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Introduction

by Robert Rabin*

This volume is a progress report of investigations on compounds of lead in the environment. All of the research included was sponsored initially by the National Science Foundation's (NSF's) Office of Interdisciplinary Research (OIR) and later, under the NSF's Research Applied to National Needs (RANN) Program.

Set up in 1969, the Office of Interdisciplinary Research deliberately sought to motivate investigators to work in interdisciplinary teams to examine selected societal problems. For example, we felt that many aspects of environmental pollution transcended traditional boundaries of media and scientific inquiry. Implementation of such interdisciplinary research would require the characterization and measurement of specific pollutants; investigation of the physical and chemical processes involved in their transport, deposition, and fate; ecological compartmentation; and mobility and effects within species, populations, and ecosystems. All of this work would be planned and conducted under a goal and a subset of specific research objectives, usually by scientists at a single institution.

In the winter of 1971, the OIR philosophy was incorporated into the RANN Program, which, in turn, was established as a new foundation directorate named Research Applications. The latter was administratively equivalent to such existing directorates as Education and Research. Within RANN, a Division of Environmental Systems and Resources was organized, and the Trace Contaminants Program became operational. Although this Program matured under RANN, its first grants for interdisciplinary research on lead were provided by OIR from the fiscal year 1969 budget. Lead research continued to be a major program enterprise through fiscal year 1976.

RANN's sponsorship of lead research by teams of scientists became rooted chiefly in three institutions: the University of Missouri at Rolla (point source pollution from lead mining, milling, and smelting

operations in a forest ecosystem), the University of Illinois (lead deposition and fate in a predominantly cropland ecosystem), and the Colorado State University (atmospheric chemistry and physics and lead transport processes). The program evolved to include smaller, but scientifically significant projects directly related to human health and a joint deciduous forest ecosystem study between teams from the University Missouri at Rolla and the Oak Ridge National Laboratory, recently renamed Holifield National Laboratory (HNL).

Throughout the course of these studies, progress was characterized by many meetings and seminars attended by scientists of the grantee institutions; exchanges of samples from field expeditions; and collaborations on chemical analyses and data reductions. Information exchange with industrial managers and scientists was strongly encouraged by the NSF program managers and, indeed, many in the industry took advantage of and benefited from this policy. Similarly, exposure to in-house work by the lead industry and their concerns provided university researchers and their students with a more complete view of the national problem.

The RANN Program insists that within its scope of work, each grantee institution incorporate user-related outreach efforts so that data in useful form are rapidly made available to local and regional environmental managers. Through the years, RANN-sponsored lead research results have had considerable exposure before the officials of the U.S. Environmental Protection Agency (EPA), local and state environmental agencies, and the concerned industries. The development of such user relationships has never been encouraged as a substitute for, or to subvert channels normally used to communicate research results. However, when public policymakers required relevant data before promulgating decisions affecting environmental quality, scientists who produced such data support with public funds have responded to this need.

In 1972 the National Academy of Sciences (NAS) published *Lead: Airborne Lead in Perspective*, one of a series of evaluations of current knowledge of selected air pollutants. The NAS report on lead dealt largely with biological effects and clinical manifesta-

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tions in man and with animal toxicity. But the report, in its recommendations for further research, also noted aspects of the problem that had been little studied. RANN's support, anticipating some deficiencies in knowledge recognized by the NAS, focused chiefly on improved understanding of the atmospheric behavior of lead compounds, chemical characterization, and analytical methods applicable to a broad range of field sampling in various ecosystems, and susceptibility of animals and plants to lead. With few exceptions, such support concentrated on the nonhuman aspects of lead in natural ecosystems. In effect, this RANN volume can be viewed as a companion to the earlier NAS report, extending findings in some areas and examining in detail aspects not previously covered.

Some of the data reported here may prove to be controversial or are still incomplete. For example, uptake of lead compounds in plants through root systems depends on transport systems and soil physics, chemistry, and mechanics, none of which is well understood. The mode and extent of foliar uptake also require much more study, and the relationship of soil microbes to plant health in the presence of anomalously high soil concentrations of lead (and other metals) is not clear.

In other respects, the overall picture is less occult. Analytical methods have improved; the analyst is considerably more cognizant of matrix effects and other pitfalls, and the use of standard reference materials is now widespread. Input-output (mass balance) analysis of lead in natural ecosystems is possible and can be a powerful method to identify sinks of high concentration for further research. Physical modeling in wind tunnels of atmospheric lead in simulated city canyons has provided new information on urban atmospheric transport mechanisms. Considerably more data are now available on the potential of airborne lead to form ice nucleants related to weather modification. The following chapters address these and other aspects in detail. Additional research needs and recommendations are summarized at the conclusion of each chapter, and part VI overviews progress and needs as a whole.

