Seasonal and diurnal variations of the size distribution of atmospheric sulfate particles

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ABSTRACT

Measurements were carried out to determine the seasonal and diurnal variations of the size distribution of sulfate particles. The results of these measurements show that there is an unambiguous seasonal variation which is caused by the changes of the relative humidity of the air. On the other hand no diurnal variation was found because during the sampling time the relative humidity was smaller than the value necessary for the phase transition of the particles. The measured growth with increasing relative humidity of the mass median radius of sulfate particles is practically comparable with the theoretical growth of a pure ammonium sulfate particle having a 0.14 μ dry radius. On the basis of these findings the mechanism of the sulfate particle formation is briefly discussed.

Introduction

Some data of the size distribution of water soluble particles were previously presented (Mészáros, 1968). However, it should be pointed out that these distributions were based on measurements carried out during a relatively short time period. Therefore in this paper the results of an extensive sampling program are described, when the sampler was operated during 200 days (in the period from March, 1967 to February, 1969). This makes it possible to group the data in the summer (April–September) and winter (October–March) half years. Independently of these samplings, daytime and night measurements were made to estimate the diurnal variation.

In this work only the size distribution of sulfate particles is discussed. It is assumed that these particles are mainly composed of ammonium sulfate. The size distribution of ammonium particles was also measured in this program, but it is difficult to compare their size distributions with that of sulfate nuclei because an important ammonium excess was found (Mészáros, 1968).

The samples were taken and analysed in the Aerological Observatory of Budapest in the same way as described by Mészáros (1968). It is to be noted, however, that the membrane filter samples (fifth stage in a Casella cascade impactor) were corrected by collection efficiencies measured by two filters connected in series behind the impactor (these collection efficiencies for Aitken sized sulfate particles were around the value of 90%).

Seasonal variation

The fraction of sulfate particles in terms of percentage of the total mass for the different size ranges and seasons is given in Table I. The size limits in the first column are defined as radii having 50% collection efficiency on the different stages of the sampler. One can see from these data that there is an unambiguous seasonal variation of the size distribution, whereas the total concentration, in agreement with previous findings (Bónis, 1968; Georgii *et al.*, 1968), remains practically constant. In the winter months the sulfate fraction in the giant range is larger, while in the range of Aitken particles it is smaller than in the summer. On the other hand, in the large size range the relative amount of the sulfate mass is the same in the two half-years.

To obtain a better understanding of the seasonal variation of the size distribution of sulfate particles, the data were plotted on logarithmic probability paper (Fig. 1). It is to be noted that in the summer half-year only such measurements were considered when all the four stages

Table 1. *Size distribution and concentration of sulfate particles in the summer and winter half-year (second line: days of sampling)*

Size range, μ	Summer, % 80 days	Winter, % 120 days
$r > 3.6$	5	8
$3.6 > r > 1.2$	6	12
$1.2 > r > 0.46$	40[a]	16
$0.46 > r > 0.14$		25
$r < 0.14$	49	39
$\Sigma \mu g\, m^{-3}$ STP	5.3	4.7

[a] In the summer half-year during 45 days the third stage of the impactor was not operated.

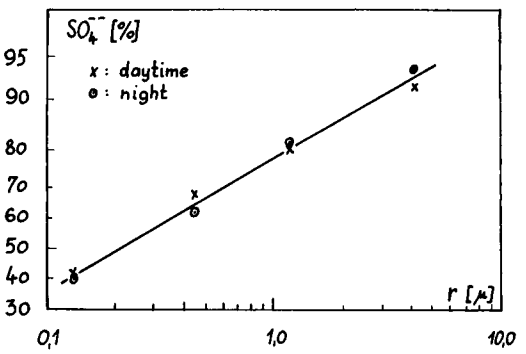

Fig. 2. Size distribution of sulfate particles in daytime and night (the ordinate indicates in per cent the mass of the particles of radius smaller than r).

of the impactor were operated (35 days). It is seen from this figure that sulfate particles are about two times larger in the winter than in the summer, but the form (dispersion) of the distribution is the same. Thus, in the summer the mass median radius is 0.11 μ, while it is 0.24 μ in the winter half-year. The upper geometric deviation, the measure of dispersion defined as the ratio $r_{90\%}/r_{50\%}$, is about 10 independently of seasons.

