' intention.

REFERENCES

[1] BARNES R. A., *The long range transport of air pollution*, JAPCA, Vol. 29 (1979), p. 1219.

[2] BARVIE L. A., GEORGII H. W., *An experimental investigation of the absorption of SO_2 by water drops containing heavy metal ions*, Atmos. Environ., Vol. 10 (1976), p. 743.

[3] BUFALINI M., *Oxidation of SO_2 in polluted atmospheres — a review*, Environ. Sci. Technol., Vol. 5 (1971), p. 685.

[4] HRYNIEWICZ R., OLIWA L., *Oznaczenie siarczanów w pyłach atmosferycznych i opadach*, Ochrona Powietrza, Vol. 20 (1970), p. 20.

[5] NEWMAN L., *Atmospheric oxidation of SO_2: a review as viewed from power plant and smelter plume studies*, Atmos. Environ., Vol. 15 (1981), p. 2231.

[6] *Sulfur oxides and suspended particulate matter*, Environmental Health Criteria 8, World Health Organization, Genewa 1979.

[7] WAGGONER A. P., WEISS R. E., AHLQUIST N. C., COVERT D. S., WILL S., CHARLSON R. J., *Optical characteristics of atmospheric aerosols*, Atmos. Environ., Vol. 15 (1981), p. 1891.

WYZNACZANIE REAKTYWNOŚCI PYŁÓW ZAWIESZONYCH PRZEZ BADANIE PRZEJŚCIA DWUTLENKU SIARKI W SIARCZANY

Badano tworzenie się związków siarki w reakcji SO_2 z pyłem zawieszonym. Zaproponowano metodę określania intensywności chemisorpcji zachodzącej w tego typu procesach. Metoda ta polega na odpowiedniej interpretacji zależności między masą pyłu (m_d) zebranego na filtrze a stężeniem siarczanów (C_{SO_4}) zawartych w tym pyle. Według autorów współczynniki funkcji $C_{SO_4} = f(m_d)$ i $C_{SO_4}/m_d = f(m_d)$ mogą być miarą podatności pyłów zawieszonych na reakcję z SO_2.

BESTIMMUNG DER REAKTIONSFÄHIGKEIT VON SUSPENDIERTEN STÄUBEN ANHAND DES ÜBERGANGES VON SCHWEFELDIOXYD IN SULFATE

Untersucht wurde die Bildung von Schwefelverbindungen die während der SO_2-Reaktion mit sus pendierten Stäuben entstehen. Beschrieben wird die Bestimmungsmethode der Intensität der Chemosorption, die bei diesen Prozessen stattfindet. Die Methode beruht auf einer entsprechenden Interpretation der Relation zwischen der auf dem Filter abgeschiedenen Staubmasse (m_d) und der – im selben Staub festgestellten – Sulfatkonzentration (C_{SO_4}). Nach den Anschauungen der Verfasser, können die Funktionskoeffiziente $C_{SO_4} = f(m_d)$ und $C_{SO_4}/m_d = f(m_d)$ ein Maßstab der Reaktionsfähigkeit sein.

ОПРЕДЕЛЕНИЕ ХИМИЧЕСКОЙ АКТИВНОСТИ ЗАВЕШЕННЫХ ПЫЛЕЙ В ИССЛЕДОВАНИЯХ ПЕРЕХОДА ДВУОКИСИ СЕРЫ В СУЛЬФАТЫ

Было испытано образование соединений серы в реакции SO_2 с завешенной пылью. Предложен метод определения интенсивности хемисорбции, проходящей в процессах этого типа. Этот метод основан на соответствующей интерпретации зависимости между массой пыли (m_d) собранной на фильтре и концентрацией сульфатов (C_{SO_4}) содержащихся в этой пыли. По мнению авторов, коэффициенты функции $C_{SO_4} = f(m_d)$ и $C_{SO_4}/m_d = f(m_d)$ можно считать мерой податливости завешенных пылей на реакцию с SO_2.