The Production of Potential Ice Nuclei by Gasoline Engines[1,2]

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ABSTRACT

Potential ice nuclei, particles which become ice nuclei when properly treated, are produced in automotive exhaust. They are activated by iodine vapor and are believed to be lead particles originating from the tetraethyl lead mixed with the fuel. The sensitivity of nucleation measurements provides an excellent method of counting submicron lead particles and monitoring the automotive component of air pollution. Measurements reported here show that the production of potential ice nuclei by a gasoline engine is at least 2×10^{7} per gram Pb at -10C, 1×10^{10} per gram Pb at -15C and 1×10^{12} per gram Pb at -20C.

Some simple calculations are presented, showing that large enough numbers of potential ice nuclei are produced by the routine burning of gasoline to be useful in cloud and weather modification research. In particular, a DC-6 aircraft burning 6 gal min^{-1} of gasoline should produce at least 4×10^{11} nuclei sec^{-1} at -20C.

It is demonstrated that ethylene diiodide can be added to the gasoline supply of an automobile and that the automobile will then act as an inexpensive source of large numbers of ice nuclei.

1. Introduction

Schaefer (1966) and Morgan (1967) recently demonstrated that lead particles originating from the combustion of gasoline containing tetraethyl lead in automobile engines can be converted into ice nuclei (probably lead iodide) by exposure to iodine vapors. The particles may then be counted using an ice nuclei counter. This provides a method for detecting submicroscopic lead particles and monitoring the automotive contribution to air pollution both in and remote from cities. At the same time this reaction presents a source of potential ice nuclei that can be activated for use in cloud modification studies.

The objective of this study is to examine the lead iodide reaction from the latter point of view, to determine whether combustion-produced lead particles constitute a large enough source of potential ice nuclei to be significant in such cloud modification activities as hail prevention and rainfall augmentation. A full study of the problem poses the following questions:

1) How many nuclei are available from engines?
2) How many nuclei are in the air?
3) What is their horizontal and vertical atmospheric distribution?
4) What is their diurnal concentration variation at the ground and aloft?

This study is restricted to the determination of the output of lead particles from an internal combustion engine. Some attention has been given to the number of potential ice nuclei in urban air and their diurnal variation at ground level (Morgan, 1967), but the concentration at upper levels has not yet been investigated.

2. Lead iodide as an ice nucleus

Lead iodide has not received much attention as a practical agent for cloud seeding in the United States. Its properties have been studied (Schaefer, 1954, 1966; Harris *et al.*, 1963), but the general feeling has been that its water solubility [0.04 gm $(100\ ml)^{-1}$ as compared with 8×10^{-6} gm $(100\ ml)^{-1}$ for silver iodide] prevents it from being effective in clouds. Bakulina *et al.* (1962) and Gromova *et al.* (1962), in the Soviet Union, find that one gram of lead iodide can produce 10^{11} nuclei at -10C. They and others (Sulakvelidze, 1966; Gaivoronskii *et al.*[4]) have reported the use of lead iodide in cloud modification experiments.

In our study the lead iodide particles (if such they indeed be) were counted with an NCAR acoustical ice nucleus counter (Langer *et al.*, 1967). In this instrument the particles are submitted to rather severe treatment in terms of their temperature-humidity history. Air sampled by the counter is first heated and humidified by passage over a hot water surface (about 50C) and then cooled rapidly to below freezing temperature.

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[4] Gaivoronskii, I. I., A. I. Kartsivadze, A. A. Ordzonikidze and Ju. A. Seregin, 1967: On artificial modification of hail processes. Paper presented at the XIVth General Assembly of the IUGG, Lucerne, Switzerland.

The particles are thereby submitted to considerable water supersaturation and possible dissolution but they apparently survive this treatment in large numbers. From this we might infer that these particles can survive warm cloud conditions and be available as active ice nuclei in the cold parts of clouds.

