On the size distribution of water soluble particles in the atmosphere

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(Manuscript received July 4, 1967)

ABSTRACT

The size distribution of the mass concentration of some water soluble materials was measured by an impactor of three stages and membrane filters. It was found that about the half of the mass of sulfate and ammonium particles is in the range of Aitken nuclei. The size distribution of sulfate particles depends on the relative humidity of the air: more nuclei are in the Aitken size range if the relative humidity is smaller. The size distribution of chloride particles is rather different from that of sulfate and ammonium particles: only a small fraction of the total mass is in the Aitken range. Considering the stoichiometric proportion of the ammonium sulfate, it is an ammonium excess, which is greater in the case of smaller particles. It is not impossible that this ammonium excess is caused by the presence of ammonium hydroxide. It follows from these results that in the Aitken size range there are many sulfate and ammonium particles which may be active cloud nuclei even over the continents.

Introduction

It is well known that the investigation of water soluble atmospheric particles is very important from the point of view of cloud physics. On the other hand, for many problems in air chemistry (origin, transport and removal rate of particles) the size distribution of particles of different chemical composition is also of interest.

The size distribution of soluble particles containing sulfate, chloride and calcium was widely studied in Hungary by gelatin substrates sensitized by suitable reagents. The results of these studies were reported earlier (see Mészáros & Mészáros, 1966). These studies demonstrated that these techniques were only able to identify the relatively pure larger particles (Mészáros, 1964*b*), the number concentration of which is practically negligible considering the number of fog and cloud droplets. The so-called single particle methods (Lodge, 1962) are unfortunately not capable of counting the mixed and smaller particles ($r < 0.5$ μ). It is known that Lodge's group in the USA is making great efforts to overcome these difficulties (Lodge & Frank, 1966) but detailed results have not yet been published. Thus it seemed best to make bulk analyses in the different size ranges in spite of the fact that "the particulate status of the collection ceases to have meaning" (Lodge, 1962) in this way.

The classical measurements of this type were carried out by Junge (1963), but he has not captured and analysed the Aitken particles. The present author (Mészáros, 1966) classified particles in two size ranges ($r > 0.3$ μ and $r < 0.3$ μ), but two intervals are, of course, not sufficient to estimate the size distribution.

For these reasons new samplings of atmospheric aerosols were carried out, using a multiple stage impactor and a membrane filter to obtain information on the size distribution of the mass concentration of different ions. The details and results of these measurements are presented in this paper.

Collection of particles

Atmospheric particles were collected with the help of a Casella cascade impactor (on clean glass slides) backed up by membrane filters (type: Synthesia; nominal pore size: 0.85 μ). These filters collect all nuclei with a 8.3 % mean penetration (Lodge & Swanson, 1964). The original third stage of the Casella impactor was not operated, thus particles were collected in four intervals. The collection efficiency of the different jets of the impactor was redeter-

Table 1. *Minimum detectable concentrations in solutions and in the atmosphere for a 200 m³ sample of air*

Ions	μg/ml	μg/m³
NH_4^+	0.20	0.025
SO_4^{--}	2.0	0.25
Cl^-	0.3	0.075

mined according to May (1945), because the suction rate employed was higher than that indicated by the company and because a particle density of 1.5 g/cm³ was assumed. Usually the suction rate decreased somewhat with increasing sampling time and atmospheric pollution but 1.7 m³/h is a good approximation for mean operating conditions. In this case the particle classification is as follows:

Stage 1 $r > 3.8\ \mu$,
2 $3.8 > r > 1.2\ \mu$,
3 $1.2 > r > 0.14\ \mu$,
4 $r < 0.14\ \mu$.

It can be seen that the first two stages collect approximately the giant particles and the third and fourth stages the large and Aitken particles respectively.

In order to assure sufficient accuracy of the chemical analyses (mainly in the case of sulfate ions) the sampling times were five days, but it is to be noted that impactor slides and filters were changed daily.

Analytical procedure

After completion of sampling all stages were washed with 25 ml of distilled water. These solutions were filtered and analysed for ammonium by colorimetric methods and for sulfate and chloride by nephelometric methods. The concentration of ammonium was measured by a Nessler reagent prepared according to Egnér *et al.* (1955). The concentration of sulfate was determined from the turbidity of the barium sulfate suspension according to Keily & Rogers (1955), while chloride was measured by silver nitrate.

Table 1 gives the minimum measurable concentrations in the solution and in the atmosphere for a 200 m³ sample of air. It was found that for concentrations higher than those listed the analyses were reliable and reproducible.

