Remarks about chemical methods used in aerosol researches

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ABSTRACT

Measurements were carried out to determine the mass-concentration of sulfate and chloride particles in the atmosphere. The identifications were done partly by the so-called single particle method (gelatine technique), partly by bulk analysis. Great differences were found between the results obtained by them. A possible explanation of the discrepancy is given.

1. Introduction

The identification of the chemical nature of an aerosol can be carried out in two different ways: by bulk analysis and by single particle method (LODGE, 1962). The former consists of the mass-determination of a certain chemical element of an aerosol sample dissolved in a small quantity of distilled water, while the latter technique makes also possible the determination of the numerical concentration and the size distribution. In a program concerning the estimation of the water-soluble component of atmospheric particles from the point of view of the cloud physics, measurements were carried out in Hungary to identify chlorides (MÉSZÁROS, 1964*a* and 1964*b*), sulfates (MÉSZÁROS, 1963) and calcium (MÉSZÁROS, 1964*c*) by gelatine layers impregnated with silver nitrate, barium chloride, and potassium ferrocyanide + ammonium chloride respectively (single particle method). Considering the mass of water-soluble materials (MÉSZÁROS, 1963) and the origin of chloride particles in the large size range (MÉSZÁROS, 1964*a* and 1964*b*), the results obtained in this way fairly differ from those of JUNGE (1956) gained by the bulk method at different places of the world.

It seemed to be interesting to determine whether these differences are caused by the different physico-geographical locations or by the different chemical techniques. For these reasons analyses were made, employing the bulk method, to identify sulfates and chlorides at the same place (Aerological Observatory of Budapest), where the majority of single particle measurements was carried out. In some cases the mass-concentration of chloride particles was simultaneously determined by both techniques.

2. Experimental procedure

Atmospheric particles were captured, using an impactor of circular jet (MÉSZÁROS, 1964*b*) on clean glass slides or on slides covered by gelatine layer containing silver nitrate. The impactor has about 50 per cent collision efficiency in case of chloride particles with a radius of 0.3 μ; therefore the values presented in this paper relate to the size range $r \geq 0.3$ μ. When using the bulk analytical technique several cubic meters of air were sucked and the sample was washed out by some millilitres of distilled water. After filtration the obtained solution was analysed by nephelometric methods using a Pulfrich photometer (Carl Zeiss, Jena, East-Germany). The chloride was tested by silver nitrate, while the mass of sulfate ions was determined from the turbidity of the barium sulfate suspension induced according to KEILY and ROGERS (1955). Concerning the magnification factor, in the case of gelatine technique, the value $M_f = 6.0$ was used in a sense proposed by METNIEKS (1958).

3. Results

Samplings were carried out in the period March–April 1964. During this time sixteen samples were taken for sulfate and twenty-two for chloride. In fifteen cases simultaneous measurements of chloride particles were made

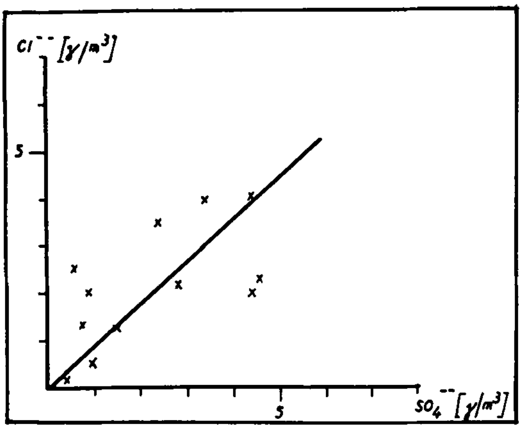

FIG. 1. Relation of chloride concentrations with those of sulfate ions in atmospheric aerosol. All values were measured by the bulk method.

employing the gelatine technique. The mass-concentration of sulfates changed in the range 0.4–6.4 γm^{-3} with a mean value 2.6 γm^{-3}, while the concentration of chlorides determined by bulk analysis fluctuated between 0.02 and 4.1 γm^{-3} (mean value: 1.5 γm^{-3}). This means that the agreement with Junge's values is rather good (JUNGE, 1956), but there is a great difference between results obtained at the same place by the two different techniques. The chloride concentration by bulk method, for example, was the greatest in anticyclonic situations in spite of the fact that the number of chloride particles measured during two years by gelatine layers was nearly always much more under cyclonic weather conditions (MÉSZÁROS, 1964*a*). In Fig. 1 the connection between sulfate and chloride mass-concentration is plotted. It is discernible that there is an approximately linear relation between them, i.e., the greater chloride masses occur when the air is polluted by local sources (greater sulfate concentration). This is in discrepancy with earlier results gained by gelatine technique (MÉSZÁROS, 1964*b*).

TABLE 1. *Connection between concentrations of chlorides measured simultaneously partly by the gelatine technique, partly by the bulk analysis.*
All values are given in γm^{-3}.

Gelatine 0, or $< 10^{-3}$	10^{-3}–10^{-2}	10^{-2}–10^{-1}	10^{-1}–10^{-0}
Bulk analysis			
4.1	3.5	4.0	0.9
2.3	2.5	1.3	0.8
1.3	0.02	0.5	
0.5	0.04	0.1	
0.2			
Mean			
1.68	1.52	1.47	0.85

On the other hand, the mass-concentrations calculated from single particle measurements are much smaller (MÉSZÁROS, 1963) than those obtained by the bulk method. Table 1 shows the connection of concentrations of chlorides in γm^{-3} measured simultaneously partly by the gelatine technique, partly by the bulk analysis. It is visible, that there is a great disagreement between them. However, in fresh maritime air masses when the single particle method gives the greatest concentrations (>0.1 γm^{-3}) the agreement is rather good. The discrepancy is the greatest, when the concentration measured by gelatine technique is low or zero, i.e. in continental air masses (MÉSZÁROS, 1964*b*).

4. Possible explanation of differences

It is very difficult to explain this phenomenon in a satisfactory manner, which cannot be attributed to the possible fluctuation of the magnification factor. Nevertheless a possible interpretation is proposed. In fresh maritime air the chloride particles coming from the ocean practically do not contain insoluble fraction, more exactly the majority of the mass of the particles is water-soluble. In contrary with that, in local (or continental) air-masses the man-made particles are mainly mixed in such a manner that the mass of the water-soluble fraction is very small compared with that of the insoluble nucleus. That is, insoluble particles are covered by a thin solution pellicle, the identification of which is not possible by the gelatine method. This means that the single particle method is suitable only for relatively pure solution droplets or water-soluble particles (in the cloud physics for the sea-salt nuclei, for instance), but in continental locations from the point of view of the atmospheric chemistry or of the atmospheric pollution the bulk analysis must be used. Of course, it is possible that this explication is not entirely correct, but it seems to be sure, according to these results, that the calculation of the mass of a chemical element from single particle measurements, or the calculation of the numerical concentration from bulk analysis is not advisable, except under maritime conditions in the case of chloride particles.

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