3. Experimental techniques and results

a. Gasoline engine exhaust treated with iodine. Air samples containing potential ice nuclei were collected in aluminized mylar bags with capacities of 135 and 600 liters. Since the NCAR counter has an upper counting limit of 1000 ice nuclei (liter)$^{-1}$, the air samples had to be diluted with filtered air so that the potential ice nuclei concentration would not exceed this limit. The potential ice nuclei were than activated with iodine, by transferring air from a small air chamber, saturated with iodine at 25C, to the bag with a 50-ml glass syringe. The addition of the first 50 ml of iodine vapor saturated air activated most of the potential ice nuclei, but the usual procedure was to add a few hundred milliliters of iodine saturated air to compensate for wall losses and to activate all the potential ice nuclei present in the air sample.

After considering the various methods of burning the leaded fuel, such as spraying into burners, we decided to use an internal combustion engine. This would make our results usable for predicting the output of potential ice nuclei in a city, or by a given number of automobiles.

A single-cylinder, 10-hp Kohler engine was fitted with a cotton-pack intake filter and a "T" joint in the exhaust pipe from which samples could be withdrawn. Sampling was accomplished with a large syringe, directly from the end of the "T" fitting. At the moment of its introduction into the bag, the sample was at a temperature somewhere between that of the exhaust (in excess of 600F) and ambient. This involved an uncertainty in the volume of the sample, but no simple way of overcoming this problem was found; to have cooled the sample to ambient temperature before insertion into the bag would have entailed large losses to the walls of the cooling vessel. Because of the uncertainty (overestimation) of the sample volume, the concentrations of potential ice nuclei measured in this way are underestimated to some degree.

For low dilutions (of the order of 10:1), the exhaust air was run directly into the 135-liter bag, and approximately 60 liters of this, at ambient temperature, were put into the 600-liter bag.

No attempt was made to assess the importance of engine rpm and load conditions, although these factors are no doubt of some importance (Hirschler and Gilbert, 1964). The engine was run at the speed imposed by its governor and no loads were applied. The fuel flow was measured with a burette and stopwatch at 20 ml min^{-1}. Air flow through the engine was measured, with a hand anemometer in the intake tube, at 400 liters min^{-1}.

The Aitken count was used as an index of coagulation and sedimentation loss and to indicate successful dilution of the sample. A Gardner small-particle counter was used for this purpose. The Aitken count of the full strength exhaust was always in excess of 10^7 particles ml^{-1}, the upper limit of the instrument scale. This rapidly decreased by coagulation, which rendered measurements at full strength rather difficult. Most measurements were made at dilutions between 10:1 and 10^4:1, a factor to be considered in evaluating the results, since in a natural situation the dilution of the exhaust probably takes place more slowly than in the case where the sample was immediately diluted by 10^3:1. Some coagulation of the diluted sample must take place, but this process would not be nearly as rapid as for an undiluted sample confined within the sampling volume. Coagulation can be expected to modify the temperature spectrum of the potential ice nuclei in a manner other than simply the decreased nuclei concentration that is considered in studies of Aitken nuclei. During coagulation of a given size distribution of ice nuclei, the concentration of small particles is decreased; the concentration of large particles is increased. The temperature spectrum of the ice nuclei distribution in this process would be shifted so there would be less ice nuclei at lower temperatures (small particles) and relatively more ice nuclei at warmer temperatures (large particles).

The final estimate of the temperature activity "spectrum" of iodine-treated automobile exhaust is given in Fig. 1 (curve with open circles). The curve is concave upward over part of its length. This could be real, but could also represent the result of coagulation and sampling at different dilutions at different temperatures. The concentration at the lowest temperature was estimated at a dilution of 10^4:1, and dilution proceeded downward to 10:1 at the warm end of the curve. Thus, coagulation may have enhanced the values on the left and right portions of the curve—on the left (low dilutions) by creating large particles and on the right (very high dilutions) by its absence. For comparison Fig. 1 includes Fletcher's theoretical activity curve for silver iodide (Fletcher, 1962) and the output of the Colorado State University modified Skyfire silver iodide generator (Grant and Steele, 1966).

b. Open flame experiments. To make a quantitative check on the differences between leaded and unleaded gasolines without the complicating factor of a possibly contaminated engine, the following experiment was conducted. Filtered air was passed through a 20-1 bell jar, in which gasoline, supplied through a hypodermic needle, was burned over a small bed of sand. A 10-ml glass syringe acted as a reservoir and fuel pump. A 50-ml glass syringe containing a few iodine crystals imbedded in a cotton pad was then used to inject measured volumes of iodine-saturated air into the chamber. The rate of fuel burning was about 0.02 ml min^{-1} with

