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ON THE ADEQUACY OF MEASURING METHODS AS APPLIED TO THE DETERMINATION OF ATMOSPHERIC POLLUTION FROM SULPHURIC ACID AND SULPHATES

The methods commonly used for measuring total sulphates in the atmosphere are found to be inadequate. To obtain a full identification of the sulphur dioxide conversion products present in the atmosphere it is necessary that the measuring system consist not only of a filter paper set, but also of a scrubber for the absorption of sulphuric acid vapour. When the absorbing solution is made up of sodium tetrachloromercurate, it will be possible to determine the quantity of fixed sulphur dioxide and sulphuric acid vapour.

1. INTRODUCTION

The most common technique of air pollution control in the vicinity of an emission source is measuring the concentration of airborne sulphur dioxide. Sulphur dioxide belongs to the class of primary pollutants. At levels commonly found in industrialized areas, sulphur dioxide is converted and rendered hazardous through interactions which occur in the atmosphere under the influence of sunlight, moisture and other environmental factors. The products of this conversion are sulphuric acid and sulphates, which persist in a liquid form and a solid form, respectively, to yield the atmospheric aerosol.

Measured atmospheric concentrations of sulphuric acid and its salts considered jointly were found to be markedly lower than the concentration of the starting compound, sulphur dioxide. This finding made the environmental scientists and engineers believe that the conversion reaction went slow. Low degrees of conversion $(c_{SO_4^{2-}}) / (c_{SO_2} + c_{SO_4})$ were measured even in the vicinity of coal-fired power plants or smelters which are known to create particularly favourable conditions for the conversion of sulphur dioxide [2], [5], [8]. The objects of interest release air pollutants that make the oxidation reaction go faster. These are nitrogen ox-

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des, hydrocarbons and heavy-metal enriched particulates [4]. Notwithstanding what was expected, airborne concentrations of compounds containing sulphate ions never exceed $0.1 \text{ mg SO}_4^{-2}/\text{m}^3$. This finding directed our attention to the problem of measuring methods.

By far the most common method applied for determining the total atmospheric concentration of the conversion products is the filter paper procedure [3], [4], [6]. On these filter papers, only deposits of solid particles including sulphates of a grain diameter greater than the filter pores 0.3 to 0.6μ are obtained. Liquid particles, e. g. sulphuric acid vapours, leave the deposit enter the atmosphere. Thus, the results obtained via the above route do not seem to enter reflect the actual pollution level.

2. MEASURING METHODS

The determinations of airborne sulphur dioxide, sulphuric acid vapour and particulate sulphate involved identical sampling sets. Each of them consisted of a TFA-810 filter paper capable of depositing 0.1 - $10.0 \mu\text{m}$ diameter solid particles, a scrubber containing sodium tetrachloromercurate solution, 25 cm^3 , a gas meter and a suction pump. The flow rate averaged lower than $150 \text{ dm}^3/\text{h}$. Each sampling procedure took 24 h. The filter was shaken in distilled water to determine the concentration of particulate sulphate. The absorbing solution was used for determining the content of sulphate ions and the quantity of fixed sulphur dioxide. When any metals were absent in the absorbing solution, the increment in sulphate ion content was the result of sulphuric acid sorption only.

The analytical methods were as follows: zirconium alizarinate decomposition for sulphate [1] and the colorimetric method (a modified version of the West and Geake method [7]) to measure sulphur dioxide in the ambient air. Metals were analyzed by atomic absorption spectroscopy.

All of the measurements comprised the immediate environment of a lignite-fired power plant. Analyses were performed for a total of 140 absorbing solutions and 140 filtrate samples obtained from washing the filter paper with distilled water.

3. DISCUSSION OF RESULTS

Table gives the concentrations of some airborne sulphur compounds measured in the vicinity of the power plant. Analyses showed that water-soluble sulphates deposited on the filter paper, whereas sulphate ions and sulphur dioxide persisted in the absorbing solution. Apart from some cations, sodium and mercury, occurring in the original absorbent none of the absorbing solutions included cations which constituted the components of the atmospheric aerosol, i.e. calcium, magnesium, potassium, copper, iron and aluminium. This means that all of the sulphate particulates have deposited on the filter paper while sulphuric acid vapour and

Table

Some of the sulphur species concentration measurements
in the vicinity of the power plant
Stężenia niektórych związków siarki w pobliżu elektrowni

Measurements	Concentration, mg/m ³		
	Sulphur dioxide	Sulphuric acid vapour	Particulate sulphate
1	0.0341	0.553	0.0833
2	0.0313	0.617	0.0828
3	0.0259	0.496	0.0773
4	0.0223	0.495	0.0698
5	0.0334	0.554	0.0793
6	0.0314	0.486	0.0662
7	0.0377	0.510	0.0608
8	0.0361	0.616	0.0685
9	0.0206	0.306	0.1225
10	0.0379	0.404	0.092

