

## THE COMPOSITION OF HYGROSCOPIC PARTICLES IN THE ATMOSPHERE

By *S. Twomey*

Commonwealth Scientific and Industrial Research Organization

(Manuscript received 8 February 1954)

### ABSTRACT

The composition of the larger ( $> 10^{-12}$  g) hygroscopic particles in the atmosphere was investigated, with use of a phase-transition method. Particles were collected on stretched spider webs exposed from an aircraft, and samples were taken in both maritime and continental air in different meteorological and geographical situations. It was found that the great majority of hygroscopic particles was composed of sea salt, sometimes in combination with insoluble material. A chemical test on individual particles indicated that no appreciable decrease in chloride content or replacement of chlorides by carbonates took place. Only occasionally were large soluble particles, other than sea salt, detected.

### 1. Introduction

Current theories of rain formation in warm clouds postulate the existence in the cloud of a small population of droplets larger than the majority. Such droplets can grow rapidly by the collection of the smaller cloud droplets, eventually becoming raindrops. For this reason, considerable attention has recently been directed to the large hygroscopic particles in the atmosphere. These particles are much rarer than ordinary condensation nuclei, but extend in size to about  $10^{-8}$  g; they are usually assumed to consist of minute crystals of sea salt [1], although some workers in the field have expressed opinions to the contrary [2].

In a previous paper [3], a technique was described by which large hygroscopic nuclei were collected on spider webs, and the individual particles were identified. It was found that, in maritime air at least, the large ( $> 10^{-12}$  g) nuclei were almost certainly composed of sea salt. In this paper, the nature of the large hygroscopic nuclei in continental and modified maritime air is discussed. A separate chemical test on the chloride content of both maritime and continental hygroscopic nuclei is also described.

### 2. Apparatus and method

*Phase-transition measurements.*—The phase-transition method of identifying hygroscopic airborne particles, together with the associated apparatus, has been described previously [3]. The technique involved the collection of the particles by stretched spider webs, exposed from a light aircraft for periods ranging from 10 to 60 min; the collected particles were subsequently exposed to an air stream of controlled humidity and constant temperature. On increase of the humidity, a hygroscopic particle became liquid at a relative humidity which was shown to depend on the chemical

composition of the particle. It was found that particles collected from maritime air, and also residual particles from sprayed sea salt, underwent a phase change at about 75 per cent relative humidity—which was also the theoretically predicted value for sodium chloride. This indicated that the collected particles were, in fact, crystals of sea salt.

This technique was used for the collection and identification of hygroscopic nuclei sampled in flights over southeastern Australia in different meteorological conditions. As a further check on the scope and limitations of the method, experiments were carried out in the laboratory to determine the phase-transition points for artificial nuclei, produced by spraying concentrated solutions of various pure chemical compounds on spider webs and allowing the droplets of solution to evaporate. The residual particles usually ranged from 2 to 20  $\mu$  in diameter. Table 1 shows the

TABLE 1. Phase-transition points for various artificial nuclei.

Compound	Transition point (per cent relative humidity) at 20C		Remarks
	Predicted	Observed	
K <sub>2</sub> SO <sub>4</sub>	97	97	
Na <sub>2</sub> SO <sub>3</sub>	95	85	Phase changed consistently at indicated value
Na <sub>2</sub> SO <sub>4</sub>	93	91	Change in crystal appearance at 84–88 per cent
KHSO <sub>4</sub>	86	87	
KCl	84–86	86	
(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	80–82	80	
NH <sub>4</sub> Cl	79–80	80.5	
NaCl	75	75–77	Solution gradual, not immediate as with sea-salt
NaClO <sub>3</sub>	75	66	Very definite, and consistently at 66 per cent
CoCl <sub>2</sub>	67	67	
NaBr	58	57	
NaHSO <sub>4</sub>	52	55(?)	Apparent drops at 55 per cent; remained opaque to 73 per cent
Mg(NO <sub>3</sub> ) <sub>2</sub>	53	56	
K <sub>2</sub> CO <sub>3</sub>	43–45	45	

relative humidities at which a number of common compounds were found to undergo the solid-liquid transition; the relative humidity in equilibrium with a saturated solution has also been tabulated for each compound. It is seen that in all but two cases the transition occurred at or near the predicted value.