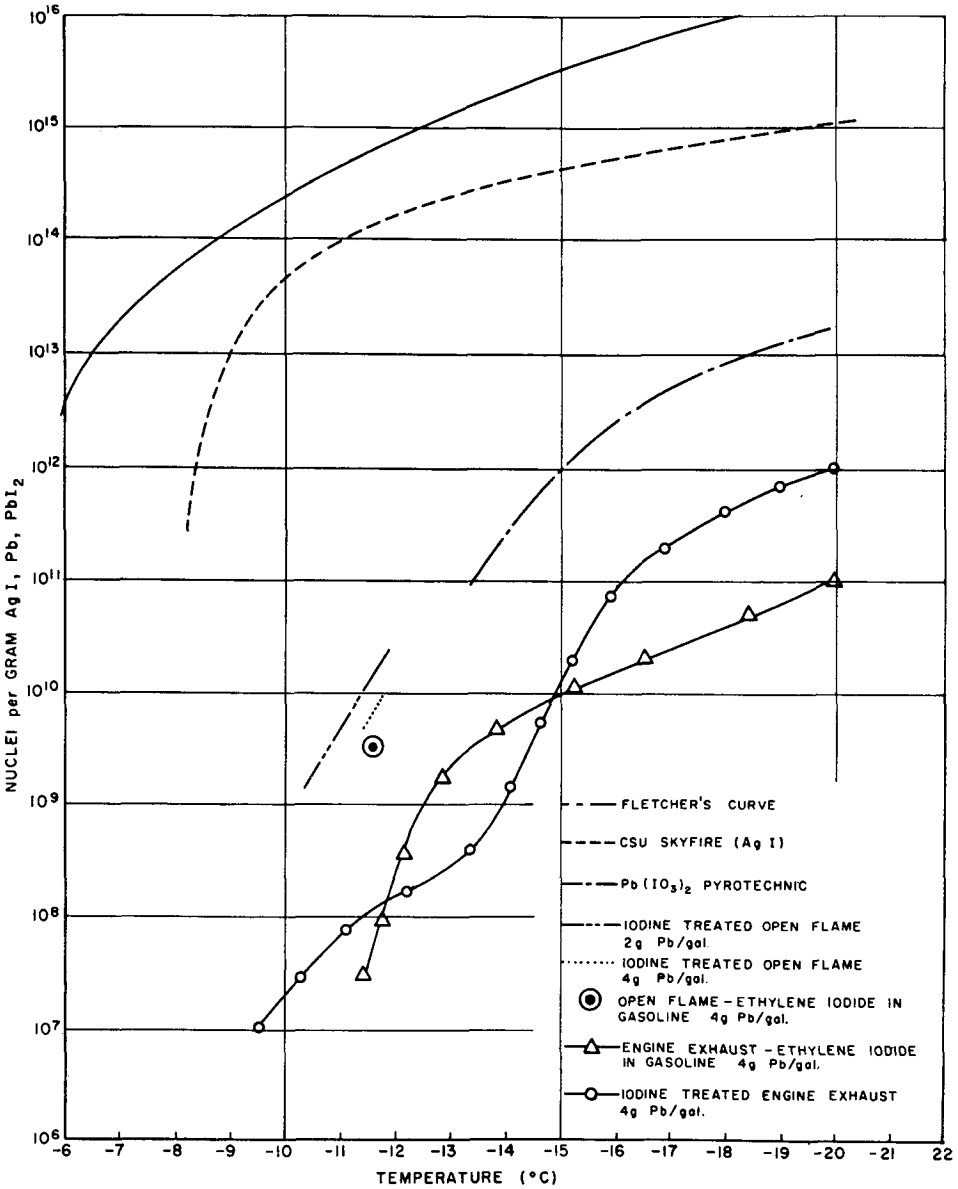

FIG. 1. Ice nucleus production per gram of lead in gasoline, compared with other theoretical and practical ice nucleus producing systems.

air circulation being 10 liters min^{-1}. This is only 4% of the fuel-to-air mixture found in the engine.