Diurnal variation

Twenty-eight daytime (from sunrise to sunset) and 28 night (from sunset to sunrise) samplings were carried out during the period February to July, 1969, to estimate the diurnal variation. Ten of these daytime–night samples were taken in the winter, while the other measurements were made in the summer half-year. Fig. 2 shows the size distributions obtained in this way. It can be seen that practically there is no difference between them. This constatation is also valid for the total mass concentration of sulfate particles which was found to be about the same in the daytime (4.8 $\mu g\ m^{-3}$ STP) and night (5.8 $\mu g\ m^{-3}$ STP). These findings are in agreement with the results of Wagman *et al.* (1967) gathered for polluted atmosphere in U.S.A.

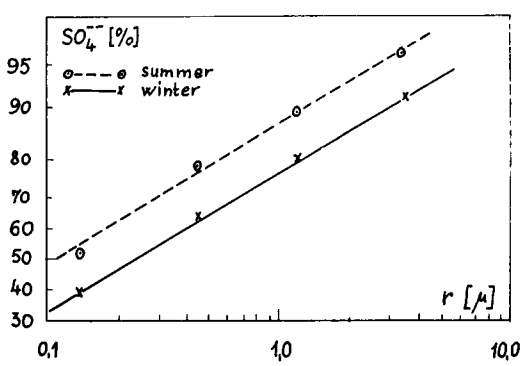

Fig. 1. Size distribution of sulfate particles in the summer and winter half-year (the ordinate indicates in per cent the mass of the particles of radius smaller than r).

Cause of the seasonal variation

It was previously found that, in agreement with expectation, the size distribution of sulfate particles depends upon the relative humidity of the air. Thus, Wagman *et al.* (1967) showed that the mass median diameter of sulfate particles becomes larger if the relative humidity increases. They concluded, however, that "... any attempt presently to construct a theoretical humidity dependence for comparison with these results would be extremely tenuous ...". On the other hand Mészáros (1968) demonstrated that the fraction of the sulfate mass in the Aitken size range decreases with increasing relative humidity. These conclusions were based upon measurements carried out during a short sampling period, thus it is of interest to re-examine this problem in detail.

In this program the sampling times were five days. For one sampling period the average relative humidity was determined from observations of three hours. The mean fractions of sulfate particles in different size ranges as a function of the relative humidity are shown in the

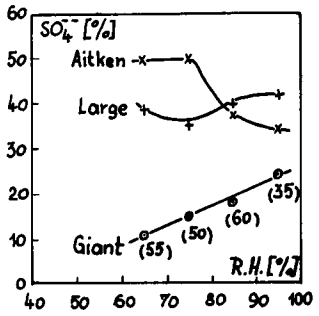

Fig. 3. Fraction of the mass of sulfate particles as a function of the relative humidity of the air (numbers in parenthesis are the sampling days).

Fig. 3. It can be seen that with increasing relative humidity the fraction in the giant range increases, in the large range it practically remains constant while in the Aitken range, after a certain value (75%), it decreases. The march of the Aitken sized sulfate particles makes it possible that the phase transition takes place around 80% relative humidity.

Fig. 4 shows the connection between the mean mass median radius and relative humidity (crosses in the figure). The solid line gives the theoretical curve calculated for an ammonium sulfate particle having a 0.14 μ dry radius. These calculations were made according to Mészáros (1969) for $T = 273$ K°. It can be seen that the agreement between the measured points and the theoretical curve is good. It is interesting to remark that for any types of mixed particles the agreement was worse, in spite of the expectation.