A number of phase transitions in common compounds are illustrated in fig. 1. One compound, how-

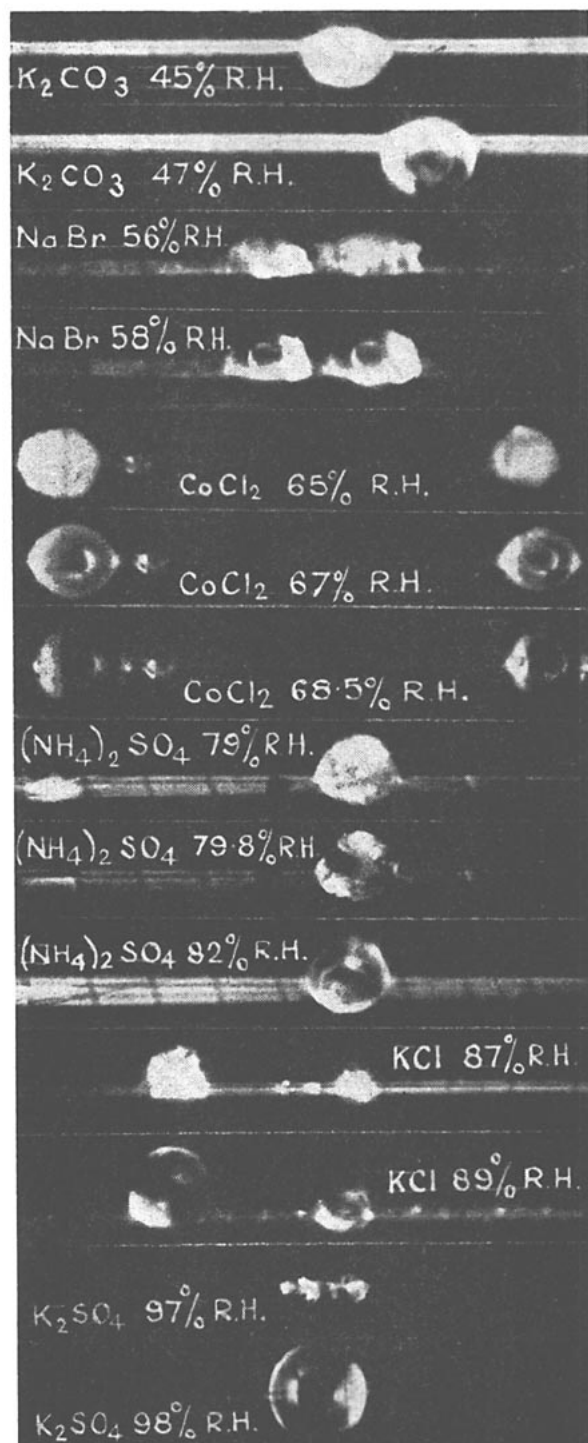


FIG. 1. Photomicrographs of actual phase transitions in a few common chemical compounds.

ever gave anomalous results; this was sodium carbonate, for which the predicted phase-transition point (*i.e.*, the relative humidity in equilibrium with the saturated solution) was 92 per cent. When droplets of sodium carbonate solution were sprayed on spider webs, the residual solid particles underwent a phase change in the region 70–75 per cent relative humidity, but growth was not appreciable until a relative humidity of about 85 per cent was reached. The point at which the phase transition occurred was somewhat variable, and the apparently liquid droplets appeared opaque until the relative humidity was raised further. When sodium carbonate, prepared in a fine powder by crushing and desiccating the hydrated crystals, was brushed on spider webs in the solid state, it was found on one occasion to give a well-defined phase transition at 90 per cent relative humidity, but on repeating the experiment an equally well-defined transition occurred at 84 per cent relative humidity. As a result of this behavior (connected perhaps with the ease with which this salt is hydrolysed) sodium carbonate could not be identified by the phase-transition method. With this one exception, however, each compound tested had a definite phase-transition point which was not affected by the previous history of the particles or the method of deposition; the phase-transition point could therefore be used with confidence to help identify these compounds.