EPA's attempt to regulate lead additives in gasoline has been nullified by recent judicial action.¹ In this case, the majority held that EPA could not show that auto lead emissions contribute significantly to blood lead levels, thereby endangering the public health. The issue is complicated by the concern for energy conservation. Leaded fuel is more efficiently burned in internal combustion engines of high compression, an important consideration under present petroleum market conditions. On the other hand, the catalytic converter is now in wide use in new cars to reduce other auto emissions. Lead in fuel poisons the catalyst however, and rapidly destroys the utility of the converter. To solve this problem, use of unleaded fuel is specified by manufactur-

ers of new cars. Some saw a solution to the lead problem in the phaseout of older cars without recourse to regulating the lead content of fuel.

Recent evidence of catalytic converter failure to perform to specifications on the road, even when lead-free fuel is used, and the release by the converter of sulfuric acid mist is disturbing. These observations, coupled with the concern over platinum scarcity and unpoven capability (on a national scale) to sufficiently recycle it from used converters, will likely keep the lead issue before us. The universality of the catalytic converter thus seems doubtful, and other technological solutions for reducing emissions may call for leaded fuel use in the short run.

In the current adversarial climate, some observers seek solace in the possibility that crude oil prices, deregulation of domestic "old oil" prices, more efficient auto engines, and new car costs will aggregate to produce conservation in automobile usage. A downward shift in life style incurred by forced conservation is unlikely to be accepted gracefully by Americans. The automobile is not viewed as a luxury, and the industry complex that produces it and insures its use is pervasive and highly important to the national economy. People of the United States may choose to forego many necessities and amenities before conservation has any major effect on fuel and lead consumption. Neither conservation nor engine retrofit technology seems to be a satisfactory solution to the problem of emitted pollutants. Social and economic issues involved in the use of the auto in life in the United States tend to confound the central problem of lead as a public health hazard, because lead usage is not easily divorced from all the other aspects.

As scientists we still have work before us. We have neither demonstrated to the satisfaction of the courts a cause and effect relationship between automotive lead emissions and depreciation of public health, nor have we excluded this as a possible or even likely event. We also have incomplete confidence in our knowledge of ecological effects.

I am indebted to Prof. Ben. B. Ewing, Robert Metcalf, Herbert Laitinen, and Dr. Gary Rolfe of the University of Illinois at Urbana-Champaign; Prof. Harry Edwards of the Colorado State University; and Prof. Bobby Wixson and Charles Jennett of the University of Missouri at Rolla. Under their leadership many people (including me) were educated and inspired. Highly significant contributions to the total philosophical and experimental approach were made in the biomedical sciences by Prof. George Wetherill and Dr. Michael Rabinowitz of the University of California at Los Angeles and by Paul Hammond of the University of Cincinnati Medical School. In ecology and analytical chemistry the same is to be said of the team at HNL headed by the indefatigable Drs. William Fulkerson, W. D. Shults, and Robert Van Hook. I also gratefully note the warm support, forbearance, and advice of Drs. Stanley Auerbach and David Reichle of the Environmental Sciences Division, HNL.

¹U.S. Court of Appeals for the District of Columbia Circuit; No. 73-2205 (various industrial organizations versus EPA); argued Sept. 9, 1974; decided Jan. 28, 1975.

Dr. Randy Boggess, Professor Emeritus, University of Illinois, as senior editor of this volume, served as counselor, shepherd, helmsman, and midwife. All of us are humbled by his wisdom, talents, and dedication.

The research reported herein was followed by our scientific colleagues in industry. At NSF we frequently sought their cooperation, consultation, and scientific collaboration. Special thanks are owed Drs. Gary Ter Haar (Ethyl Corp.), Emmett Jacobs (E. I. du Pont de Nemours & Co., Inc.), Jerry Cole and Don Lyman (International Lead Zinc Research Organization), and Mr. Norman Anderson (AMAX, Inc., and COMINCO) and his colleagues in competition in the lead-mining operations in Missouri.

Many persons in the Federal Government were devoted critics and helpmates to all of us. I acknowledge our gratitude particularly to Ray Johnson (Department of the Interior, later at NSF), Lindsay Norman (Interior), Herbert Wiser (EPA), William

"Hub" Allaway (Agriculture), John Lagerwerff (Agriculture), and to those in the Bureau of Mines and the Forest Service connected with lead mining in Missouri.

The strength of the NSF partnership with the research teams was enhanced by the empathy and encouragement afforded my colleagues and me by the NSF management. I especially appreciate the support of Drs. Joel A. Snow and Alfred E. Eggers, Jr., and the splendid constancy of Drs. Philip Johnson and Raymond Johnson.

