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THE EFFECT OF SAMPLING CONDITIONS ON THE CONCENTRATION OF SULPHURIC ACID FOUND IN URBAN AIR

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by

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French Version in Press J. Envir. Anal. Chem., July 1971

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AIR POLLUTION CONTROL DIRECTORATE

DEPARTMENT OF THE ENVIRONMENT

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#### CANADA

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#### ABSTRACT

By means of a specific method for the measurement of sulphuric acid in air, the authors have studied the effects of flow rate and the sampling time upon the concentration of sulphuric acid found. The samples were taken at constant flow rate for varying periods of time and also at varying flow rates with the time held constant. A diminution of the concentration of sulphuric acid found in air, expressed in micrograms per cubic metre, is observed for increases in flow rates and sampling times.

The neutralization of sulphuric acid at the surface of the glass fibre sheet would seem to be the most plausible explanation.

#### INTRODUCTION

In a previous work, we have described a specific method for the measurement of sulphuric acid in urban air (1). We have, at the same time, mentioned the following limiting conditions:

- 1. Possible reaction of sulphuric acid with other compounds sampled.
- 2. More or less complete collection of sulphuric acid by glass fibre filters.

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By means of such a method, it then becomes possible to study whether there is a variation in the concentration of sulphuric acid as measured in air. We considered it expedient, first of all, to measure the effect of sampling time upon the concentration of sulphuric acid found while varying the sampling conditions.

#### EXPERIMENTAL

In a preliminary series of experiments, we sampled for fixed periods of time, for example for 24 hours using seven samplers operating at different flow rates. In a second series of experiments, the samples were taken at constant flow during varying periods of time in order to obtain a 24 hour sample and several others of 6, 8 or 12 hours were taken during the same period of time. All the sampling instruments used (Hi-Vol), were calibrated by means of two different methods before starting the experiments. The analytical method for sulphate has been described in the previous paper (1).

#### RESULTS AND DISCUSSION

Figure 1 illustrates some results obtained according to the first sampling method. The curve of the relative concentration of sulphuric acid is shown as a function of the volume sampled. The concentration at a volume of 1800 cubic metres is considered equal to unity. Each point on the curve represents the mean of 9 samples. The concentration of sulphuric acid diminishes as the volume, that is, the flow, increases. A relative concentration of 2.0 corresponds to a volume of 900 cubic metres. For a doubled volume, the concentration is halved. We have found it impossible to sample at a lower flow rate because the instruments used cannot function under these conditions.

The results obtained according to the second method of sampling are summarized in the curve of the relative concentration of sulphuric acid as a function of sampling time, Figure 2. The concentration at 24 hours is considered equal to unity. Seventy two samples were taken to obtain this curve. The flow rate of the apparatus was about 45 cubic

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feet per minute. It is noticeable that the concentration of sulphuric acid diminishes very rapidly, during the first hours of sampling, finally diminishing at a rate much less rapid after ten hours. According to this curve, the concentration of sulphuric acid at 12 hours sampling is 1.35 times greater than for a period of 24 hours. A sampling volume of 800 cubic metres corresponds to this period of 12 hours. We have seen previously, from Figure 1, that the relative concentration of sulphuric acid for a volume of 800 cubic metres is 2.25 times greater than that for a volume of 1800 cubic metres. It then follows, that the flow of air through the filter has a greater influence on the diminution of the concentration of sulphuric acid than does the time of sampling. By constructing the curve of the logarithm of the concentration of sulphuric acid as a function of the sampling time, some additional information can be obtained. It is seen that two straight lines can be drawn, which leads one to believe that we have to do, possibly, with two different reactions. The first reaction, at the beginning of sampling, is very rapid, and the other, slower, manifests itself at the end of sampling. Or, alternatively, there may be one reaction, which is governed by two different factors, of which the influence of one disappears after 7 hours sampling.

This decrease in the concentration of sulphuric acid, with the time and flow rate of sampling, can also be due to other factors such as the increase in the concentration of particles on the surface of the sheet, the composition of the sheet itself and the composition of the sample of air. Two phenomena can explain this diminution, evaporation and the neutralization of the sulphuric acid during sampling.

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It is difficult to explain by one of these reactions, in unequivocal fashion, the decrease in concentration of sulphuric acid according to the results obtained. In all cases, the neutralization of sulphuric acid at the surface of the sheet, would seem to be the principal reason. In the course of developing this method for the measurement of sulphuric acid, we were using standards of ammonium sulphate or of sulphuric acid for the calibration curve. It was a question of placing a known volume of the standard solution in the bottom of the petri dish and after evaporation, one proceeded to microdiffusion. During these earlier experiments, we had observed that it was impossible to carry out the diffusion of the sulphuric acid if the acid is placed upon a sheet of glass fibre. There is complete neutralization by the formation of a non-volatile or non-decomposable sulphate at the temperature used for measurement. A recent paper by Benarie and Nonat (2) shows that it is impossible to recover by microdiffusion, sulphuric acid placed on the surface of a sheet of glass fibre even after washing of these filters with sulphuric acid followed by rinsing. An acid washing is unable to eliminate the fixative power of glass fibre sheet for sulphuric acid.

This property of glass fibre sheet seems to be the principal cause of the variation of the concentration of sulphuric acid with respect to the method of sampling. On the other hand, there should not be complete elimination of sulphuric acid because of more or less direct contact of the particles with the sheet. The more the volume sampled increases the more the number of particles increases and as a result more intimate contact is established between the sheet and the particles. There then results a very rapid decrease in the concentration of sulphuric acid.

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#### CONCLUSIONS

One may summarize the possible explanations of the decrease in sulphuric acid by studying Figure 4. One observes, here, that the total quantity of sulphuric acid, at the surface of the sheet, remains constant for a given period, which reinforces the statement that the volume has no influence on the concentration of sulphuric acid. It would seem to be, therefore, a question of neutralization rather than evaporation. On the contrary, it is observed that this total concentration decreases as a function of time according to the second method so that a minimum is reached after 6 hours.

One may suppose that there has been neutralization of the sulphuric acid in proportion to the increase in the quantity of particulates. At the end of 6 hours, there should have been complete coverage of the sheet by the particulates from which the level of neutralization is decreased. There is then increase in the total concentration of sulphuric acid due to the decrease in the speed of neutralization, which is then controlled by what could be a diffusion phenomenon.

#### SOMMAIRE

A l'aide d'une méthode spécifique pour le dosage de l'acide sulfurique dans l'air urbain, les auteurs ont étudié les effets du débit, et, du temps d'échantillonnage, sur la concentration de l'acide sulfurique. Les échantillons furent prélevés, à débit constant pendant des périodes de temps variables, et à débit variable pendant des périodes de temps constantes. On observe une diminution dans la concentration de l'acide

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sulfurique, exprimée en microgrammes par mètre cube, pour une augmentation du débit et du temps d'échantillonnage.

La neutralisation de l'acide sulfurique a là surface des feuilles de fibres de verre semble être l'explication la plus plausible.

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# FIGURE CAPTIONS

1 Relative concentration sulphuric acid versus volume.

2 Relative concentration sulphuric acid versus sampling time.

3 Log relative concentration sulphuric acid versus sampling time.

4 Total relative concentration sulphuric acid versus sampling time.

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