When unleaded gasoline (Indolene) was burned in this chamber and iodine introduced, the measured ice nucleus concentration was surprisingly high—1000 $liter^{-1}$ at −15.5C, falling rapidly to 0.9 $liter^{-1}$ at −13.3C. Pure, redistilled isooctane showed very little activity, 2 $liter^{-1}$ at −19.5C, which led us to believe that the unleaded gasoline though lead-free by automotive standards, had become contaminated to the extent of a few milligrams of lead per gallon. Gasoline with a lead content of 2 gm gal^{-1} showed activity some 10^3 to 10^4 times greater than the unleaded gasoline, 5×10^3 $liter^{-1}$ at −11.8C and 3×10^2 $liter^{-1}$ at −10.3C.

It is noteworthy that at −10C the number of nuclei produced per gram of lead by the open flame is about an order of magnitude greater than that produced by the engine. Probably all the lead in the fuel of the open flame appears as small particles, while the engine expels most of its lead (more than 90% by weight) as particles 1 μ in diameter or larger (Hirschler and Gilbert, 1964). Interesting, too, is that the efficiency of the open flame compares favorably with the efficiency of a lead iodate pyrotechnic generator (Finnegan *et al.*[5]), also shown in Fig. 1.

[5] Finnegan, W. G., L. A. Burkardt and P. St. Amand, 1967: The pyrotechnic generation of freezing nuclei. Paper presented at the Conference on Physical Processes in the Lower Atmosphere, Ann Arbor, Mich.

c. Experiments with synthesized fuel. Indolene has some 50 chemicals mixed within its formulation (McEwen, 1966). As mentioned above, when supposedly lead-free Indolene was burned in the chamber in the presence of iodine vapor, some ice nuclei were produced. This suggested that possibly some other nonlead constituent of Indolene might also produce ice nuclei in the presence of iodine vapor. Terpenes in the presence of iodine vapor have been found to result in the formation of ice nuclei (Rosinski and Parungo, 1966). Although Indolene with a tetraetheyl lead formulation did show a 10^3 to 10^4 greater ice nuclei production than Indolene without tetraethyl lead, it was necessary to prove that simply the presence of lead and iodine together could result in the formulation of ice nuclei when a volatile fuel was burned.

A number of fuels were synthesized in the laboratory using isooctane, tetraethyl lead, ethylene dichloride, ethylene dibromide, and some aromatic fuels such as benzene, toluene and xylene. When these fuels were burned in the chamber in the presence of iodine vapor, no ice nuclei would be detected either in the formulas containing no tetraethyl lead, which was expected, or in the formulas containing tetraethyl lead (4 gm Pb gal^{-1}), which was not expected. The conclusion drawn is that the Indolene formulation contains some unidentified agent(s) that acts as a catalyst in the reaction that forms lead iodide from the combustion of Indolene containing tetraethyl lead in the presence of iodine vapor.

Subsequent investigations with the combustion of fuel by flame led to the conclusion that lead and iodine present in a burning fuel are necessary but not always sufficient to produce ice nuclei. The fuels noted above were mixed in various proportions and the additional chemical, ethylene diiodide, was included. No mixture of the fuels that did not have both tetraethyl lead and ethylene diiodide was capable of producing ice nuclei.

A first attempt to add one formula weight of ethylene diiodide to each formula weight of tetraethyl lead met with limited success. We noted that the characteristic violet color of free iodine (from decomposition of ethylene diiodide in the fuel) did not persist in any mixture that contained tetraethyl lead. When one formula weight of ethylene diiodide was added, the violet color soon faded, leaving a colorless liquid. It seems obvious that the free iodine from the decomposition of ethylene diiodide reacted with the tetraethyl lead to form a compound where one or more of the ethyl radicals had been replaced with iodine. These latter compounds are not efficient agents for the production of ice nuclei.

When a small amount of a fuel was mixed with an additional small amount of isooctane containing approximately 10 formula weights of ethylene diiodide and burned immediately, the production of ice nuclei was quite pronounced. Again, when leaded Indolene was added to the fuel, the ice nuclei activity proved to be greater than for any other fuel mixture when utilizing the 10 formula weight addition of ethylene diiodide dissolved in isooctane.

