Determination of sodium cations in atmospheric particles[1]

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ABSTRACT

A method of detecting sodium ion in atmospheric particles using the magnesium salt of 8-amino-1-naphthalenesulfonic acid is described. The preparation of the reagent is outlined. The reaction product appears as small clusters of soft white or brownish-white needles, which may be readily identified under the optical microscope. A calibration curve is given for the particle-reaction site ratio, using sodium chloride as the calibrating material. Results of field tests of the method are presented.

Introduction

The detection of small quantities of sodium ion is one of the more difficult analytical procedures, due to the great solubility of most sodium salts. DRANITSKAYA (1956) reported the use of 8-amino-1-naphthalenesulfonic acid as a gravimetric reagent for sodium ion. It was found that with this reagent the sodium ion content of very small particles could be determined using the general method of collection on Millipore filters developed by LODGE (1954). When this procedure is applied to atmospheric particles, the presence or absence of sodium ion may be measured with considerable accuracy. Thus it is possible to calculate sodium content in relation to other anions which may be present, particularly in connection with sodium-chloride ratios in atmospheric studies.

Reagents

The reagent used was the magnesium salt of 8-amino-1-naphthalenesulfonic acid. Because the solubility of the magnesium salt in water is 111 g/liter whereas that of the sodium salt is 6.3 g/liter, the reaction is:

$$Mg(H_2NC_{10}H_6SO_3)_2 + 2\,Na^+ \rightarrow 2H_2NC_{10}H_6SO_3Na\downarrow + Mg^{++}$$

The magnesium salt was prepared by adding six grams of 8-amino-1-naphthalenesulfonic acid to six grams of magnesium carbonate in 50 ml of distilled water and heating gently until evolution of CO_2 had ceased. The excess magnesium carbonate is removed by filtering the dark purple supernate into a brown bottle. The reagent is stable for three weeks. To each portion used for reaction, as it is used, a few crystals of solid sodium chloride are added with vigorous stirring to saturate the solution with respect to sodium. This affords more quantitative precipitation of the particles on the filter.

If the Millipore filter is allowed to dry after treatment with the reagent, a crystalline deposit forms on the back of the filter. Most of this deposit is eliminated, without loss of the small particles in the sample, by using a saturated solution of the sodium salt of 8-amino-1-naphthalenesulfonic acid as a wash solution. This wash solution is prepared just before use by mixing equal parts of the reagent solution and 10 per cent sodium chloride solution in a centrifuge tube. The soft precipitate is centrifuged out and the supernate discarded. The precipitate is washed with a small portion of distilled water and recentrifuged. This supernate is also discarded. A small amount of the soft precipitate on the end of a stirring rod is mixed with two cc of distilled water, and this saturated solution is used for the wash. This must be freshly prepared every four hours.

Procedure

The membrane filter with the collected sample is floated, sample side up, on the surface of 4 ml of the reagent in a small petri dish. It is convenient to carry out the saturation of the

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reagent with sodium chloride in the petri dish just before the filter is placed on it. The reaction is very rapid and the reaction product somewhat soluble, so the filter is removed after five seconds and transferred at once to a piece of blotting paper soaked with the wash solution. After washing for 10 seconds, the filter is placed on a dry blotter and dried in a desiccator. When dry, the filter is mounted in immersion oil for examination in an optical microscope. Under polarized light, the reaction product is seen as small clusters of soft white or brownish-white needles. If the precautions of saturating the reagent and wash solutions with the sodium product are not followed, the reaction will not be quantitative for the smallest particles, due to the slight solubility of sodium 8-amino-1-naphthalenesulfonate (DRANITSKAYA, 1956). Some of the salt from the saturated wash may remain on the back of the filter, but this will not interfere if the microscope is carefully focussed. Potassium and ammonium ions do not interfere.

The size ratio particle-reaction site is calibrated in the usual manner (LODGE *et al.*, 1956) by counting and measuring the diameters of a series of particles and corresponding reactions. Sodium chloride was used as the calibration material. There is evidently no greater variation in growth rate from one batch of reagent to another than there is internal variation among the samples. This internal variation is quite large. Twelve calibration samples were prepared; of these three had small particles, five had medium-sized particles, and four had large particles. The number of particles and reaction sites was determined as a function of diameter for each sample, and the numbers in each size class were summed first for the three groups and then for the full twelve samples. The ratios of reaction-site diameters to particle diameters were obtained from plots of diameter against cumulative percentage on log probability paper for each pair of particle-reaction counts.