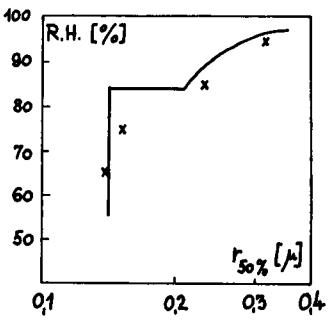

Fig. 4. Connection between the relative humidity and the mean mass median radius (crosses). The solid line indicates the theoretical connection for an ammonium sulfate particles having a 0.14 μ dry radius. Number of sampling days as in the former figure.

Taking into account that in the summer and winter half-year the average relative humidity for the sampling period was found to be 69% and 86% respectively, the seasonal variation can easily be explained on the basis of relative humidity changes alone (see Figs. 3 and 4). It also follows from these figures that below humidities of 80–85% the size distribution must be practically the same which gives an explanation that no diurnal variation was found. That is, during the daytime and night samplings the mean relative humidities were 67% and 74% respectively.

Thus, according to Figs. 3 and 4, it is possible to draw the conclusion that the mean size distribution for the summer half-year refers to the distribution of dry particles. In the case of dry particles about 50% of the sulfate mass is in the Aitken size range, while in the large and giant size ranges the corresponding values are 40% and 10%, respectively. Of course, an important fluctuation can be observed around these mean values.

Discussion

It is well known that two explanations have been suggested for the formation of sulfate particles (Junge, 1960): photochemical oxidation of sulfur gases in the gas phase and their catalytic oxidation in cloud droplets. Georgii *et al.* (1968) propose that the temporal and spatial uniformity of the mass concentration of sulfate particles can be explained by the latter process. The results presented in this paper also show that the sulfate mass concentration is independent of seasons and parts of the day. Further, the dispersion of the size distribution is always constant which suggests that the same sulfate formation (and modification) process is permanently operating and only the size of particles is changing as a function of the relative humidity. This formation process cannot be the photochemical oxidation in contrast with the previous assumption of the present author (Mészáros, 1968). Thus it seems that the catalytic oxidation is the main cause of the sulfate formation. In this case the average size of sulfate particles should be explained by this mechanism. Assuming a 8 μ average cloud droplet radius and a 5 μg/ml sulfate concentration in cloud water, it is a simple matter to show that after the evaporation of such a droplet an am-

monium sulfate particle of 0.125 μ dry radius is obtained. This value is in good agreement with the mean mass median radius of dry particles measured in this program.

Finally it is to be noted that the above conclusion does not exclude the possibility that photochemical processes are acting in the lower atmosphere. According to this model the *mass concentration* and the size distribution of the sulfate mass can be explained by the catalytic oxidation alone. However, there is no intention here to suggest that this mechanism is necessarily satisfactory for the explanation of the *number* of small sulfate particles. Thus Clark & Withby (1967) recently observed that the number of atmospheric particles (sulfate ?) in the range of 0.001–0.015 μ increases considerably in midday hours (mainly in weather without clouds), but the mass concentration of these particles seems to be too low even if their number concentration is very important.

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СЕЗОННЫЕ И СУТОЧНЫЕ ВАРИАЦИИ РАСПРЕДЕЛЕНИЯ ПО РАЗМЕРАМ ДЛЯ СУЛЬФАТНЫХ ЧАСТИЦ В АТМОСФЕРЕ

Были проведены измерения для определения сезонных и суточных вариаций распределения по размерам сульфатных частиц. Результаты измерений показывают, что существуют определенные сезонные вариации, вызываемые изменениями относительной влажности воздуха. С другой стороны, суточных вариаций найдено не было, потому что во время забора проб относительная влажность была меньше, чем это необходимо для фазовых переходов в частицах. Измеренный рост среднего по массе радиуса частиц сульфатов с увеличением относительной влажности практически сравним с теоретическим ростом частицы чистого сернистого аммония, имеющей радиус в сухом состоянии 0,14 *мкм*. На основе этих результатов кратко обсуждается механизм формирования сульфатных частиц.