The above experiments were conducted with the ice nucleus counter at a temperature of −12C. No attempt was made to determine the comparative efficiency of the various fuel mixtures as carriers for the production of lead iodide from the combustion of fuels containing tetraethyl lead and ethylene diiodide.

d. Activation of potential ice nuclei at the source. The activation of potential ice nuclei in gasoline engine exhaust requires introduction of iodine by some means. We did this by injecting a saturated iodine-air mixture into the sample bags with a syringe. Another way of activating these potential ice nuclei consists of mixing ethylene diiodide with the leaded gasoline to activate them at their source. We are aware of no reason for this causing harm to the engine. One formula weight (5.2 gm gal^{-1}) of ethylene diiodide was added to Indolene gasoline containing 4 gm Pb gal^{-1} and burned in both the engine and the open flame chamber. The specific yield of ice nuclei was very close to the yield found with post-combustion addition of iodine vapor in both cases, as is seen in Fig. 1. It would appear reasonable to expect that with an optimum addition of the ethylene diiodide, the specific yield might be even higher than by post-combustion treatment.

e. Discussion of experimental technique. We believe that our experimental technique underestimates the number of potential ice nuclei. There are several reasons for this. First is the uncertainty in the sample volume, mentioned previously. Second is simple loss due to handling during transfer by syringe to the bag. There is also some loss caused by a phenomenon that we did not uncover until rather late in the study. Initially, we set the water temperature in the humidifier at as low a value as would yield a good cloud in the cloud chamber and assumed that this was sufficient to insure activation of all the nuclei. On one occasion, however, the water temperature was increased considerably and the count was observed to increase (Fig. 2). In subsequent trials we found that this increase with increasing humidifier temperature continued up to some point, after which the count decreased with further temperature increase. The temperature at which the peak count occurred varied from one trial to another, probably partly as a result of the initial humidity of the sample air. At warm chamber temperatures (−10 to −12C) the peak occurred at water temperatures somewhere near 55C; at cold chamber temperatures (−19 to −21C) it occurred somewhere near 40C water temperature. Our interpretation of this phenomenon centers about the inefficiency of the humidifier and the considerable solubility of lead iodide, as compared with the solubility of silver iodide, in water. The humidifier with which the counter is equipped requires rather high water temperatures to form a cloud in the cold chamber. A humidifier recently tested at NCAR is capable, by exposing the air more completely to the water surface,

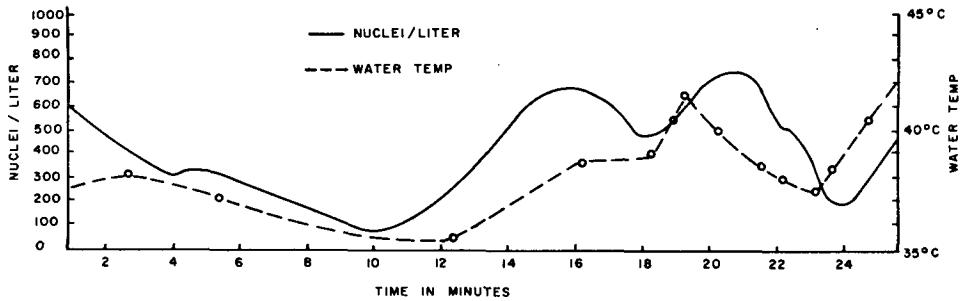

FIG. 2. The effect of humidifier water temperature on ice nucleus count. Chamber temperature, −11.3C.

of maintaining a good cloud in the cold chamber at much lower water temperatures.

The significance of the water temperature is that the higher it is, the greater is the cooling rate of the air as it enters the cold chamber. At high temperatures, much of the water is lost to the cold walls and does not appear as cloud water. Temperature differences between the cold wall and the adjacent saturated air of as much as 70C in the upper part of the chamber are probably possible. In such a case the cooling rate would be so rapid that high supersaturations would occur in the air, with the result that a droplet would form on the soluble lead iodide particle, which then would dissolve and no longer be available as an ice nucleus. At the point at which we observe the peak counting rate, the loss due to wetting and dissolving of the particles probably equals the count-increasing effect of increasing cloud liquid water content. Both processes probably are taking place simultaneously even before the peak is reached. This would mean that we never detect the full concentration of ice nuclei with this system. It is also likely that particles are carried by the large flux of vapor to the walls of the upper part of the chamber and are lost to the glycol coating.

