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# ADVISORY

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Reference No. 50-63

An airborne flame photometer and  
its use in the scanning of  
marine atmospheres for sea-salt particles

WOODS HOLE, MASSACHUSETTS

WOODS HOLE OCEANOGRAPHIC INSTITUTION

Woods Hole, Massachusetts

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An airborne flame photometer and its use in the scanning of marine atmospheres for sea-salt particles.

by

A. H. Woodcock and A. T. Spencer

Technical Report No. 14  
Submitted to the Office of Naval Research  
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November 1956

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Director

An airborne flame photometer and its use in the scanning  
of marine atmospheres for sea-salt particles

A. H. Woodcock and A. T. Spencer

Introduction

Evidence of the association of bubbles in the sea with sea-salt nuclei in the air and of the connection between these nuclei and salts in solution in rain waters (see references 1, 2, 15, 17 and 19), has directed our attention to problems requiring more knowledge of the quantities of these nuclei in the atmosphere. In some of these problems, an instrument was required which would make possible a rapid scanning from aircraft of the distribution of salt of certain particle size ranges in the lower layers of marine atmospheres. In these air layers and in the clouds which are often found in them, the difference in the horizontal and vertical distribution of the weight of sea salt per unit volume of air commonly amount to several orders of magnitude (16). Hence, no great instrumental accuracy was initially needed to obtain a useful exploratory tool.

Methods presently available for obtaining the weight of salt per unit volume or weight of air\*\* are very slow and laborious. A further objection to most of these methods is that the quantities measured often represent average values along extended air paths, due to the necessarily prolonged time required to obtain an adequate sample. Hence these methods are not useful where rapid and rough mapping of the distribution of sodium-bearing particles in the lower layers of marine atmospheres is required.

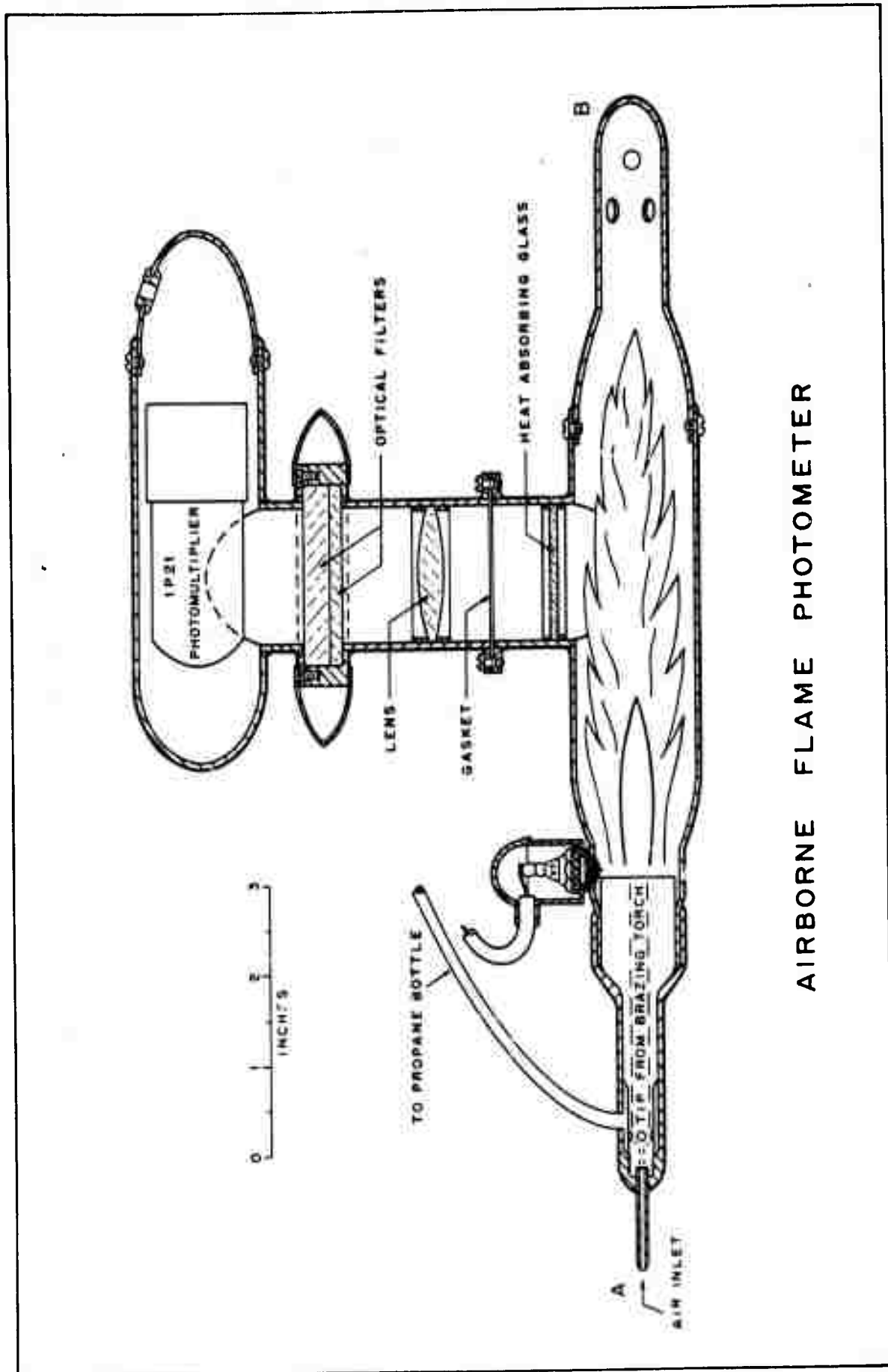
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\*\*For filtration methods see references 4 and 8, and for impingement methods see references 5, 9, 10 and 18.

Soudain (11) and Vonnegut (14) have developed a useful instrument which applies the principles of flame-photometry to the problem of detection of sodium-bearing aerosols. Their instruments are laboratory models, capable of giving relatively instantaneous indications of these aerosols. However, neither author calibrated his instrument in terms of the weight of sodium per unit volume of air nor adapted it for use in aircraft.

The purpose of this paper is to describe briefly a flame photometer designed for use in an airplane, (see Figures 1 and 2) to discuss its use in conjunction with a different method of measuring airborne salt, and to give some of the first data obtained. This instrument measures and records the average voltage output of a photocell which is exposed to the sodium flashes in a flame. This voltage output has been related to the quantity of sea-salt particles in the air, by comparison with direct simultaneous sampling of these salt particles, so that it provides a rapid indication of the weight of sea-salt present. The justification for this comparison of sodium-flash intensity, as represented by the photocell output, to the mass of sea-salt particles in the atmosphere, is to be found in the work of Junge (see reference 6, p. 130). He showed that the ratio of the sodium to the chloride in the giant nuclei in marine air is about the same as this ratio in sea salts. Hence, it was expected that the sodium flash intensity would be a nearly constant function of the quantity of sea salt in the air, since the ratio of sodium to total salts in sea salt is a constant.