*Chemical tests.*—Cauer [2] has suggested that the chlorides in sea salt may be changed rapidly to carbonates when droplets of sea water are carried into the atmosphere. Consequently it seemed necessary to find some means by which hygroscopic nuclei collected could be tested to ascertain whether any loss in chloride, or the presence of carbonates, could be detected.

A combination of the "isopiestic" method of Woodcock and the chemical method of Seely [4], for the detection and measurement of chloride particles, provided a method by which chloride content could be measured. Using a gelatin film sensitized with mercurous fluosilicate, Seely found that distinctive "halos" were produced by chloride particles; in the case of sodium chloride particles, the diameter of a halo was found to have a sensibly constant ratio of 8.5 to the equivalent spherical diameter of the particle producing the halo.

For the present purpose the experimental procedure was as follows. Glass slides were exposed in the atmosphere, subsequently placed in a stream of air of constant high humidity, and the droplets formed on the hygroscopic nuclei were measured and their positions noted. The slides were then dried out, and a sensitized gelatin film, prepared by Seely's method, was lowered onto the surface of the glass slides; the halos produced by the various particles were then

measured. In this way, a graph of halo diameter *versus* particle diameter could be obtained for particles sampled in different air masses or produced artificially by spraying the slides.

A direct test for the presence of carbonates was carried out as follows. A strip of very fine filter material (Lovell Co. "Millipore") was impregnated with an alcoholic solution of phenolphthalein and partially dried out. The sensitized strip was then carefully pressed onto slides carrying the particles being tested. If the test was carried out in humid air (to ensure that hygroscopic particles had grown into droplets), particles containing soluble carbonates produced distinctive red spots which persisted for some minutes. It was not possible to determine sensitivity limits of the method, but single particles of sodium carbonate with mass of the order of  $10^{-9}$  g produced spots which were very easily seen with the naked eye; from a sodium-chloride-sodium-carbonate mixture containing 5 per cent sodium carbonate, particles of the same size produced spots which were much fainter, but still visible, particularly under low magnification.

*Proportion of insoluble material in nucleus.*—A mixed nucleus, containing a proportion of insoluble material (such as a salt nucleus which at some time collected a minute particle of clay or similar material), could be examined by measuring the diameter of the droplet formed when the mixed particle was exposed to an air stream at two values of relative humidity. If the corresponding values of equilibrium salinity and droplet density were  $S$  and  $\rho$ , and  $S'$  and  $\rho'$ , respectively, and the volume of the droplets (including the solid portion)  $V$  and  $V'$ , respectively, it can easily

TABLE 2. Phase-transition observations.

Category	Relative humidity (per cent) at phase transition	Per cent of total number of nuclei in category	Number of occasions on which category was found
I	73-76	90	25
II	80-82	2	1
III	87	1	1
IV	91-93	3	5
V	undefined	4	—

be shown that the proportion of sea salt in the mixed nucleus was, by volume,

$$\alpha = [1 + (k - 1)d/(\rho S - k\rho'S')]^{-1},$$

where  $d$  = density of sea salt ( $2.2\text{g/cm}^3$ ), and  $k = V\rho S/V'\rho'S'$ . In the case of an unadulterated sea-salt nucleus,  $k = 1$ .

### 3. Experimental results

Flights were made over New South Wales during the late summer and autumn of 1953, during which samples were taken from 500 to 10,000 ft above ground level and in different air masses under different meteorological conditions. Further flights were carried out during the winter of 1953, when southwesterly (post-frontal) air streams were followed from south Australia to near the coast of New South Wales. Phase-transition measurements were made on over 3000 hygroscopic particles. The relative humidities for phase transition of particles ( $> 10^{-12}$  g) fell into the categories set out in table 2.