My partners, Drs. Richard Carrigan, Ronald Goor, and Marvin Stephenson, made my years with RANN's Trace Contaminants Program most rewarding. Their public service is in the best tradition of the NSF.

Finally, I am grateful to the many scientists and their students supported by the RANN program. Their degree of motivation and dedication made my work seem effortless by comparison.

PART I

Characteristics, Monitoring, and Analysis

PHYSICAL AND CHEMICAL CHARACTERISTICS OF ENVIRONMENTAL LEAD

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INTRODUCTION

This chapter deals with the physical and chemical nature of lead-containing species in the environment. It is specifically concerned with the activities of the research groups at Colorado State University, the University of Illinois at Urbana-Champaign, and the University of Missouri at Rolla that bear upon this subject. Reference will be made to the work of other investigators only if this work provided the impetus for further study by the three university groups, supplied information required in the formulation of research plans, yielded data that could be used to check the validity of experimental results and their interpretation, or discussed techniques that are of general value.

The term "physical characterization" bears upon those physical properties of lead-containing species that are significant in terms of transport, physical interactions with other substances, deposition in various environmental "compartments", physiological activities, removal mechanisms, etc. As such, the discussion is concerned with such general physical properties as particle size and distribution, phase relations, solubility, surface characteristics, washout efficiency, morphology, crystal structure, and the experimental methods for the determination of physical properties.

The term "chemical characterization" bears mainly upon the chemical composition of lead-containing materials in the environment. The chemical form of lead will determine solubility in water and biological fluids, the extent to which lead is fixed in soils, and the types of chemical reactions occurring in the atmospheric, aquatic, and soil environment. It is,

therefore, of primary importance to determine the physical nature and chemical forms of lead (or other trace elements) in the environment if its behavior is to be understood and its environmental impact evaluated and predicted.

The characterization of environmental lead will be considered in terms of lead-containing material (1) emitted into the atmosphere, water, or soil; (2) existing in the atmosphere; (3) existing in water, either in solution or suspension; (4) occurring in soils; and (5) present in biological organisms. Consideration will be given to specific effects of environmental lead in terms of such processes as atmospheric washout.

LEAD EMISSIONS INTO THE ENVIRONMENT

Lead-containing material is introduced into the environment from a variety of sources. The principal input, however, is from the combustion of lead-containing fuels used in internal combustion engines, the combustion of lead-containing coal or fuel oil, and activities in lead mining and refining. The extent and geographical distribution of such emissions are considered elsewhere. A major source of lead input into the environment is the exhaust from automobiles. Most of the research at Colorado State University and a large portion of that at the University of Illinois are devoted to problems associated with this lead source. Work has also been reported from the University of Illinois bearing upon environmental lead introduced from the combustion of coal. Investigators at the University of Missouri are primarily concerned with lead originating from mining, smelting, and refining. The physical and chemical characterization of such emissions, before physical or chemical changes that occur in transport or deposition, will be considered in the following discussion.

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Automotive Emissions

This section deals with the characterization of lead-containing gaseous and particulate matter emitted from internal combustion engines fueled with leaded gasoline and with a study of the physical and chemical nature, under controlled laboratory conditions, of simulated automotive emissions.

Physical Characterization: Purdue et al. [1] have reported that a minimum of 90 percent of the lead emissions in the exhausts of internal combustion engines using leaded fuel are particulate, and the remaining 10 percent may be organic lead vapors (presumably uncombusted lead alkyls). The lead antiknock formulation may include, in addition to organic halogen compounds acting as scavengers, any or all of $\text{Pb}(\text{CH}_3)_4$, $\text{Pb}(\text{CH}_3)_3(\text{C}_2\text{H}_5)$, $\text{Pb}(\text{CH}_3)_2(\text{C}_2\text{H}_5)_2$, $\text{Pb}(\text{CH}_3)(\text{C}_2\text{H}_5)_3$, and $\text{Pb}(\text{C}_2\text{H}_5)_4$. Menne and Corrin [2] found that in ambient air adjacent to a heavily traveled highway, the only lead alkyl detectable was $\text{Pb}(\text{CH}_3)_4$; concentrations ranged from 1 to 20 percent of the total lead concentration. The implications of these results will be discussed later. Lead alkyl concentrations in air up to $2 \mu\text{g}/\text{m}^3$ have been reported by Laveskog. [3]

