

## Gaseous Iodine Measurements and Their Relationship to Particulate Lead in a Polluted Atmosphere

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### ABSTRACT

Gaseous iodine and particulate iodine and lead samples were collected simultaneously in a polluted atmosphere using activated charcoal and membrane filters. Concentrations of gaseous iodine varied from 10–18 ng m<sup>-3</sup> and particulate iodine from 2–15 ng m<sup>-3</sup> as determined by neutron activation analysis. The total iodine concentration found in this work is approximately twice that found in the unpolluted marine atmosphere. Lead concentrations varied from 0.4–3.7 μg m<sup>-3</sup> as determined by atomic absorption spectrophotometry.

There is an apparent relationship between the concentration of total particulate matter in the air and the ratio of particulate iodine to gaseous iodine. This relationship is consistent with laboratory investigations of gaseous I<sub>2</sub> adsorption onto combustion aerosols reported by other investigators. Calculations indicate that the concentrations of gaseous iodine measured in this work should be sufficient to activate all lead containing particles to ice nuclei in a polluted atmosphere. It is suggested that large concentrations of ice nuclei are not generally observed in polluted air at ground level because the reaction of lead and iodine at the concentrations observed in this work proceeds slowly.

### 1. Introduction

There has been considerable interest recently in the possibility of weather modification by the formation of ice nuclei from air pollution products. Schaefer (1968a, 1969) has demonstrated evidence of such ice nuclei at and below inversions near large polluted cities. Schaefer (1966, 1968a, b, 1969), Morgan (1967) and Hogan (1967) have suggested that ice nuclei can be formed by the reaction of elemental iodine vapor and lead aerosols from automobile exhaust and gasoline vapors, and have shown that these reactions do occur in the laboratory. Schaefer (1968a) found that the burning of wood chips followed by the addition of auto exhaust will produce large concentrations of ice nuclei, and he suggested that the combustion of such substances might release sufficient quantities of iodine to react with lead aerosols to produce ice nuclei in polluted areas.

The concentration of I in the atmosphere as reported in the literature is extremely variable. Many values which are often quoted are those obtained in Europe in the 1920's (Von Fellenburg, 1926; Cauer, 1930). However, Cauer (1937) has reported that these earlier measurements, which generally did not distinguish between gaseous and particulate components, were highly contaminated by the burning of seaweed along the northern European coast. This was the commercial method of obtaining I<sub>2</sub> prior to the mid 1930's. Recent

atmospheric iodine measurements have ranged from a few nanograms of particulate iodine in marine air (Duce *et al.*, 1965, 1967) to several micrograms per cubic meter of presumably both gaseous and particulate I (Eggleton *et al.*, 1963; Paslawska and Ostrowski, 1968). It is not known if these differences in I concentration are real or if the differences are a result of analytical or collection methods. Duce *et al.* (1965) attempted to measure gaseous iodine using a carbonate bubbler preceded by a filter arrangement. Their values ranged between 2 and 18 ng m<sup>-3</sup> in the Hawaiian marine atmosphere. Recently, the first reliable measurements of gaseous I in the marine environment have been made by Moyers (1970) in Hawaii using the technique described in this work. His results suggest an average concentration of 8±3.5 ng m<sup>-3</sup> for gaseous I in an unpolluted marine atmosphere.

The purpose of this work was to measure lead and iodine simultaneously in a polluted atmosphere for the first time and to investigate how the I concentration (especially gaseous) in this environment is affected by the degree of particulate air pollution. An evaluation of the relationship between atmospheric I and Pb should lead to a better understanding of the possibility of weather modification due to the formation of ice nuclei in polluted air.

### 2. Experimental procedure

Samples of gaseous iodine as well as particulate iodine and lead were collected simultaneously in Cambridge, Mass., during the summer of 1969. The

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collection site was located on a roof  $\sim 10$  m above the ground in an industrial area near the Massachusetts Institute of Technology. The particulate samples were collected on Millipore type EH and HA filters which have acceptable blanks for I and Pb. The gaseous I was collected on activated charcoal which was pre-cleaned by heating to 750C for two weeks in a vacuum approximately  $10^{-5}$  cm Hg. This produced charcoal with an iodine blank of 2–5 ppb. An electrostatic precipitator was used to remove the particulates from the air stream prior to collection of gaseous iodine on the charcoal. Tests with the 8-day radioactive iodine tracer  $^{131}\text{I}$  and with sea salt aerosols indicated that neither the ozone produced by the precipitator nor the corona discharge itself will alter the concentration of gaseous  $\text{I}_2$  by more than 3–4%.