sulphur dioxide have passed through the filter. Thus, the usability of filter papers for measuring the concentration of sulphate-ion compounds raises serious doubts. While filter papers may be of utility as applied to airborne sulphate sampling, they become useless when applied to the measurement of sulphuric acid concentration without being saturated — e.g. with alkalis — prior to the measuring procedure. As shown by the data in table, it was not so much sulphur dioxide (which had been reported so far to be the main contributing factor) as the sulphuric acid that accounted for the atmosphere pollution level. Airborne sulphur dioxide concentrations were generally close to one hundredth of mg SO₂/m³ and were obviously lower than those of sulphuric acid vapour which in most instances approached one tenth of SO₄⁻²/m³. Sulphate concentrations averaged between 0.06 to 0.12 mg/m³. It is interesting to note that atmospheric concentrations of sulphuric acid vapour measured near the power plant are several dozen times as high as the admissible value (NDS_{24h} = 0.1 mg/m³). The total sulphate ion concentration values measured in the area of interest are significantly higher than those reported by other investigators for similar objects. Thus, the values measured by FORREST and NEWMAN [2] range from 0.039 to 0.078 mg/m³ for the power plant plume and from 0.028 to 0.040 mg/m³ for the ground level. MEAGHER and coworkers [5] give concentration values for the plume which vary from 0.0020 to 0.0994 mg/m³. Similar results were reported by our research group in 1982 [8], because the measuring method applied in that study involved filter papers alone. It became obvious that both the literature data

quoted here and our own results described airborne concentrations of sulphates alone. These led to an inadequate interpretation of the measured results and, consequently, to considerable errors in the estimates of atmospheric pollution from compounds containing sulphates ions. Analyses of the absorbing solution have revealed that the sulphate ion content measured there is from 2.5 to 9 times as high as that determined in the filter deposit.

The application of such measuring methods, that enable determination of all the airborne sulphur compounds mentioned, makes it possible to give an adequate characterization of the conversion reaction for sulphur dioxide. The conversion of sulphur dioxide in the vicinity of the power plant was found to go fast, because measured concentrations of conversion products (specifically those of sulphuric acid) were much higher than those of the substrate, i.e. sulphur dioxide. But reliable data will not be achieved until direct measurements in the stack plume are performed.

The application of the modified measuring method shows that sulphur dioxide emissions are responsible for sulphuric acid formation in the atmospheric air. It is therefore advisable that air pollution control involve not only measurements of sulphur dioxide concentrations, but airborne sulphuric acid as well.

4. CONCLUSIONS

1. Airborne sulphur dioxide concentrations measured in the vicinity of coal-fired power plants are generally low (approximately one hundredth of $\mu\text{g}/\text{m}^3$) and show a relatively poor tendency to increase.

2. The atmospheric air around the sulphur dioxide emission source is also characterized by the presence of sulphuric acid and sulphates as polluting factors. Both the products of the conversion reaction occur at concentrations evidently higher than those of the substrate.

3. In areas exposed to sulphur dioxide emissions, air pollution control should involve not only measurements of sulphur dioxide concentrations, but also airborne sulphuric acid. A full characterization of air pollution from the two sulphur compounds and sulphates may be achieved by applying a modified measuring method which involves filter papers and sodium tetrachloromercurate solutions. The application of filter papers alone enables determination of airborne sulphates only.

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METODY POMIARU ZANIECZYSZCZENIA POWIETRZA ATMOSFERYCZNEGO KWASEM SIARKOWYM I SIARCZANAMI

Powszechnie stosowane metody pomiaru całkowitej siarki w powietrzu atmosferycznym nie są dokładne. Układ pomiarowy, który dawałby pełny obraz produktów konwersji dwutlenku siarki w powietrzu, powinien składać się nie tylko z sączka bibułowego, ale również z płuczki pochłaniającej pary kwasu siarkowego. Określenie stężenia dwutlenku siarki i par kwasu siarkowego jest możliwe, gdy pochłaniaczem jest roztwór czterochlorortęcianu sodowego.

ÜBER DIE UNANGEMESSENHEIT DER BISHER ANGEWANDTEN METHODEN ZUR BESTIMMUNG DER LUFTVERSAUCHUNG MIT SCHWEFELSAURE UND SULFATEN

Es wird festgestellt, da die bisher angewandten Methoden zur Bestimmung des Gesamtsulfateninhalts in der Luft ungeeignet sind. Eine zuverlässige Identifizierung der Schwefeldioxidumwandlungsprodukte verlangt wesentliche Abänderungen im Me verfahren. Es ist empfehlenswert, das bisher angewandte Me system zusätzlich mit einem Wascher auszustatten. Als Auffanglösung durfte Natriumtetrachlormerkurat angewendet werden. Das auf diese Weise modifizierte Me verfahren gestattet eine genauere Bestimmung der Schwefeldioxid- und schwefelsauredunstmengen.

МЕТОДЫ ИЗМЕРЕНИЯ ЗАГРЯЗНЕНИЯ АТМОСФЕРНОГО ВОЗДУХА СЕРНОЙ КИСЛОТОЙ И СУЛЬФАТАМИ

Широко применяемые методы измерения всех соединений серы в атмосферном воздухе неточны. Измерительная система, которая давала бы полное представление о продуктах конверсии двуокиси серы в воздухе, должна состоять не только из бумажного фильтра, но и из промывной склянки, поглощающей пары серной кислоты. Определение концентрации двуокиси серы и паров серной кислоты возможно, если поглотителем является раствор тетрахлоромеркуроата натрия.