#### A Brief Description of the Instrument

The instrument, shown in section in Figure 1, consists of an enclosed gas burner, or torch into which a mixture of air and propane gas is introduced. The mixture is ignited in flight by a spark which



## AIRBORNE FLAME PHOTOMETER

Fig. 1 Schematic drawing of airborne flame photometer.

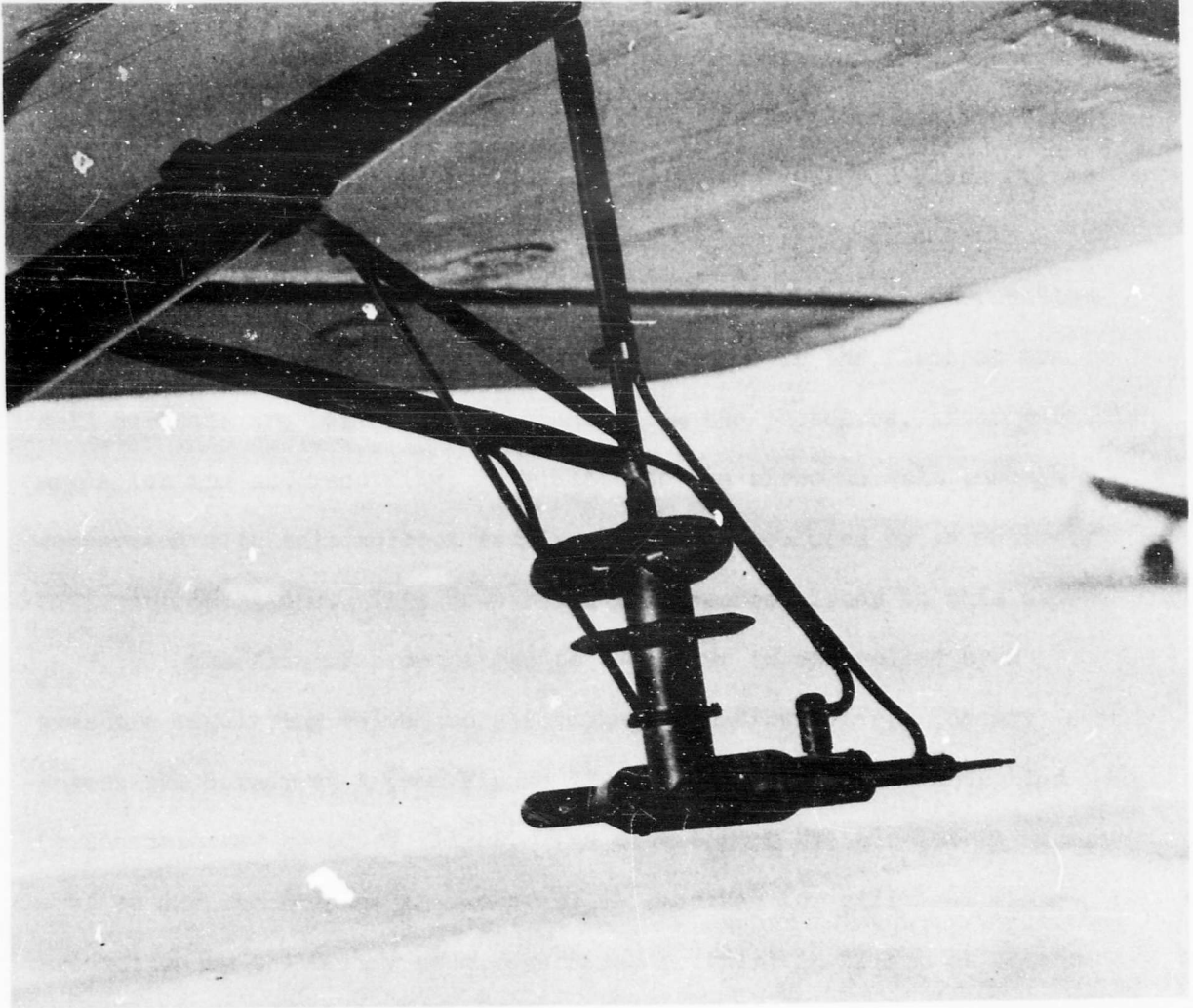


Fig. 2 Photograph of flame-photometer housing mounted under the wing of a small aircraft.

crosses the gap between the center electrode of the spark plug and the outer edge of the burner. Figure 2 shows the mounting of the flame photometer under the wing of an aircraft.

The flame is viewed by a 1P21 photomultiplier tube through a lens and a multi-layer interference filter. This filter has its transmission peak at 5892A, and includes an additional colored glass filter for the elimination of side bands.

The output voltage of the photomultiplier tube is a function of the light from the sodium flashes which occur in the flame as the salt aerosols are heated. This signal from the phototube, after suitable amplification and recording, is related to the airborne salt through comparison with salt aerosol samples taken and measured by an entirely different technique. This comparison is discussed later in this paper.

The flow of propane gas to the flame is controlled by a pressure regulating valve and a floating-ball flow meter. The air enters the burner at A (see Figure 1) at a speed which is controlled by the selected speed of flight. The diameter of the air intake orifice and the propane intake pressure required for efficient flame production by the burner were determined by trial in flight at speeds of 70 to 105 m.p.h. It was found that the best flame characteristics for this instrument were obtained at an air speed of about 90 m.p.h., an air intake orifice diameter of 2.36 mm and a propane flow rate of about 57 gms. per hour.

#### Calibration.

The sea-salt-particle sampling technique, which was used to indicate the range of usefulness of the output voltage of the photomultiplier tube as a measure of airborne salt, is one which has been described by Woodcock (15 and 18) and further tested by Twomey (13)

and Crozier (3). This technique involves the exposure to the air of small glass slides and the subsequent measurement with a microscope, under constant relative humidity conditions, of the salt aerosols impinged upon them. When these aerosols are crystalline particles they range in size from about 1 to  $10\mu$  radius and they are known to contain over 90 per cent of the total mass of sea salts usually present in marine air (see Junge, 6, pp 135). The amplifier used with the flame photometer, as presently designed, is sensitive to only the larger of these particles.

In comparing techniques in flight, the small glass slides were exposed simultaneously with the operation of the photometer and the recording of the output voltage of the photomultiplier tube. Over seventy comparative tests have been made in the lower atmosphere (altitude 200 to 7,000 feet) over the sea in the Florida and West Indian regions. During these tests many factors, such as air speed, airplane flight attitude, propane gas flow, phototube supply voltage, etc., which were found to effect the photocell output voltage, were held reasonably constant.

Figure 3 shows the results of these comparative tests. Graph (A) in this figure gives the earlier observations made over the ocean east of Pompano Beach, Florida and graph (B) gives the latest data from the Virgin Island area. The large apparent increase in the photocell output voltage on graph (B), as compared to graph (A), is due to increased amplification of the signal in a later model of the instrument. This later model also had an increased sensitivity to the larger sodium flashes. The two diverging lines are introduced among the observed points in order to show the maximum error of the isopiestic method (i.e.  $\pm 20\%$ ; see reference 18, p. 181), as applied to the problem of determining the weight of sea-salt particles on the glass slides. These sodium data will be discussed later in this paper (see p. 9).