The gaseous and particulate iodine samples were analyzed by neutron activation using the M.I.T. reactor ( $\phi_{th} \approx 2.3 \times 10^{13}$  neutrons  $\text{cm}^{-2} \text{sec}^{-1}$ ). For each sample the charcoal and one-half of the Millipore filter were sealed in polyethylene vials, irradiated for 20 min, and added to separate flasks containing 10 ml of hot, 1M NaOH solution and  $\sim 30$  mg of iodate carrier. Following oxidation and reduction steps to exchange the radioactive iodine with the carrier, the iodine was chemically purified using a modification of the procedure of Duce and Winchester (1965). Subsequent washings indicated that this procedure resulted in quantitative exchange between the radioactive  $^{128}\text{I}$  and the  $^{127}\text{I}$  carrier. The iodine, as a AgI precipitate, was then beta-counted using a gas flow proportional counter with an automatic sample changer. Standards were used with each sample to ensure accurate results.

The particulate Pb was removed from the second half of the filter with ultrasonic agitation in 0.1N  $\text{HNO}_3$ . This solution was then analyzed using a Perkin-Elmer 303 Atomic Absorption Spectrophotometer.

### 3. Results and discussion

The results of the analyses are presented in Table 1. Two types of weather characterized the sampling period. Samples 1–5 were collected during predominantly hazy days with weak westerly winds, i.e., winds blowing from the land. Samples 6–12 were collected during days of clear, cool weather and brisk easterly winds blowing from the sea. There is a statistical difference in the concentrations of Pb and particulate I for the two different meteorological conditions. For samples 1–5 the average lead concentration is  $2.9 \pm 0.7 \mu\text{g m}^{-3}$  and the average particulate iodine concentration  $10.5 \pm 3.5 \text{ ng m}^{-3}$ . For samples 6–11 the average lead concentration is  $1.1 \pm 0.6 \mu\text{g m}^{-3}$  and the average particulate iodine concentration  $4.0 \pm 2.4 \text{ ng m}^{-3}$ . Analysis of these averages by the *t* test indicates that for samples collected under the two different meteorological conditions, the concentration averages are statistically different for both particulate I and Pb at a 1% significance level. The

TABLE 1. Concentrations of gaseous iodine and particulate lead and iodine collected in Cambridge, Mass.\*

Sample no.	Date (1969)	Time (EST)	Gaseous iodine ( $\text{ng m}^{-3}$ )	Particulate iodine ( $\text{ng m}^{-3}$ )	Particulate lead ( $\mu\text{g m}^{-3}$ )
1	2 Sept.	1000–1800	—	—	2.04
2	3 Sept.	0630–1130	17.8	9.9	2.31
3	4 Sept.	0645–1145	11.0	9.6	3.32
4	4 Sept.	1200–1630	18.5	15.4	3.70
5	4–5 Sept.	1645–0530	12.7	7.2	3.30
6	5 Sept.	0530–1545	13.7	3.2	$0.68 \pm 0.10$
7	15 Sept.	1240–1900	—	1.9	$1.33 \pm 0.20$
8	15–16 Sept.	1900–0550	14.4	2.8	$0.45 \pm 0.10$
9	16 Sept.	0550–1620	12.5	3.9	1.84
10	16 Sept.	1620–2340	10.2	8.0	$1.66 \pm 0.25$
11	16–17 Sept.	2340–0540	14.7	—	$0.39 \pm 0.10$

\* All analytical uncertainties are  $\pm 10\%$  unless otherwise indicated.

values shown for the lead concentrations are within the range of values reported by the U. S. Public Health Service (1962, 1968) for the Cambridge-Boston area.

The gaseous I concentrations show two interesting characteristics. First, the concentration of gaseous iodine varies much less with changing meteorological conditions than particulate iodine and lead. The average gaseous I concentration for samples 1–5 is  $15.0 \pm 3.5 \text{ ng m}^{-3}$  and  $13.1 \pm 2.4 \text{ ng m}^{-3}$  for samples 6–11. Second, the average concentration of gaseous I for all samples is  $13.9 \pm 2.8 \text{ ng m}^{-3}$ , which is less than twice the average value, and within the range of values observed in the unpolluted marine atmosphere by Moyers (1970). This indicates that, at least in this study, if a pollution source exists for I, this source is apparently not adding large quantities of gaseous iodine to the atmosphere relative to that coming from the sea. The most commonly suggested pollution source of I is fossil fuels, and it is possible that the amount of pollution iodine is seasonally dependent, with more I added to the air in winter and less in summer.