Results

The samples were taken in the garden of the Aerological Observatory of Budapest during the period March 30 to May 27, 1967. This observatory is located outside the built-up area, about 15 km south-east of the city centre. The sampler was operated at 2 m above ground level and was protected against precipitations. During the indicated period eleven samples were taken (during April 9–12 no samplings were made). All samples were analysed for ammonium, nine for sulfate and two for chloride. The fraction of these ions in terms of percentage of the total mass for the different size ranges is given in Fig. 1. The results of the first two stages are presented together, considering the lesser importance of these ranges. It can be seen that, considering the ammonium, in the majority of cases the largest fraction is found in the Aitken size range. For sulfate the situation is slightly different. In five out of nine cases the higher values are in the range of large particles. This means that ammonium is associate with somewhat smaller particles than sulfate.

The mean percentage values of all measurements are given in Table 2. One can see that the mass of ammonium and sulfate ions is roughly equal in the large and Aitken size ranges. The two chloride tests show that in this case only a small fraction of the total mass is in the Aitken range as contrasted with ammonium and sulfate particles.

It is to be noted that an inverse relation was found between the fraction of sulfate particles in the Aitken size range and relative humidity as shown by the data in Fig. 2. This means that the size, and consequently the size distribution, of sulfate particles depends on the relative humidity, i.e. particles are hygroscopic in nature.

The data in Fig. 2 make it probable that in the free atmosphere (less humidity) a substantial fraction of the sulfate mass is found in the Aitken range, in agreement with the estimate of Martell (1966). It is interesting to note that this phenomenon was not observed in the case of ammonium.

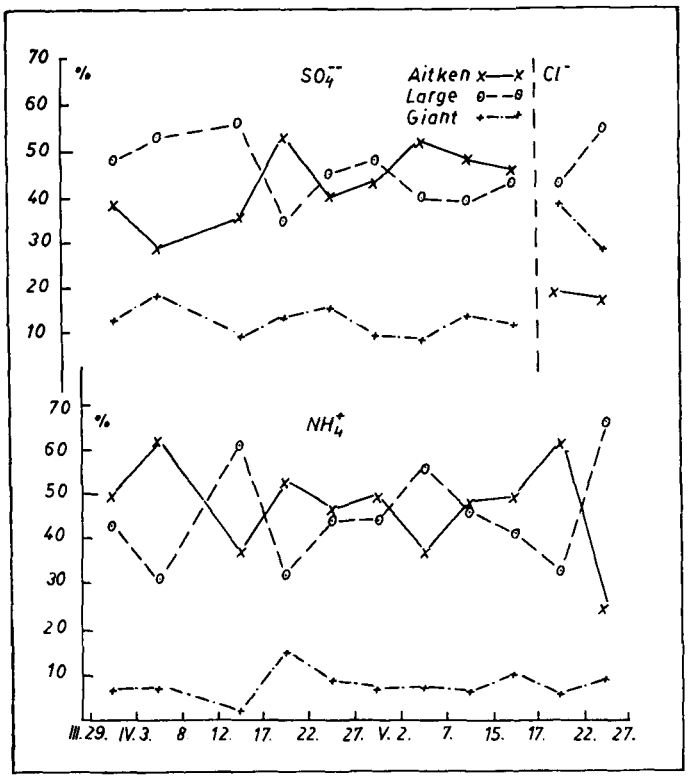

Fig. 1. Fraction of the mass of water soluble materials in different size ranges during the sampling period.

Possible origin and composition of water soluble particles

First of all, it seemed to be of interest to see if the ratio of sulfate to ammonium corresponds to that of ammonium sulfate or not. The Figs. 3*a*, 3*b*, 3*c* and 3*d* show the relation of the mass of these ions in the different size ranges. The solid lines indicate the stoichiometric proportion. It can be seen that the relation is best in the case of large particles, in agreement with Junge (1963). But it is also obvious that, except for the giant particles, there is an excess of ammonium, in contrast to Junge's findings (1963). The data of Table 3 show that this excess is greater in the case of smaller particles. In a previous paper (Mészáros, 1966) it was

Table 2. *Mean fractions of water soluble materials in different size ranges*

	NH_4^+, %	SO_4^{--}, %	Cl^-, %
No. of samplings	11	9	2
Giant	8	12	33
Large	45	45	49
Aitken	47	43	18

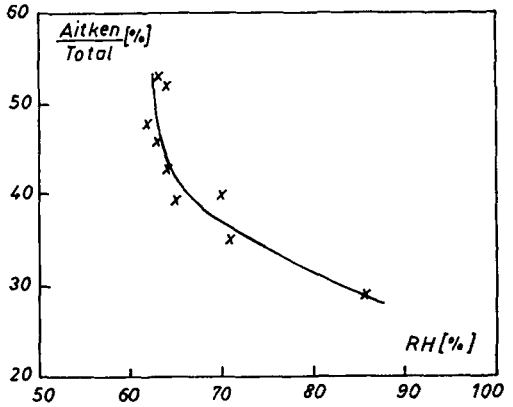

Fig. 2. Relation between the fraction of sulfate particles in the Aitken range and the relative humidity.