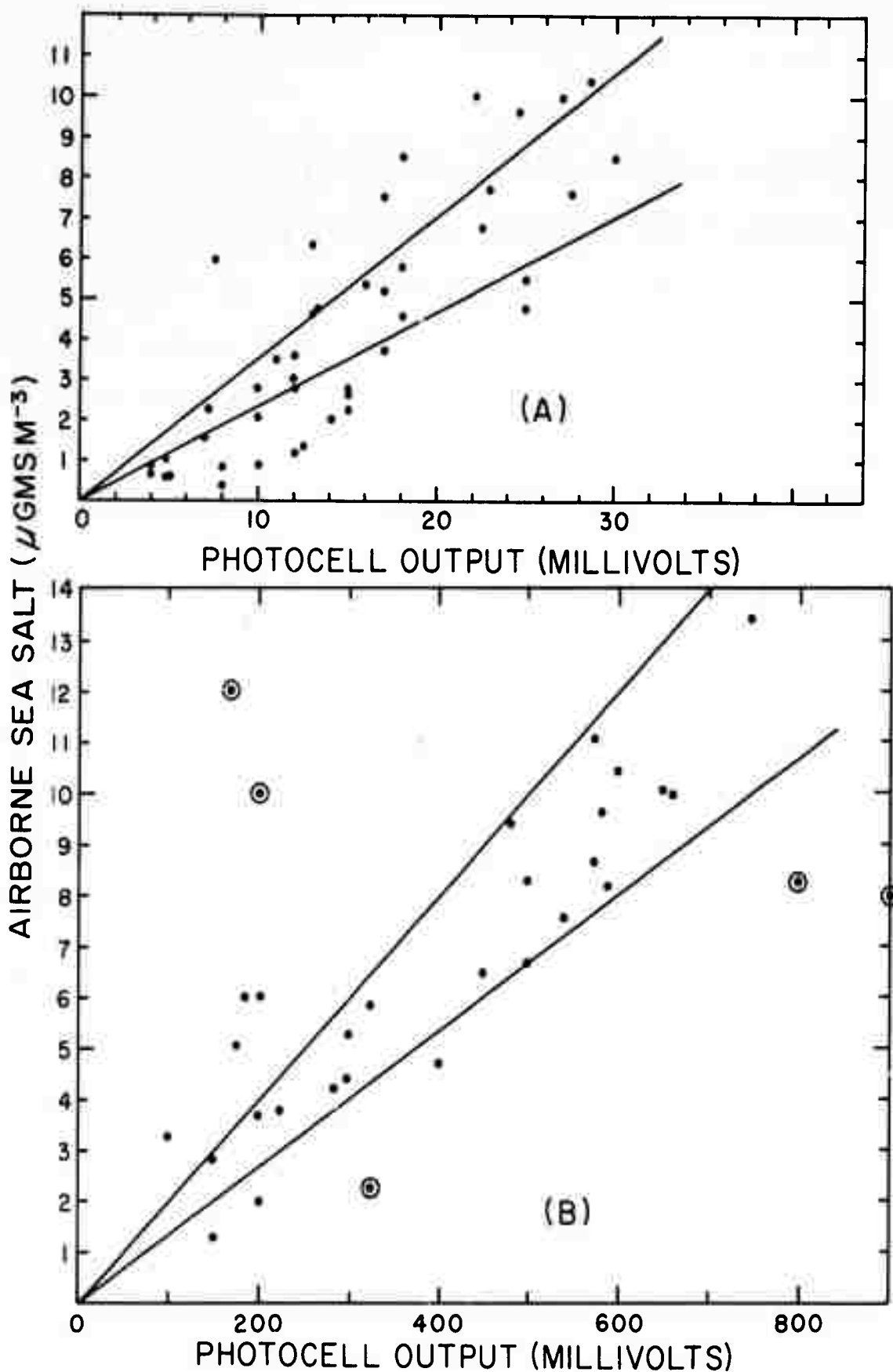


Fig. 3 A comparison of the average photocell output voltage, during the periods (30 to 100 seconds) required to obtain the sea-salt particle samples, to the total quantity of sea salt. Graph A shows the results obtained in the region of Pompano Beach, Florida, and graph B shows those obtained near St. Thomas, V. I. The diverging lines indicate the maximum error to be expected in the isopiestic method. The quantities of sea salt represented by the circled points were derived by extrapolation from a partial sampling of the total range of particle size. These values are therefore subject to the uncertainties of partial sampling (see text).

### Collection Efficiency

May (9) and many other workers have emphasized the importance of "isokinetic" conditions in the intake orifices of aerosol samplers in order to insure that a representative number of particles enter. In other words, with the intake orifice facing directly into the wind, the air velocity within the orifice should equal that in the main airstream on the outside. Lower or higher air speeds within the orifice will alter the number of particles which can enter, and hence will alter the apparent concentration of particles in the free air.

In the first exploratory studies of atmospheric sodium particles, no suction was applied to the tail pipe (see B, Figure 1), in order to speed the flow of air through the flame chamber. Hence, internal friction caused the rate of flow of air inside the intake orifice tube (A) to be somewhat less than the air speed of the aircraft. This was demonstrated by placing the instrument in an air stream of a known velocity and measuring the quantity of air passing out of the vent pipe.

Figure 4 shows the observed inflow amounts at various air speeds compared to the ideal isokinetic inflow. Note that the measured air inflow at 80 m.p.h. was about 17 per cent less than ideal, and at 90 m.p.h. about 11 per cent less. These data were obtained with the flame turned off. However, operation of the flame was found to have no measurable effect upon the air inflow rate.

It was sufficient for our present purposes to demonstrate that the amounts of particulate sodium which do enter the orifice and flame, produce a varying average sodium flash signal which is quantitatively related to the varying average amounts of sea salt sampled on the glass slides. It is thought that the above near-isokinetic-flow values assure a collection efficiency which is quite high enough for the initial exploration discussed here.