A comparison of particulate and gas samples in the unpolluted marine atmosphere gives a ratio of particulate to gaseous iodine of 0.25–0.50 (Moyers). In Cambridge it was found that the samples collected during the period characterized by easterly winds and low lead concentrations had a particulate-to-gaseous-iodine ratio which ranged between 0.2 and 0.8, while during the period of westerly winds and high lead content the ratio was 0.5–0.9. Clough *et al.* (1965) have suggested that adsorption of  $\text{I}_2$  on particles from combustion processes is largely a reversible adsorption and presented the empirical relationship that the particulate-to-gaseous-iodine ratio ( $\text{Ip/Ig}$ ) should be equal to approximately  $1.5 \times 10^8$  times the mass of particulate matter in the air ( $\text{gm m}^{-3}$ ) and should be independent of gaseous iodine concentrations  $\leq 10^{-7} \text{ gm}^{-3}$ . Those values were obtained by studying the adsorption of  $\text{I}_2$  vapor (using  $^{131}\text{I}$ ) onto particles produced from the combustion of coal at various particulate matter and gaseous iodine concentrations. Thus, at a total particulate mass of  $100 \mu\text{g m}^{-3}$ ,  $\text{Ip/Ig}$  would be approximately 0.15 while at a particulate mass of  $1000 \mu\text{g m}^{-3}$  the same ratio would be  $\sim 1.5$ . The average weight of total particulate

material in Boston-Cambridge air as given by the Bureau of Environmental Sanitation, Department of Public Health, Commonwealth of Massachusetts (1968), is approximately  $90 \mu\text{g m}^{-3}$ . According to the U. S. Public Health Service (1968) the average Pb concentration in the Boston-Cambridge area is about  $1 \mu\text{g m}^{-3}$ , and this implies that lead represents  $\sim 1\%$  of the total suspended particulate matter in Boston-Cambridge air. Using the empirical formula of Clough *et al.* (1965), it would be expected that  $I_p/I_g$  should be 0.15 when the Pb concentration is  $1 \mu\text{g m}^{-3}$ . Fig. 1 shows a plot of particulate lead vs  $I_p/I_g$  for the Cambridge samples. A least-squares regression line along with the standard error of estimate  $\sigma$  of the line is also given in Fig. 1. The correlation coefficient of 0.80 for Pb vs  $I_p/I_g$  indicates that total particulate matter apparently is related to the ratio of particulate-to-gaseous-iodine concentration (if lead is assumed to be a monitor of the total particulate mass in the air). If it is assumed that the Pb concentration is approximately equal to  $1\%$  of the total particulate mass concentration, then from the regression line in Fig. 1,  $I_p/I_g$  for these samples in Cambridge can be expressed by

$$I_p/I_g = (1.8 \times 10^3)m + 0.16, \quad (1)$$

where  $m$  is the mass concentration ( $\text{gm m}^{-3}$ ) of total particulate matter in the air,  $1.8 \times 10^3$  the slope of the regression line plotted in Fig. 1, and 0.16 the y intercept of the regression line.

The standard deviation of the slope of the regression line plotted in Fig. 1 is  $\pm 0.6 \times 10^3$ . Thus, the value for the slope from this work, 1200–2400, is in fairly close agreement with the value, 1000–2000, suggested by Clough *et al.* (1965).

Schaefer (1966) estimated that air polluted by automobile exhausts can have  $\sim 10^9$  particles containing lead per cubic meter which may act as ice nuclei after exposure to  $I_2$  vapor. Schaefer (1966) further estimated that 1 gm of  $I_2$  vapor would be sufficient to activate  $10^{18}$  particles containing lead from automobile exhaust. Thus, from the two previous statements, it would appear that  $1 \text{ ng m}^{-3}$  of gaseous  $I_2$  in polluted air should activate all the lead particles in this air. Schaefer (1969) has suggested that gaseous  $I_2$  concentrations in polluted air should be considerably higher than this value. In the free atmosphere, however, Schaefer (1966) states that ice nuclei normally number from  $10^1$ – $10^4$  per cubic meter.

The measurements in Cambridge gave an average gaseous iodine concentration of  $\sim 14 \text{ ng m}^{-3}$ , and this number was relatively independent of the degree to which the air was polluted. This amount of gaseous  $I_2$ , although lower than the values generally estimated for polluted air, should be sufficient to activate all potential ice nuclei contained in an urban atmosphere polluted by automobiles. However, no one has reconciled the fact that with the measured quantities of lead and predicted quantities of iodine present in polluted air the corre-

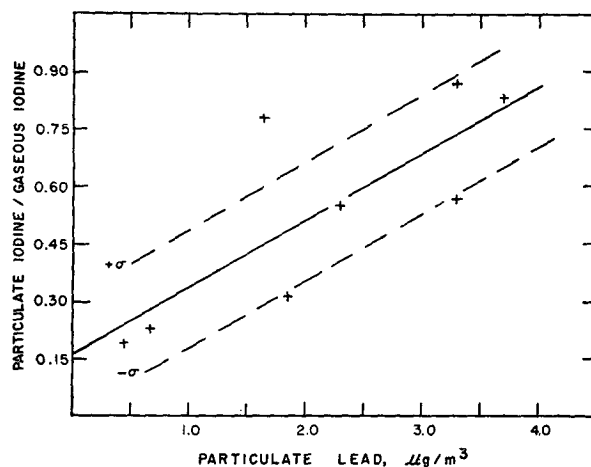


FIG. 1. Variation of the particulate-iodine-to-gaseous-iodine ratio with changing particulate lead concentration in Cambridge, Mass.