The particles of the first and most important category underwent a phase change at about the same

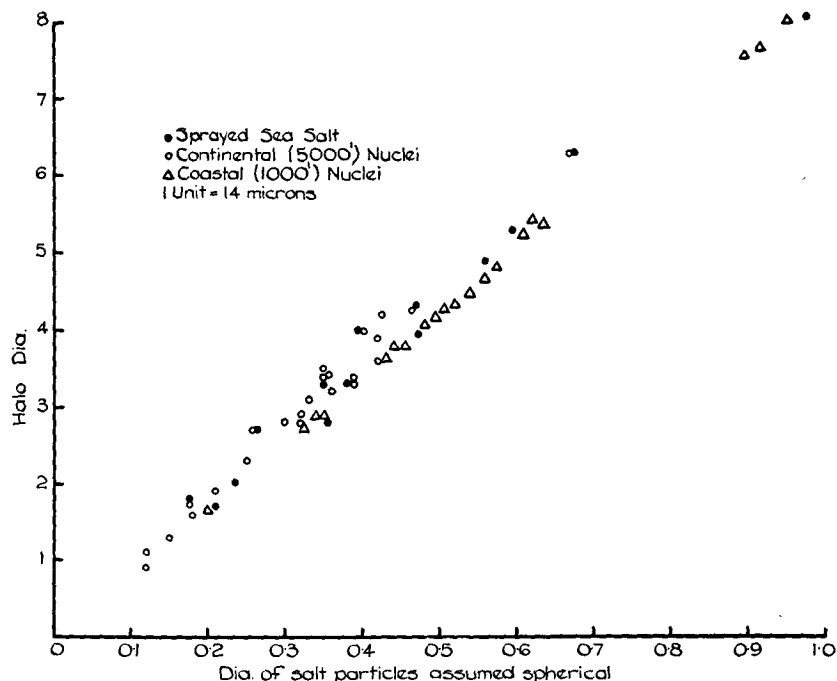


FIG. 2. Graph of halo diameters *versus* diameter of particle producing halo, latter being measured by isopiestic method of Woodcock.

point as sea salt, and it seemed certain that they were in fact composed of sea salt. Moreover, in fresh maritime air over the sea or within a few miles of the coast, all solid hygroscopic nuclei sampled were in category I. However, the possibility of replacement of chloride by carbonate, as suggested by Cauer [2], was not excluded by these measurements, due to the anomalous phase-transition properties of sodium carbonate described earlier.

The particles which underwent a phase transition between 80 and 82 per cent relative humidity were found in large numbers in samples at three levels on one day, near a large inland town. A similar result was found on no other occasion, and it is considered likely that man-made contamination in the atmosphere was responsible. Ammonium sulphate changes phase at about 80 per cent relative humidity, and it is possible that these nuclei were in fact composed of ammonium sulphate.

The particles of the third category were observed only once, and were so small that they were not visible under the microscope; but visible droplets appeared at 87 per cent relative humidity. It is possible, however, that the particles had become liquid at a lower value, and that 87 per cent relative humidity was not the true transition point. As this result was found only once, no further check on the point was possible.

The particles of the fourth category had a phase-transition point suggestive of sodium carbonate. They were found at higher levels in subsiding air masses, where the numbers of hygroscopic nuclei were very low. It is possible that they may in fact have been particles of sodium carbonate formed by the process described by Cauer.

Simultaneous measurements of particles by the isopiestic and halo methods gave the data plotted in fig. 2. The measurements were made for (a) sea salt sprayed on the slides in concentrated solution in a dark room, (b) hygroscopic nuclei sampled over the coast in fresh maritime air at an altitude of 1000 ft, and (c) hygroscopic nuclei sampled over land at 5000 ft in air which travelled at least 500 mi over land.

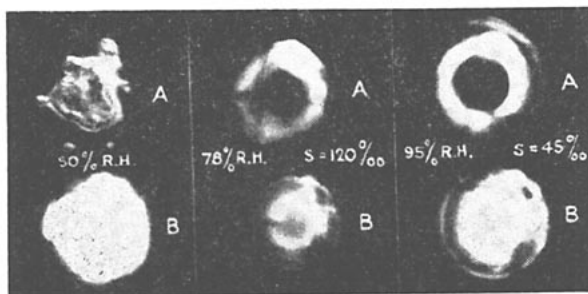


FIG. 3. Photomicrographs at successively higher relative humidities of two natural hygroscopic nuclei, one of which (B) contained high proportion of insoluble material. (Relative humidity and equilibrium salinity indicated in each case.)