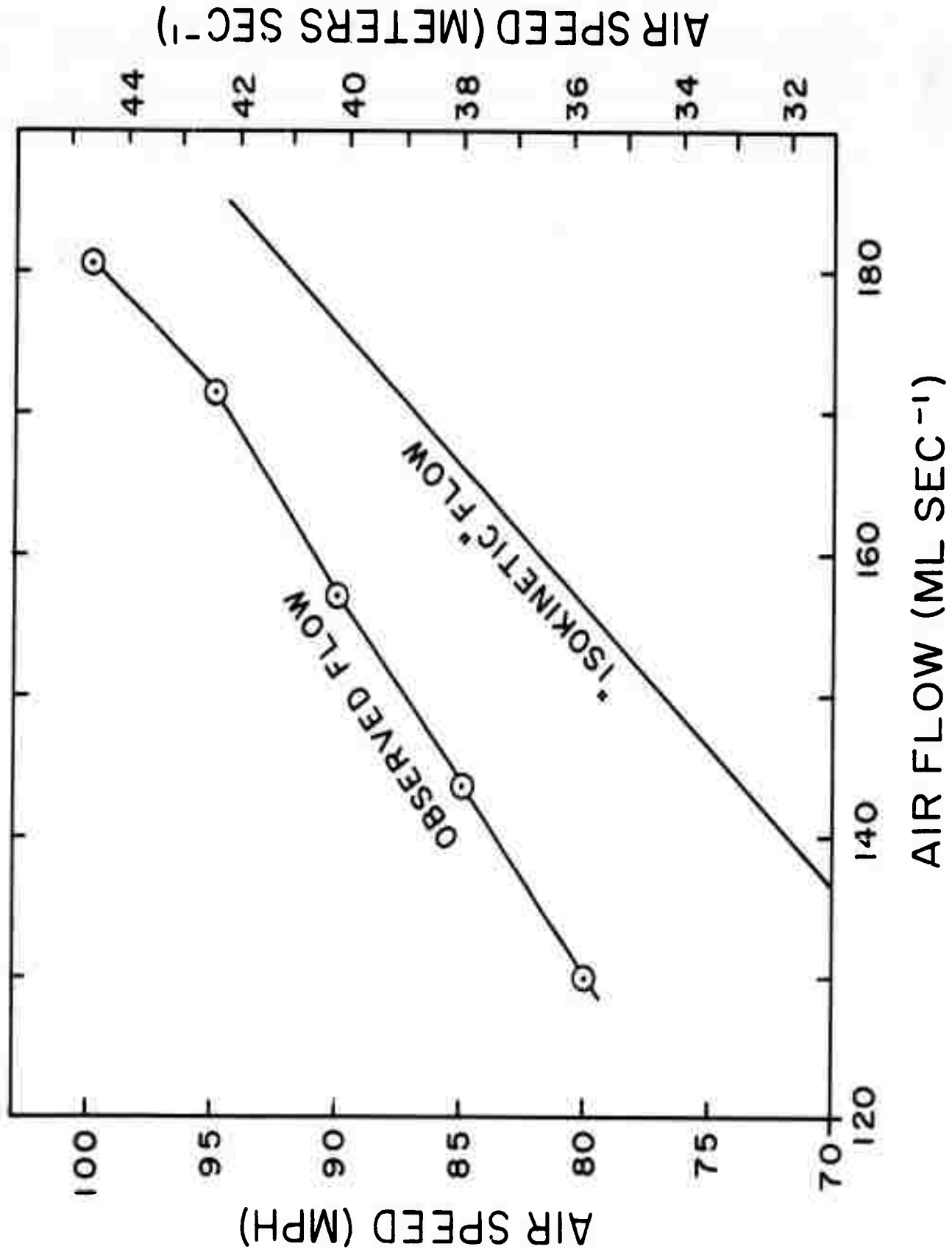


Fig. 4 Measured air flow into photometer intake orifice, compared to ideal (isokinetic) flow. Orifice inside diameter 2.36 mm.

Figures 5 and 6 show a comparison of the average sodium flash signal intensity, as indicated by the photocell voltage output, to the average quantity of sea-salt found among particles collected on the glass slides. The number of observations averaged in each case is shown near each point. It is apparent on these figures that the differences which occur in the airborne sea salt and sodium, with increasing altitude, are very similar in trend. This result was expected, since the constancy of the relationship of the sea salt, among the giant salt nuclei, to the chloride (13 and 18) and to the sodium (5) has been shown.

On Figures 5 and 6 the voltage values are also given for periods when the flame photometer was operated within relatively small nonprecipitating cumulus clouds. Due to the increased mass of the salt nuclei in the clouds (they become relatively large cloud droplets), the collection efficiency of the photometer intake orifice for these particles would be more nearly unity than for the same particles in the clear air. Thus these photometer voltages obtained within the clouds probably more nearly represent the total sodium present than do the values measured in the clear air.

It will be noted that the average photocell voltages in the clouds are similar to, but somewhat greater than, the average voltages in the sub-cloud layer of air. Until further measurements become available, this similarity is tentatively interpreted as showing that the clouds are largely composed of air which has come from the sub-cloud layer. The somewhat higher values obtained in the clouds as compared to the values in the sub-cloud layer, are thought to result from a), the tendency for the clouds to be made up of the sub-cloud air containing the highest amounts of salt (compare cloud voltages on Figures 5 and 6