The shape of the calibration curve depends in part upon the size of the original particles as shown in Fig. 1. It was found that the particle-reaction ratio was linear for particles larger than 10μ diameter. The portion of the calibration curve for particles of original diameter between 7 μ and 10 μ cannot be expressed as a simple function. Due to the difficulty of obtaining samples in which 50 per cent or more

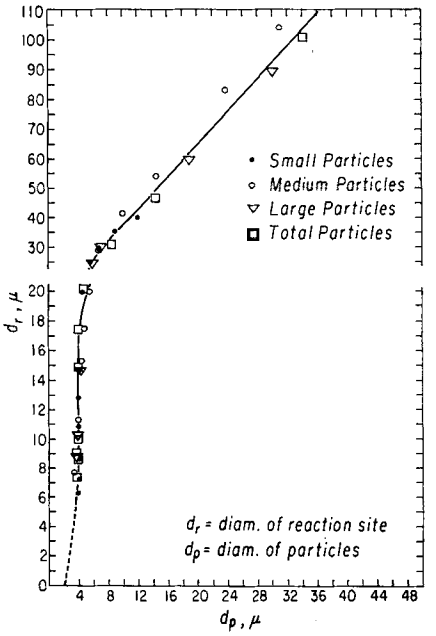

FIG. 1. Calibration curve for NaCl reacted with magnesium 8-amino-1-naphthalenesulfonate. Diameter of particle vs. diameter of reaction site.

of the particles are smaller than 7 μ, the lowest portion of the calibration curve is extrapolated, based on the probable shape suggested by individual calibrations. The apparent anomaly in the graph indicating that particles of small diameter give reactions of yet smaller diameter may be due to the solubility of the sodium salt of 8-amino-1-naphthalenesulfonic acid, causing some of the reacted material to be lost before it is viewed in the microscope. Due to the non-linearity of the curve, it is not possible to measure the standard deviation accurately, but it is probable that values obtained from the curve would be correct to within ± 5 per cent.

Field test

The method was field-tested on 30 samples collected near Rehoboth Beach, Delaware by the U.S. Weather Bureau under the supervision of Mr. Dwight M. Kline. Despite the presence inland of extensive bays and inlets the samples showed generally much lower counts when the air was from inland regions than when from the ocean. The counts of sodium and of chloride are shown in Figs. 2 and 3. It is interesting to note

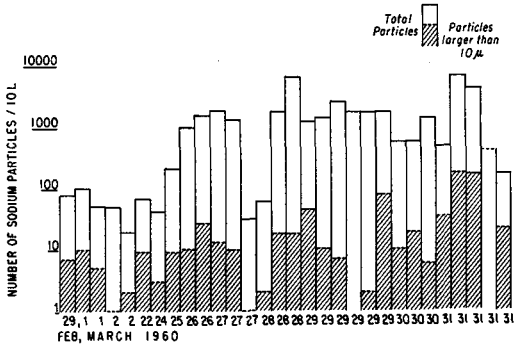

FIG. 2. Totals of sodium particles collected in the field.

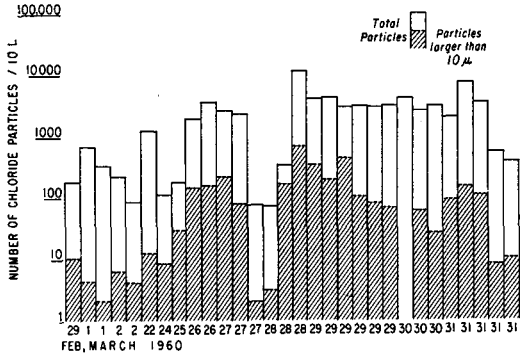

FIG. 3. Totals of chloride particles collected in the field.

that all samples through 25 March were taken in air from an inland source and that all of the others, except the first sample on the 28th were in air from the ocean or, in some cases, air with variable trajectory.

In comparing the chloride and sodium counts one concludes that a considerable amount of chloride is carried by particles containing no identifiable sodium, especially in the larger sizes and in marine air. Because of complicating factors, both meteorological and technical, an explanation of the variations will not be attempted here. Mr. Kline is examining the data in connection with other types of measurements and samplings made at this and other locations. The results of the test suggest that the method is accurate in use in the field within the usual limitations of the technique of the microscopist.

Conclusions

The method of detecting the presence of sodium ion in atmospheric particles by reacting with the magnesium salt of 8-amino-1-naphthalenesulfonic acid has been shown to be sufficiently accurate for work in the field. While somewhat unsatisfactory in stability of reagent and solubility of reaction product, it provides the first gravimetric method of measuring sodium ion in micron-sized particles.

Acknowledgement

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