It is apparent that the results obtained show no evidence that any reduction in chloride content took place.

For comparison, the regression equations between  $h$  (halo diameter) and  $d$  (diameter of salt particle, assumed spherical, deduced by the isopiestic method) were as follows:

$$\begin{aligned} \text{Sprayed sea-salt:} & \quad h = 8.7 d; \\ \text{Maritime nuclei:} & \quad h = 8.5 d; \\ \text{Continental nuclei:} & \quad h = 9.1 d. \end{aligned}$$

It is obvious that the variations in the ratio  $h/d$  were not significant.

On application of the phenolphthalein test for carbonates, no observable coloration was produced in slides exposed for relatively long periods in continental and maritime air. It seems certain, therefore, that no larger carbonate particles were present.

It was considered that, in continental air which had been circulating over land for some time, accretion by the sea-salt nuclei of the numerous insoluble particles observed in continental air might take place. On application of the final test described in section 2, above, it was found that many nuclei contained a variable, and often high, proportion of insoluble material. An extreme case is illustrated in fig. 3. It will be seen that the smaller nucleus A grew in humid air to a much greater size than nucleus B; the solid interior in B can be seen in the photomicrograph, even at the highest relative humidity. Calculation of the proportion of salt ( $\alpha$ ) in each nucleus gave  $\alpha = 100$  per cent for A and 1.5 per cent for B. The latter figure, however, was exceptionally low; in most instances, the percentage of salt ranged from 20 to 100 per cent. It must be pointed out that a nucleus containing 20 per cent salt would still be measured with fair accuracy by the isopiestic method, as the salt fraction grows on solution, at the high relative humidities used, to fifty or so times its original volume. The accretion of insoluble material was found mostly in anticyclonic air during the summer, when convective mixing was most active. Appreciable accretion was not found in post-frontal streams of westerly maritime air crossing the southeastern corner of the continent.

#### 4. Conclusions

1. The main constituent of large hygroscopic nuclei found in the atmosphere was sea salt.
2. On rare occasions, hygroscopic particles other than sea salt, probably ammonium sulphate and sodium carbonate, were encountered.
3. In continental air, particularly during the summer months, mixed nuclei were common; these consisted of sea salt mixed with insoluble material in variable proportions.

*Acknowledgments.*—The investigation was part of the research program of the Division of Radiophysics.

The writer is indebted to the Chief of the Division, Dr. E. G. Bowen, for his encouragement and advice in connection with the project. Thanks are also due to Mr. B. K. Seely, of the New Mexico School of Mines, for advising on the use of the halo method for the detection of chlorides, and to Mr. A. H. Woodcock, of the Woods Hole Oceanographic Institution, who was very helpful in advising on the application of the isopiestic method for the measurement of hygroscopic particles.

## REFERENCES

1. Woodcock, A. H., and M. Gifford, 1949: Sampling atmospheric sea-salt nuclei over the ocean. *J. marine Res.*, **8**, 177-197.
2. Cauer, H., 1949: Ergebnisse chemisch-meteorologischer Forschung. *Archiv Meteor. Geophys. Bioklim.*, **B, 1**, 221-256.
3. Twomey, S., 1953: The identification of individual hygroscopic particles in the atmosphere by a phase-transition method. *J. appl. Phys.*, **24**, 1099-1102.
4. Seely, B. K., 1952: Detection of micron and submicron chloride particles. *Analyt. Chem.*, **24**, 576-579.

---

**CORRESPONDENCE****An infrared detector for measurement of the back radiation from the sky**

By SIDNEY C. STERN and FREDERICK SCHWARTZMANN

*Chemical Corps Biological Laboratories, Camp Detrick, Frederick, Maryland*

9 June 1954

With reference to the above-titled article which appeared in the April 1954 issue of the JOURNAL, we wish to take this opportunity to acknowledge with thanks the prior efforts of Lt. Cmdr. Leo C. Clarke, USNR. Working as a team, Commander Clarke and Mr. Stern designed and developed a prototype radiometer prior to the former's departure for overseas in 1951.