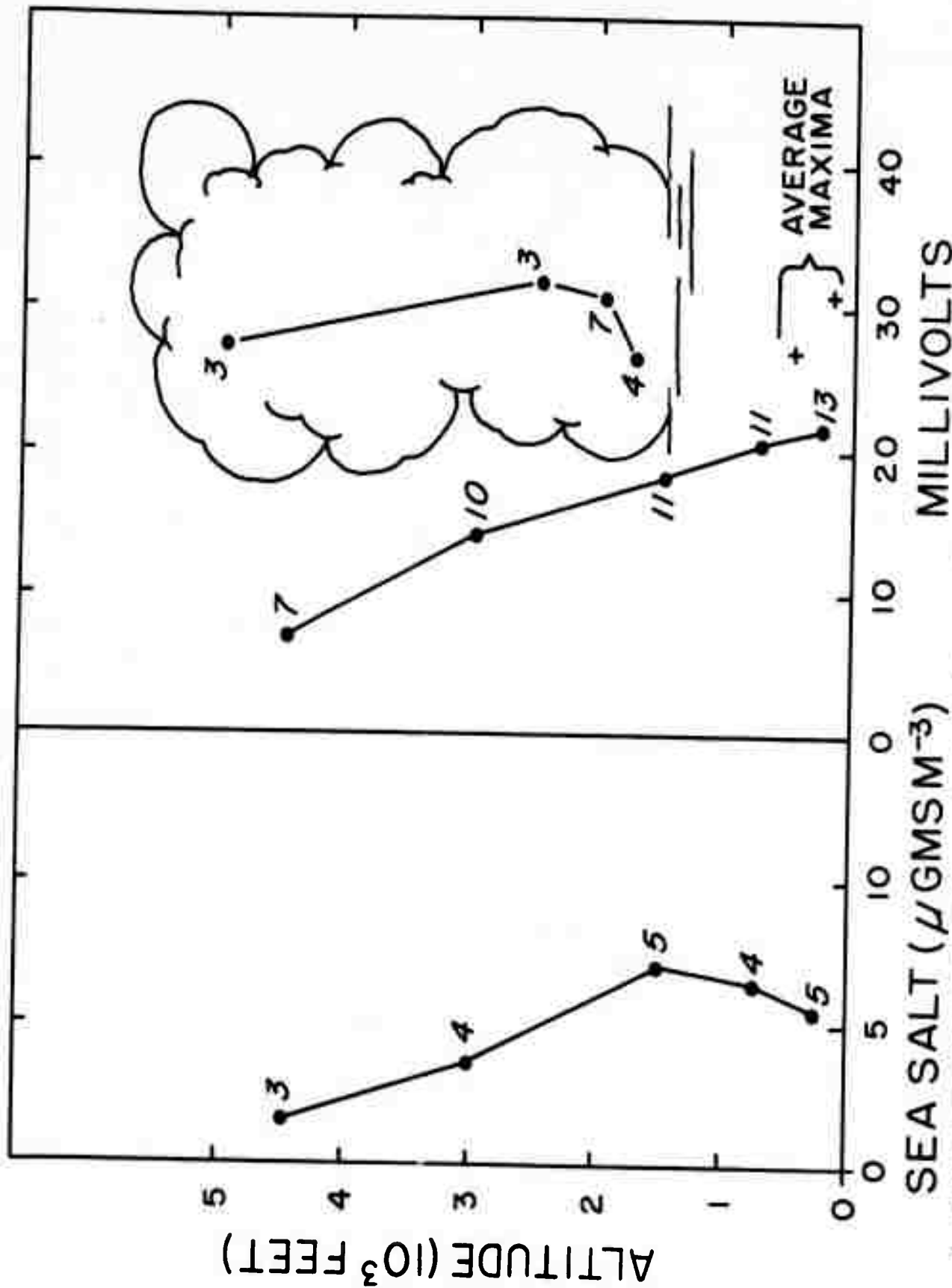


Fig. 5 Average vertical distribution of weight of sea salt in the clear air compared to the average airborne sodium in the clear air and in cumulus clouds. The sodium is represented by the millivolts output of the photoelectric cell. These measurements were made over the sea, from one-half to two miles east of Panama Beach, Florida, and during July 22, 23, 24, 25, 27, and 28, 1955. Average local surface winds force 3, ESE. See text for further discussion.

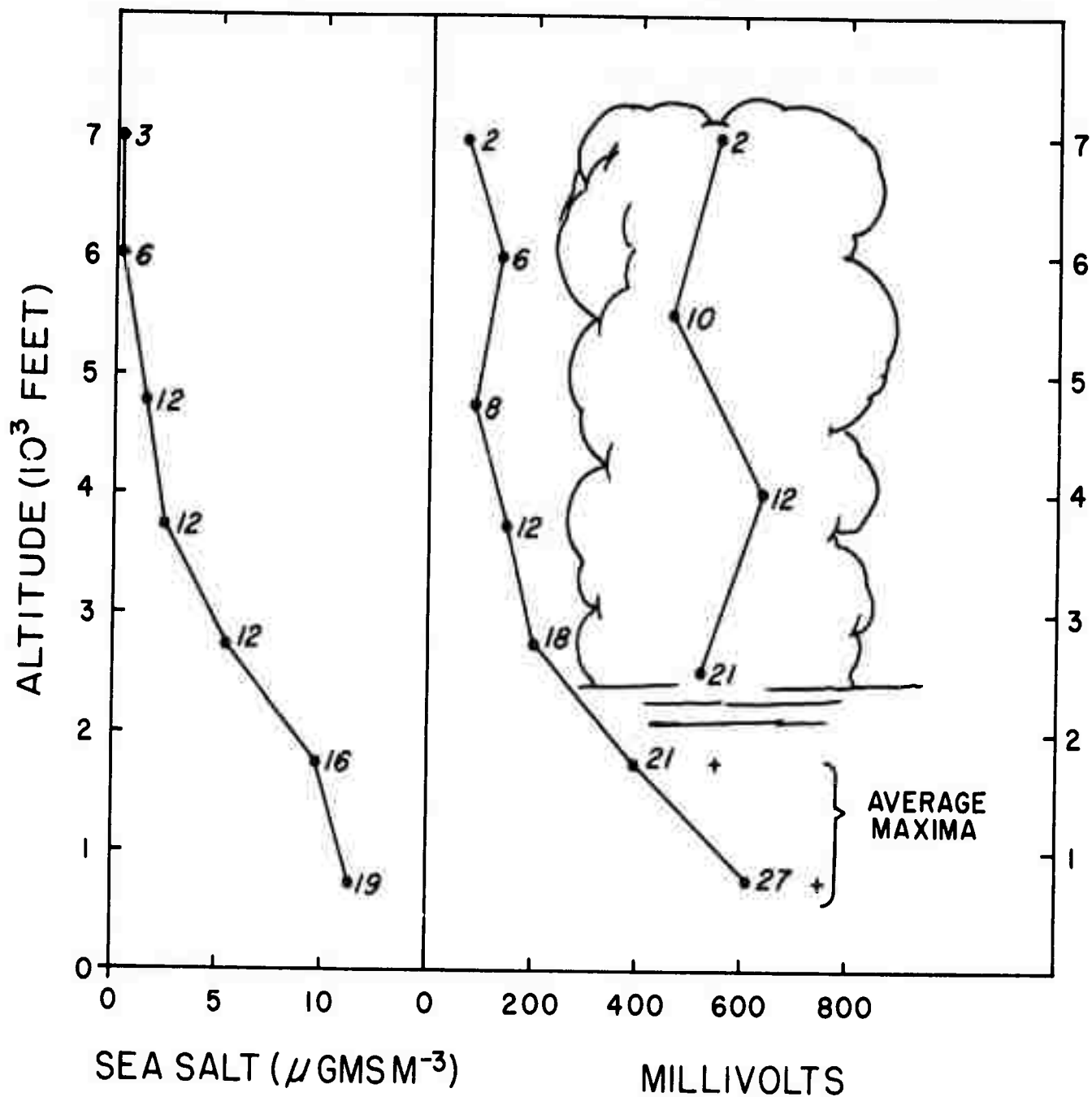


Fig. 6 Average vertical distribution of weight of sea salt in the clear air, compared to the average airborne sodium in the clear air and in small cumulus clouds. The sodium is represented by the millivolts output of the photoelectric cell. These measurements were made over the sea about five miles southeast of the island of St. Thomas, V. I., and during thirteen days between the dates May 25, 1956 and June 10, 1956. Surface winds force 3 to 5 E to ESE.

to the average voltage maxima in sub-cloud air); and b), a somewhat higher instrumental sampling efficiency in the clouds. It is very unlikely that correction for the collection efficiency error will greatly alter the relative cloud values given here. However, until this error is eliminated, these values should be regarded as tentative.

### Discussion

There is a considerable scatter of the observed points on Figure 3 beyond the + 20 per cent maximum error of the glass slide method. This is thought to be due in large part to the difficulties of properly integrating the highly variable signal from the phototube and to variations in the relative mass of salt (or sodium) present in the salt particle size range sampled by the flame photometer. The variability of the photometer signal during "calibration sampling runs" indicated that the slide samples were averaging a greatly varying quantity. The second of the above factors will be discussed in some detail later. The justification for using the photometer data at this time, despite the above rather large scatter in the calibration values, lies in the close similarity of the changes in the average photometer results, at different altitudes and positions, to changes in the average amounts of sea-salt present (see Figures 5 and 6).