4. Applications to cloud modification

a. Natural activation of exhaust particles. The possibility that exhaust-produced particles can be activated by iodine naturally present in the atmosphere must be considered. Recent measurements of iodine in the air (Duce and Winchester, 1965; Duce *et al.*, 1963, 1965, 1966; Lininger *et al.*, 1966; Winchester and Duce, 1966) rarely indicate the presence of more than a few nanograms of iodine per cubic meter, which would probably be enough to activate many lead particles if there were some efficient way to get the iodine to the particle surface. Unfortunately, we have no basis for speculation on this point.

b. Artificial activation of exhaust particles. The activation of the potential ice nuclei at their source could make it possible to treat the gasoline supply of an entire city, county, or other such unit with ethylene diiodide during an aptly chosen climatic period (hail season, rainy season, etc.) and to study any modifications to weather that result in the area. Another interesting, simultaneous application of such a large-scale experiment would be the concept of utilizing the ice nuclei produced as an air tracer. With proper distribution, a superhighway would become a line source, a city a very intense point source, etc.

It is immediately obvious that as a cloud seeding device a single gasoline engine is extremely inefficient when compared to the silver iodide generators in current use. The efficiency in terms of nuclei per gram is not all important, however, when one considers the number of cars and the amount of leaded gasoline being burned in even small cities. Possibly more important is the extended source that is created by the automobiles of a city and its suburbs.

To obtain a rough idea of the potential automobile concentration in a populated area, we may consider the following approximate figures: In the city of Denver (250 km^2) there are 250,000 registered vehicles, or 1000 vehicles km^{-2}. In a 5-county area of approximately 4000 km^2 centered on Denver, there are 600,000 registered vehicles, a density of 150 vehicles km^{-2}. Between the hours of 0700 and 1900, 192,000 cars cross the boundaries of the 1.5 km^2 area known as "Downtown Denver."

If, in a city such as Denver, there is an area of 1 km^2 that has 1000 automobiles fairly uniformly distributed and burning gasoline containing 3 gm Pb gal^{-1} at the rate of 1 gal hr^{-1} each, the rate of production of potential ice nuclei active at −20C is, according to Fig. 1, 3×10^{15} nuclei hr^{-1} km^{-2}. If after 1 hr this has uniformly diffused into a layer 1 km deep, the concentration in that layer is 3×10^{15} nuclei $km^{-3}=3$ nuclei ml^{-1}.

It is not possible to say whether this is an over- or underestimate of the real situation, but similar calculations are often displayed to illustrate the potential of fixed-point silver iodide burners. The computation for this case, involving moving sources in great numbers, is possibly closer to the truth than calculations based on the stationary generator.

In a city, the time and space distribution of gasoline consumption is continuous and complex. If traffic is heavy before the onset of vertical mixing and dilution, there is a storing-up of the particles in the lower few hundreds of feet. This would raise the surface concentration to very high values during the cooler hours of

the day. In most cities the morning traffic rush occurs at such hours. Under light-wind conditions most of the automobile exhaust output of the evening, night and morning hours would be stored until convection commenced the following day, when it would be diffused upward.

If we consider an aircraft such as a DC-6 burning 6 gal min^{-1} of gasoline (4 gm Pb gal^{-1}), we arrive at a potential output of 4×10^{11} nuclei sec^{-1} active at -20C. This compares not unfavorably with a high output silver iodide generator that produces 10^{14} nuclei gm^{-1} of AgI at -20C and consumes an acetone solution containing 120 gm AgI hr^{-1}, yielding 3×10^{12} nuclei sec^{-1}.

5. Potential ice nuclei and air pollution

Although it has not yet been demonstrated that the ce nuclei activated by iodine in city air are lead particles, we think this is the case. We had planned to make, as should be done, some parallel measurements of potential ice nuclei and mass concentration of lead in the air. In areas where automobiles are operating it may be difficult, however, to establish any relationship between the two measures since over 90% of the mass of lead exhausted by automobiles is in particles over 1 μ in diameter. A few particles as large as, say 5 μ, would have a strong effect on the mass concentration but none whatever on the potential ice nuclei concentration, which would be determined by the very fine particles. If, at some future date, these parallel measurements are made, it would be best to carry them out in some rural area, free of local traffic.