sponding quantity of ice nuclei are not observed. There may be several explanations for this: 1) the gaseous iodine observed in the atmosphere may not be elemental iodine ( $I_2$ ); 2) at the concentration of gaseous iodine and/or lead particles present in a polluted atmosphere, the kinetics of the reaction may be very slow; and 3) the carbonaceous material and non-lead inorganic materials in pollution particles may "shield" the lead from reaction with iodine.

Assuming the gaseous iodine in the marine atmosphere is  $I_2$ , Moyers (1970) has shown that the behavior and concentrations of atmospheric iodine can be explained quite well thermodynamically. If the sea is a major source of gaseous iodine in Cambridge, it would seem almost certain that at least part of this gaseous iodine will be molecular iodine ( $I_2$ ). The reversibility of the adsorption as reported by Clough *et al.* also fits well with the observations in this investigation, suggesting that the iodine is present as  $I_2$  vapor.

It is likely that a combination of 2) and 3) above may explain the low concentrations of ice nuclei observed in polluted air. The fact that Schaefer (1969) has not observed ice nuclei in ground-level polluted air, but has observed large concentrations of ice crystals, which have presumably formed on ice nuclei, at altitudes of 500–1500 m over and downwind from polluted cities, may indicate that a fairly long period of time is required for ice nuclei formation by the reaction of iodine vapor and lead containing particles.

Schaefer (1966) has shown that when air from automobile exhaust is exposed to air with "a trace of iodine vapor" present, large concentrations of ice nuclei are formed in a matter of seconds. In a typical experiment Schaefer added  $\sim 0.1$  liter of air from a bottle containing iodine crystals at a temperature of 25C. In such an experiment Schaefer (1966) reported that  $10^9$  or more ice nuclei per cubic meter will form within 10 sec. Since the vapor pressure of solid  $I_2$  at 25C

is  $\sim 0.4$  mm, this air has a partial pressure of  $I_2(g)$  equal to  $\sim 5 \times 10^{-4}$  atm when saturated. Thus, 0.1 liter of such air would contain about  $6 \times 10^{-4}$  gm of iodine, and when diluted to 100 liters in a cold chamber the resulting concentration in this chamber would then be  $6 \times 10^{-3}$  gm $^{-3}$ , i.e., more than five orders of magnitude higher than the concentration of gaseous iodine in the free air. Automobile exhaust directly from a car certainly has a concentration of Pb particles much higher than that in even the most polluted atmosphere. Thus, from reaction kinetics alone, the time required to form measurable numbers of ice nuclei may be much longer than the time required under the laboratory conditions just described.

Lead is apparently emitted from the automobile exhaust system as very small particles (Mueller *et al.*, 1964) and these particles would be expected to coalesce rather rapidly with each other and other small particles until they attain radii of 0.1–0.3  $\mu\text{m}$  (Junge, 1963). This type of growth mechanism undoubtedly results in particles with mixed amounts of organic and inorganic material, and the non-lead substances may act to "shield" the lead from reaction with iodine. In addition, the Pb compounds initially present in the automobile exhaust almost certainly undergo other chemical reactions as the particles age in the atmosphere. This might effectively render some of the Pb inert to reaction with  $I_2$ .

In summary, from this preliminary study there is evidence that total particulate matter (as monitored by particulate lead) is related to the ratio of particulate to gaseous I in polluted air in Cambridge. Although the gaseous  $I_2$  concentration is not as high as had previously been predicted for a polluted atmosphere, it appears that there should be sufficient gaseous iodine present in Cambridge air to activate all the lead containing particles to ice nuclei. The relatively low concentration of ice nuclei generally observed in polluted air compared to that observed in laboratory studies of the lead-gaseous iodine reaction may be largely due to slower reaction rates under free atmosphere conditions. The formation of ice nuclei by the lead-iodine reaction could be much more serious in any location where a pollution source of iodine would significantly raise the gaseous  $I_2$  concentration in areas of heavy automobile pollution. Thus far, no evidence of serious gaseous  $I_2$  pollution has been detected in the Cambridge area. However, it is not meant to be implied by this paper that the factors reported here are representative of areas and times other than those where and when these measurements were made. Many more measurements are required to describe the gaseous iodine concentration of polluted air and its relationship to the lead concentration of polluted air and further studies of this problem are underway in our laboratory.

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