At this stage of its development, the airborne flame photometer is regarded as an exploratory probe in areas where the differences in salt amount are great, and as a device for rapidly "roughing-in" the distributional picture of the sodium-bearing particles. There is a great difference in the time required to obtain the results by the slide method as compared the photometer method. For example the salt data from the glass slides, which are shown on Figure 6, required forty hours to produce, while the flame photometer data on this figure are the result of two hours of work.

The photometer is especially useful in areas of marked change in aerosol population, such as those which occur while ascending from the sub-cloud to the cloud and above-cloud layers and while flying through cumulus clouds. Where particle size distribution and greater accuracy are required, other methods may be used. In these cases the photometer is sometimes a valuable supplemental tool. For instance, in some of our problems it is useful to know the maximum quantities of salt present, among certain particle size ranges, along a given flight line. Previous methods required that glass sampling slides be exposed as rapidly as possible and at numerous intervals along this line. The "reading" of these many slides was very time consuming and laborious. The continuous record of the photometer makes it possible, however, to scan a flight path and then, upon reversal of course, to use this record as a guide in relocating the areas of maximum salt. Salt samples may then be taken in these areas of interest only, thus saving much time and work.

Figure 7 shows an example of an interesting horizontal difference in sodium or salt content in the air at constant altitude near an island. This difference, which is not unusual at other levels, is probably due in large part to the convergence of surface air towards the island (caused by island heating) and the consequent subsidence of the relatively salt-free air from higher levels at the off-shore location about 5 miles south of the island. It may also be due in part to increased wind force near the island causing a greater local production of salt particles by the sea surface (see reference 1 and 16 about role of wind in nuclei production).

Though we have used this instrument at low air speeds on a small aircraft, our experience has indicated that it could be readily adapted for use at the higher air speeds of larger airplanes.

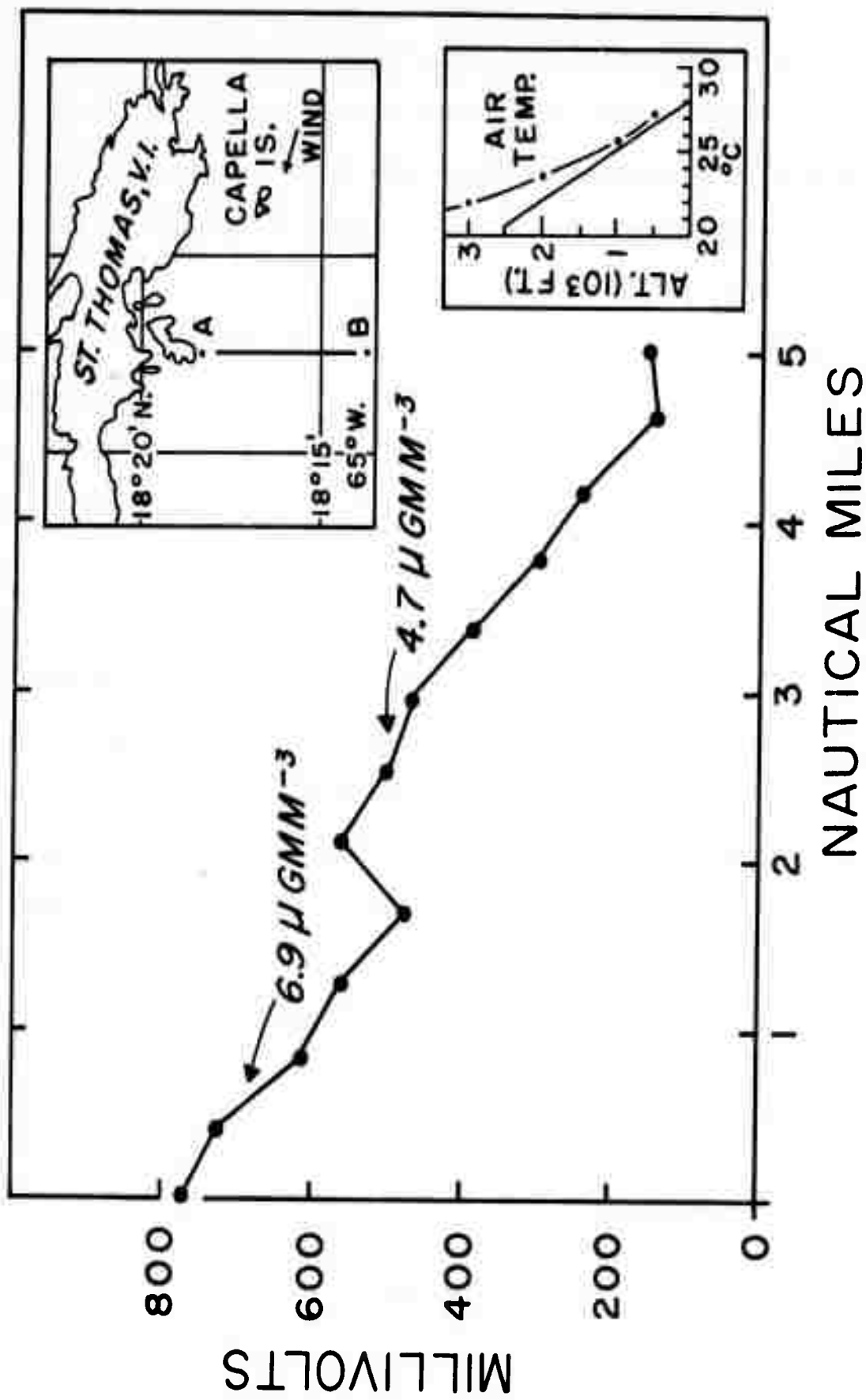


Fig. 7 An example of horizontal differences which occurred in the photocell output voltage along the flight line A B (see insert map). The weight values shown represent sea salt sampled on glass slides a short time later and in the approximate position shown by the arrow marks.  
Date: June 7, 1956, alt. 500 ft.

In using the flame photometer within clouds, it is reasonable to question the possible effects of cloud water on the flame and on the sodium flash intensity. It might be supposed that the heat required to vaporize the water on the cloud droplets passing through the flame might so lower the flame temperature that an inadequate amount of heat would remain to heat all of the sodium in each salt particle to incandescence. However, this seems unlikely since the propane burning rate of 67 grams per hour releases from 300 to 1000 times as much heat as that required to vaporize the water found in the average cloud (i.e. from 0.10 to 1 gm m<sup>-3</sup>). This excess of heat is derived assuming isokinetic flow in the orifice. With this flow, the air passes through the flame at a rate of about 0.157 liters per second at the airplane speed of 35.8 meters per second (80 mph). The heat of combustion of the propane gas is about 1380 cal per gram.

The effects of changing pressure (altitude) on the gas delivery rate of the commercial "constant flow valve" used was also measured. The maximum increase in this flow rate due to decreasing pressure with altitude was only 7 per cent. This increase produces no noticeable effect upon the flame or its sodium flash signal.