The existence of a direct relationship between lead in air and the potential ice nuclei would be of great importance for studies of urban air pollution as it would establish an excellent real-time lead detection method of extremely high sensitivity. The only reservation we hold at present stems from the demonstration by Rosinski and Parungo (1966) that terpenes, organic substances produced by plants, react with iodine to produce ice nuclei.

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REFERENCES

Bakulina, Ye. V., T. N. Gromova and P. N. Krasikov, 1962: A method for the use of aqueous solutions of lead iodide as agents in supercooled clouds and fogs. *Tr. Gl. Geofizi. Observ. A. I. Voyeykov*, No. 126, 10–15. OTS translation 63-21573, U. S. Department of Commerce, Clearinghouse for Federal Scientific and Technical Information, Springfield, Va. 22151.

Duce, R. A., J. T. Wasson, J. W. Winchester and F. Burns, 1963: Atmospheric iodine, bromine and chlorine. *J. Geophys. Res.*, **68**, 3943–3947.

——, and J. W. Winchester, 1965: Determination of iodine, bromine, and chlorine in atmospheric samples by neutron activation analysis. *Radiochim. Acta.*, **4**, 100–104.

——, ——, and T. W. Van Nahl, 1965: Iodine, bromine and chlorine in the Hawaiian marine atmosphere. *J. Geophys. Res.*, **70**, 1775–1799.

——, —— and ——, 1966: Iodine, bromine and chlorine in winter aerosols and snow from Barrow, Alaska. *Tellus*, **18**, 238–249.

Fletcher, N. H., 1962: *The Physics of Rainclouds.* Cambridge University Press, 386 pp.

Grant, L. O., and R. L. Steele, 1966: The calibration of silver iodide generators. *Bull. Amer. Meteor. Soc.*, **47**, 713–717.

Gromova, T. N., P. N. Krasikov, V. T. Lenshin, G. T. Nikandrova, M. A. Khimach and N. S. Shishkin, 1962: Experiments concerning the interaction of aqueous solution of lead iodide on supercooled clouds. *Tr. Gl. Geofizi. Observ. A. I. Voyeykov*, No. 126, 16–21. OTS translation 63-21573, U. S. Department of Commerce, Clearinghouse for Federal Scientific and Technical Information, Springfield, Va. 22151.

Harris, F. S., Jr., D. C. Sparks and R. G. Layton, 1963: Nucleation of ice on lead iodide. *J. Atmos. Sci.*, **20**, 149–152.

Hirschler, D. A., and L. F. Gilbert, 1964: Nature of lead in automobile exhaust gas. *Arch. Environ. Health*, **8**, 279–313.

Langer, G., J. Rosinski and C. P. Edwards, 1967: A continuous ice nucleus counter; its application to tracking in the troposphere. *J. Appl. Meteor.*, **6**, 114–125.

Lininger, R. L., R. A. Duce, J. W. Winchester and W. R. Matson, 1966: Chlorine, bromine, iodine and lead in aerosols from Cambridge, Massachusetts. *J. Geophys. Res.*, **71**, 2464–2475.

McEwen, D. J., 1966: Automobile exhaust hydrocarbon analysis by gas chromatography. *Anal. Chem.*, **38**, 1047–1054.

Morgan, G. M., Jr., 1967: Technique for detecting lead particles in air. *Nature*, **213**, 58–59.

Rosinski, J., and F. Parungo, 1966: Terpene-iodide compounds as ice nuclei. *J. Appl. Meteor.*, **5**, 119–123.

Schaefer, V. J., 1954: Silver iodide and lead iodides as ice crystal nuclei. *J. Meteor.*, **11**, 417–419.

——, 1966: Ice nuclei from automobile exhaust and iodine vapor. *Science*, **154**, 1555–1557.

Sulakvelidze, G. K., 1966: Results of the Caucasus anti-hail expedition of 1965. *Vysokogornyi Geofizi. Inst.*, **7**, 1–61.

Winchester, J. W., and R. A. Duce, 1966: Coherence of iodine and bromine in the atmosphere of Hawaii, northern Alaska and Massachusetts. *Tellus*, **19**, 287–292.