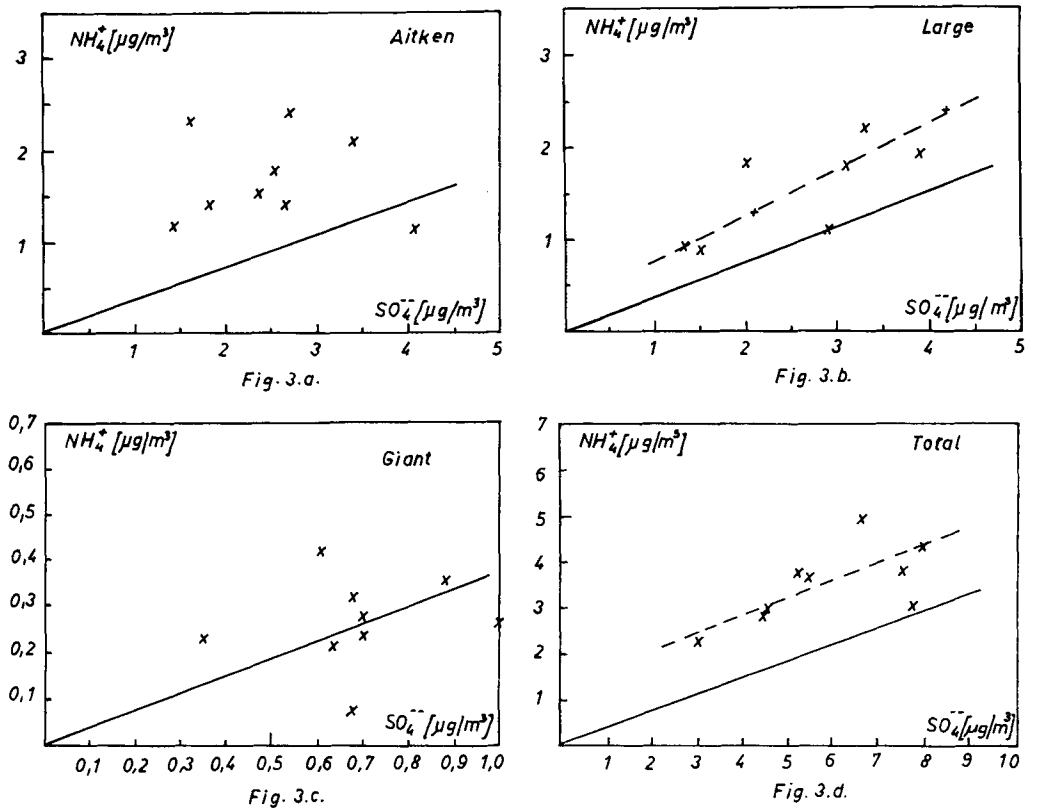

Fig. 3. Ratios of the mass of sulfate ions to that of ammonium ions in different size ranges.

suggested that this excess is probably due to some local sources and may be caused by the presence of ammonium hydroxide. To study the first question, samplings were made in an unpolluted area (Bónis, 1968). The results show that in summer the ammonium-sulfate ratio in the back-ground air of this country is close to that of ammonium sulfate, but that in winter ammonium is considerably in excess.

The presence of ammonium hydroxide was verified in the following manner: In some cases the solution, obtained by the washing-out of membrane filters operated without the impactor, was divided into two equal parts. These filter samplings were carried out one year earlier, in the same season as those discussed above. The concentration of ammonium was determined from the first part, while the second part was boiled for fifteen minutes to liberate gaseous ammonia, which was absorbed. After this the second part was also analysed. It was found that, according to thirteen measurements, the ammonium concentration is reduced by boiling to 64 % of the original concentration, indicating that 36 % of ammonium is ammonium hydroxide. It is interesting to note that reducing the ammonium-sulfate ratio of 0.63 for "Total" in Table 3 by 36 % results in a ratio of 0.40, which is close to that of ammonium sulfate. Most likely about 60 % of the ammonium was therefore present as ammonium sulfate.

Table 3. *Mean ratios of sulfate to ammonium in different size ranges*

NH_4^+/SO_4^{--}			
Giant	Large	Aitken	Total
0.41	0.62	0.66	0.63

The ammonium sulfate particles in the Aitken

size range may possibly be formed by the following process: Gaseous ammonia reacts with minute sulfuric acid particles generated by photooxidation of gaseous sulfur compounds (SO_2, H_2S) in the presence of water vapour. The primary particles, or clusters of molecules, grow rapidly by coagulation among themselves, or with other particles resulting finally in a size distribution with a maximum in the range of 0.05–0.1 μ radius (see Junge, 1963). This formation process is supported by the observation of Bónis (1968) that at the Aerological Observatory of Budapest total sulfate varies not much with the seasons in contrast to the larger sulfate particles ($r > 0.3$ μ) which show a minimum in summer. Thus in summer apparently despite the influence of convection, which will more Aitken sized sulfate particles are present tend to reduce their concentration.