As previously suggested, it is thought that one source of the errors in relating photocell output voltage to individual sea-salt samples taken with the glass slides, (see Figure 3) lies in the changing relative distribution of mass of salt among particles of different sizes. The photometer output amplifier, as presently constituted, is sensitive to an alternating sodium flash signal from the larger particles and not to signals from relatively steady sodium light. From a study of the photocell output records from the St. Thomas data, it is known that the major portion of the sodium signal comes from flashes which occur at frequencies of about one per second or less. (There was too little

amplification to detect the weaker flashes.) If we assume that the air entered the intake orifice at airplane speed (35.8 m. sec.<sup>-1</sup>), the rate at which air passed through the flame is simply the product of the cross-sectional area of the orifice (.04375 cm<sup>2</sup>) and the air speed (3.58 x 10<sup>3</sup> cm sec<sup>-1</sup>). From this product, which is 0.157 liters per second, and from the spatial distribution of the salt particles we can determine the particle weight range which produces the flashes of one or less per second. This is done, using the salt-particle distributions derived by the glass-slide technique.

Figure 8 shows graphically the cumulative number distribution of particles of various weights sampled by the glass slides over the ocean in the Virgin Island area. On this figure one can readily see that the lower limit of the weight range of particles present in numbers sufficient to cause one flash or less a second in 0.157 liters of air (i. e. about 7 x 10<sup>3</sup> particles or less m<sup>-3</sup>), is not a constant value. In fact the "lower limit weight" varies, during the several days represented, from about 1 x 10<sup>-10</sup> grams to 2.7 x 10<sup>-10</sup> grams\*. Figure 9, which shows cumulative mass distribution of the salt particles, may be used to determine the relative proportion of the total airborne salt present in nuclei larger than the limiting weight.

As a result of the variable distribution of mass in the weight range sampled by the flame photometer, the instrument probably "sees" a variable proportion of the total salt present. For example, Table I, column 7, shows this varying proportion, expressed as the ratio of the total airborne salt to the salt present in the particles larger than

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\*The fact that the air entered the orifice at a speed somewhat less than that of the aircraft will alter these values somewhat, but will not alter the basic argument concerning this source of error.

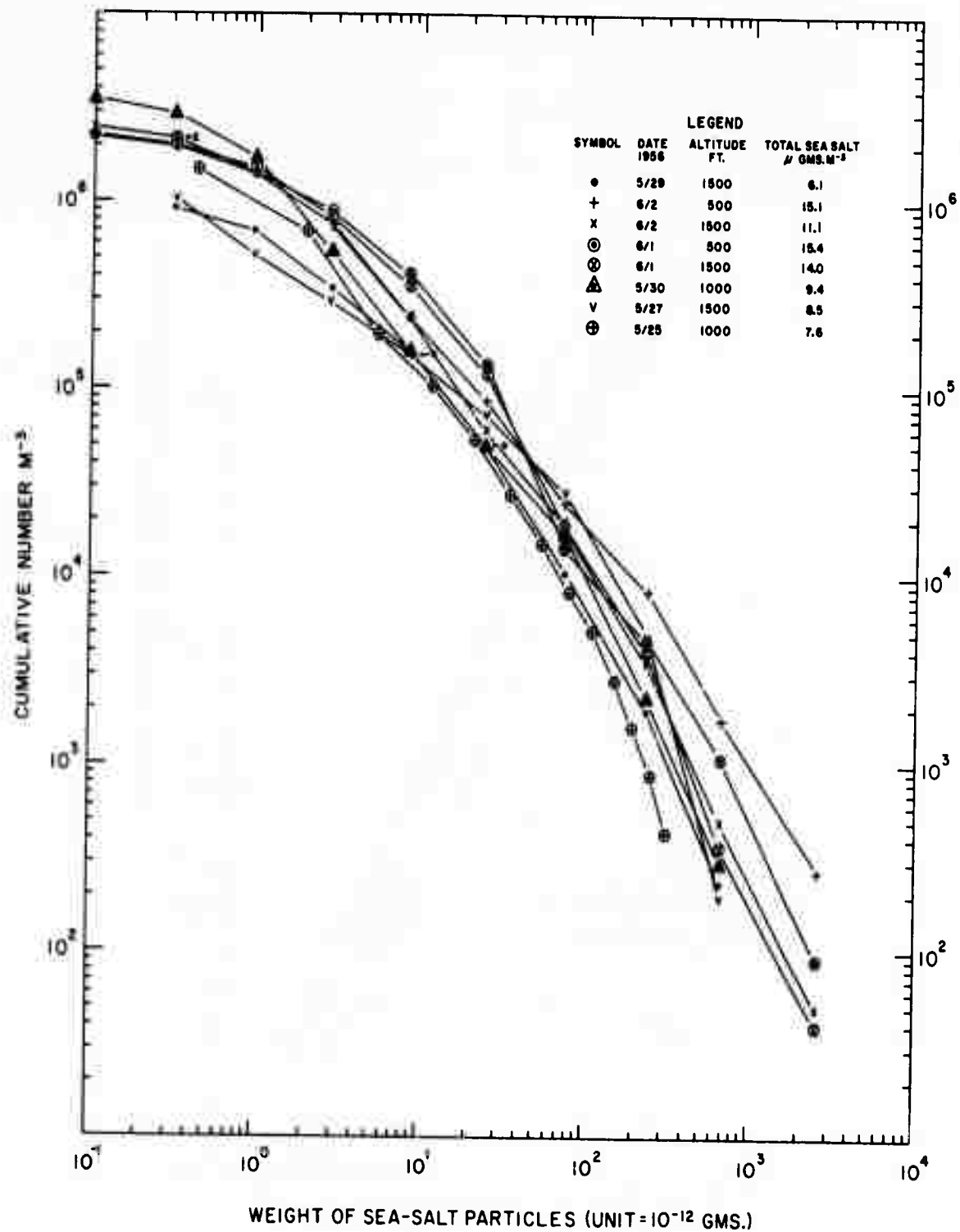


Fig. 8 Cumulative number distribution curves for the samples represented on Figure 9.

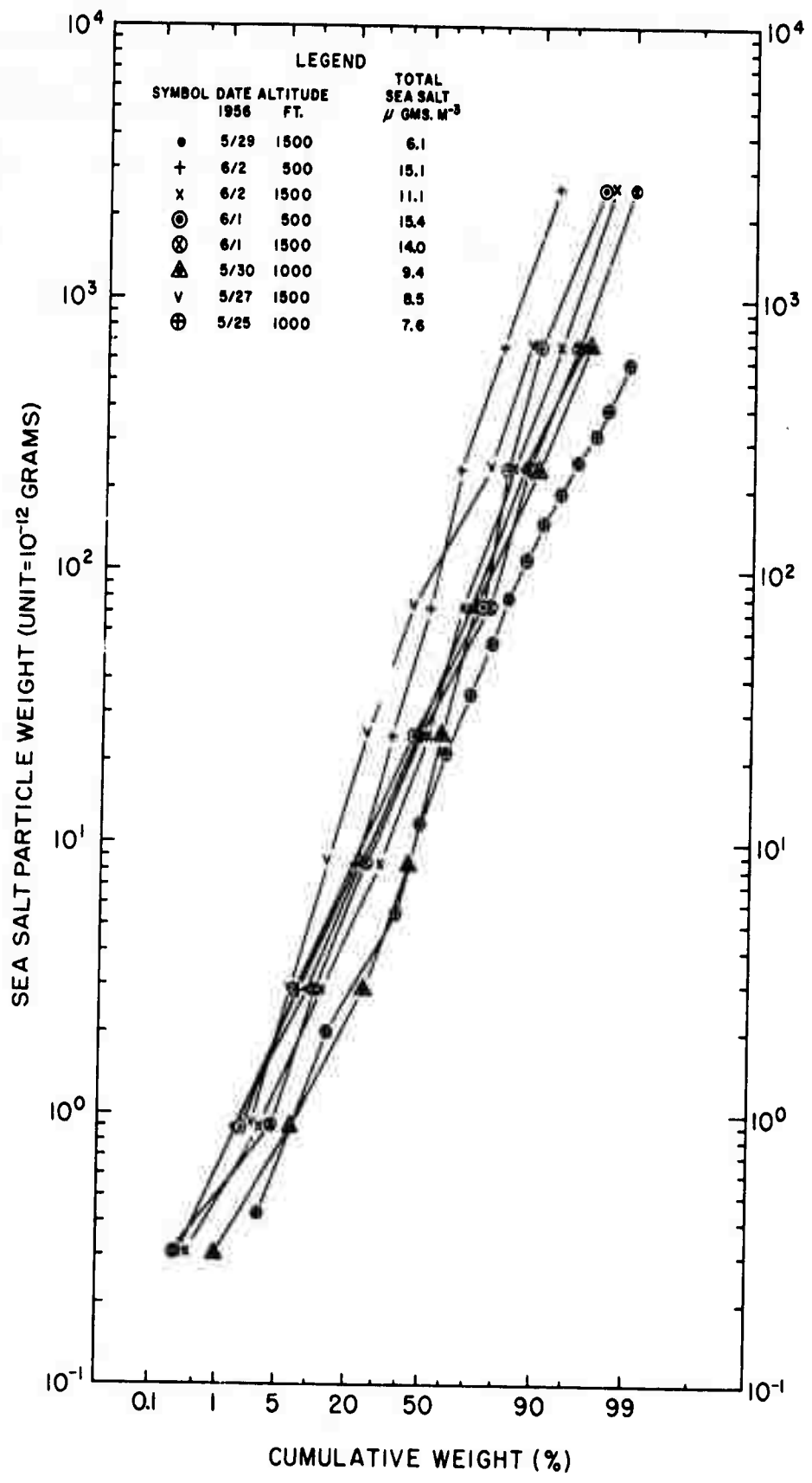


Fig. 9 Cumulative percent weight distribution curves, representing atmospheric salt-particle samples taken at the altitudes where, due to more complete sampling, the widest range of particle size was obtained. The sampling location was over the sea in the Virgin Islands region.

the above-mentioned "lower limit" particle weight. These ratios are derived from the data on Figures 8 and 9 in the following manner. On Figure 8 note that the June 2 salt-particle distribution curve, for the 500 foot level, crosses the limiting number of  $7 \times 10^3$  particles per cubic meter at a nucleus weight of  $270 \times 10^{-12}$  grams. On Figure 9 the cumulative per cent mass distribution curve for the same day and altitude shows that 34 per cent of the mass of salt was present in particles larger than  $270 \times 10^{-12}$  grams. Table I column 7 shows this and other figures for the relative mass of salt present in particles larger than the "lower limit" weight. Correction of the data for this source of error proved inconclusive. This is thought to be due to the small amount of data showing a significantly large difference and to the obscuring effects of other variables such as the error of the glass slide method.

From the above analysis it is seen that an instrument sensitive to only a portion of the range of salt particles entering the orifice should record a signal variability from changing relative mass distribution among these particles. It is clear that a variable signal does not, therefore, necessarily indicate differences in the total mass of salt in the particle size range sampled by the glass slides. Also, there is little doubt that much larger differences in the ratios  $M_2/M_1$  (see Table I) often occur. Consequently the present circuit which amplifies the photoelectric cell output voltage is now being altered to broaden its sensitivity to a greater range of sodium flash signal frequency. This is expected to remove much of the above source of error.

In the meantime the present instrument is a useful exploratory tool in those areas of the lower atmosphere where large differences in sodium content are the major features to be studied. We hope to apply

the instrument in various field studies. For instance we would like to know the differences in the salt-aerosol load of the marine air masses moving into "disturbed areas" in the North Atlantic trade-wind system. It is already known that differences in the salt load of the sub-cloud air of the order of ten to a thousand times are directly related to the speed at which this air has been moving (16). It has also been shown that these aerosols are probably connected in some way with the rain-forming process (15, 17 and 19). Hence large differences in their distribution in air which is moving into a "disturbed area" may be directly connected with the rate and position of release of heat (precipitation) in these areas.

The instrument may also be useful in testing the idea of trade-wind cloud growth by the "entrainment" of environmental air. If subsequent measurements continue to show high relative sodium content in the clouds, it will become necessary to reconsider this idea of cumulus growth, or to investigate the possibility that the clouds concentrate the larger salt particles within and near themselves. This reasoning follows from the fact that the clear air at cloud levels contains relatively small quantities of salt (see Figures 5 and 6). Hence entraining or mixing of this environmental clear air with cloud air should produce a diminishing sodium amount at increasing altitudes in the clouds. This decrease is not revealed by the data thus far.

TABLE I

Showing differences in the ratio of the computed weight of salt which produces the sodium flash signal, to the total weight of salt in all of the particles sampled by the glass slides. The symbols refer to the data of the six days when the most complete salt-particles samples were taken (see Figures 8 and 9), with the slides.

Symbol	Date	Altitude	Airborne sea-salt	Particle* weight	Total sea-salt in particles equal to or larger than (W)	M2/M1
	1956	ft.	M1 $\mu\text{gms m}^{-3}$	(W) $10^{-12}\text{g}$	M2 $\mu\text{gms m}^{-3}$	
⊕	5/25	1000	7.6	90	1.22	0.16
∇	5/27	1500	8.5	190	2.55	0.30
●	5/29	1500	6.1	100	1.58	0.26
△	5/30	1000	9.4	120	1.88	0.20
⊙	6/1	500	15.4	160	3.24	0.21
⊗	6/1	1500	14.0	155	2.24	0.16
+	6/2	500	15.1	270	5.13	0.34
x	6/2	1500	11.1	150	2.55	0.23

\*Weight of the smallest particle among the salt nuclei numerous enough to produce a maximum of one sodium flash a second. (i.e. a cumulative number of  $7 \times 10^3$  particles  $\text{m}^{-3}$ --see text)

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