It should be mentioned that in many places of the world there is rather a tendency for sulfate excess in aerosol samples. Lodge & Frank (1966) for example have recently reported "that sulfuric acid admixed with ammonium sulfate is the predominant single class of particles in the sub-micron size range". Our results in Hungary show that the sub-micron particles are probably composed of a mixture of ammonium sulfate and ammonium hydroxide. The reason for this difference remains an open question, but it should be mentioned that relatively high ammonia gas concentrations (80–100 $\mu g \cdot m^{-3}$) were observed at our observatory.

It seemed to be of interest to compare the ratio of the mass of water soluble materials to that of insoluble substances. For these reasons the mass of all atmospheric particles was directly determined, by means of membrane filters operated behind the impactor, in the size range of $r < 0.14$ μ by a micro-chemical balance weighing to an accuracy of ± 0.1 mg. On the other hand, the total mass concentration was measured by membrane filters worked simultaneously without the impactor. Considering the concentration of water soluble materials discussed earlier, it follows from the obtained data that the ratio of the mass of soluble materials to that of insoluble substances in the Aitken size range is 20 % on average. This value is far higher than that in larger ranges (it is about 7–8 % in the range of $r > 0.14$ μ). In connection of this problem it is to be noted that the earlier results of the author (Mészáros, 1966) suggest that in the range of $r > 0.3$ μ only about the 1–2 % of the particulate matter is water soluble. This means that with decreasing size the relative quantity of water soluble substances increases, and the major part of large water soluble particles can be found in the range of $0.1 < r < 0.3$ μ.

It was mentioned above that the majority of chloride particles are in the range of $r > 0.1$ μ. This indicates that the formation of these particles is different from that of the ammonium and sulfate particles. It is possible that a substantial fraction of large and giant chloride particles consisted of sea salt, since maritime air masses prevailed during the chloride sampling period over Hungary. The majority of maritime chloride particles are in the range of $r > 0.3$ μ (Mészáros, 1964*a*). But it is quite possible that some of the smaller chloride particles were of continental origin (Junge, 1963), the composition of which is completely unknown. It should be noted here that the total mass concentration of chloride particles is very small in continental areas, being of little importance as compared with that of sulfate and ammonium particles.

Cloud physical considerations

It is generally accepted that Aitken nuclei are mainly activated in condensation over the oceans, where the number of large particles is negligible (Junge, 1968). Recent observations (A. Mészáros, 1967), however, have shown that in freshly formed small cumulus clouds, even over Middle Europe, the concentration of cloud droplets is, in most cases, far higher than that of large particles. This means that a fraction of Aitken particles must be activated. The results presented in this paper suggest that this fraction is probably composed of water soluble materials, mainly of ammonium sulfate particles, the quantity of which is quite sufficient in this size range.

Acknowledgement

The author is indebted to Mr. J. Schnörch (Research Institute of Electric Power Industry of Budapest) who lent the Casella impactor, to Mrs. I. Weingartner (Meteorological Institute) who carried out the chemical analyses and to Miss. K. Pacséry (Meteorological Institute) who prepared the figures.

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О РАСПРЕДЕЛЕНИИ ПО РАЗМЕРАМ В АТМОСФЕРЕ ЧАСТИЦ ВЕЩЕСТВ, РАСТВОРИМЫХ В ВОДЕ

С помощью трехуровенной ловушки и мембранных фильтров измерялось распределение по размерам частиц, содержащих некоторые растворимые в воде вещества. Найдено, что около половины массы сульфатов и аммония находится в ядрах Айткена. Распределение по размерам частиц, содержащих сульфаты, зависит от относительной влажности воздуха: большее количество ядер находится в интервале Айткена, если относительная влажность меньше. Распределение частиц, содержащих хлориды, заметно отличается от распределения частиц с аммонием и сульфатами: только малая часть их полной массы находится в интервале ядер Айткена. Если рассматривает стехеометрическое отношение аммиака к сульфату аммония, то оказывается избыток аммония, который больше для случая малых частиц. Представляется возможным, что этот избыток аммония вызван присутствием гидроокиси аммония.

Из этих результатов следует, что в интервале ядер Айткена есть много частиц, содержащих сульфат и аммоний, которые могут быть активными облачными ядрами даже над континентами.