The particle size distributions of lead-containing particulate matter in fresh automotive exhaust have been investigated by Habibi et al., [4] Habibi, [5] Hirschler et al., [6] Hirschler and Gilbert, [7] Mueller et al., [8] and Ter Haar et al. [9] The particle size distribution varies with engine operating conditions. The chemical composition of the lead-containing particles also varies with particle size. In a general sense, however, from 20 to 30 percent of the total lead is found in particles greater than $5 \mu\text{m}$; from 50 to 70 percent in the 1 - to $5 \mu\text{m}$ range, and 5 percent or less in submicrometer particles. More than 90 percent of the emitted particles possess a diameter less than $2 \mu\text{m}$. The sizes quoted are aerodynamic sizes. It should be pointed out that the size refers to the particle itself, which contains species other than lead compounds. It is customary to express the particle size distribution of lead-containing species in terms of the fraction of total lead contained in particles of a given size range. It is thus impossible to calculate the number of particles in a given size range from the distribution function so expressed. The settling velocity of a $5 \mu\text{m}$ particle (aerodynamic size) in still air is 0.1 cm/s ; given an emission height of perhaps 3 m, the lifetime of such a particle in the still atmosphere would be 50 min.

A Digression on Particle Size: Particle sizes determined by visual observation or light and electron microscopy are geometrical sizes deduced by various techniques from a two-dimensional display. They are generally reported in terms of the radius (or diameter) of an "equivalent" sphere. Particle sizes as measured by impactors, air centrifuges (such as the Goetz spectrometer), or techniques involving the transport behavior of particles in an applied field are aerodynamic sizes and are generally expressed in terms of a sphere of unit density that possesses the same aerodynamic behavior as the

particle in question. The two size descriptions are not identical and cannot be interchanged without additional information on such parameters as shape and density. Most of the work reported on lead-containing particles involves aerodynamic sizing. This is an appropriate description, because the important factors of atmospheric transport, fallout, washout, and deposition in the lungs are determined by aerodynamic properties (and hence aerodynamic size) rather than particle geometry as expressed in geometrical size.

Exhaust Simulation: Zimdahl [10] at Colorado State University has constructed a generator for various lead salts used in plant studies with simulated lead-containing aerosol. A similar generator has been used by Grant and Vardiman [11] to investigate possible weather modifications produced by lead aerosols. However, the major study on automotive exhaust simulation has been conducted at the University of Illinois.

In order to simulate the reactions and transport of automotive exhaust particles with pure and known compounds in the laboratory, Boyer and Laitinen [12] at the University of Illinois have developed methods for the production and characterization of artificial lead-containing aerosols. Such model particulates should have a morphology and particle size distribution as similar as possible to the exhaust particles found in the environment.

Lead bromide and lead bromochloride aerosols were produced from controlled temperature melts of the pure compounds in the apparatus illustrated in figure 1-1. Through adjustment of the voltage applied to the heating coil, the melt temperature was maintained at 400°C for lead bromide (melting point of 373°C) and 450°C for lead bromochloride (melting point of 430°C). At these temperatures the va-

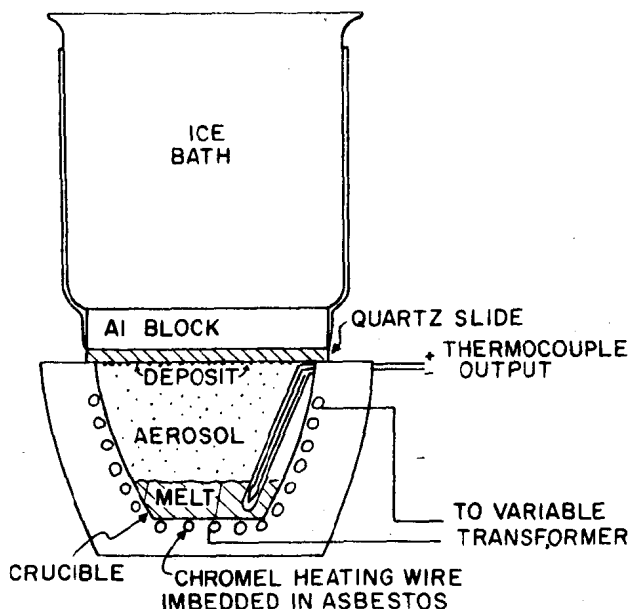


FIGURE 1-1.—Apparatus for collection of lead halide aerosol particles from controlled temperature melts.

por pressure over the two lead halides is sufficient to produce upon condensation a visible white "smoke" in the cooler region above the melt. The particles forming this smoke were collected on quartz slides for examination by electron microscopy and X-ray diffraction. The reaction chamber depicted in figure 1-2 was connected in series with the generating crucible to permit a study of the gas phase reactions of these lead-containing aerosols.

Varying the temperature of the generating crucible and reaction chamber produced changes not only in particle size distribution and morphology (as determined with the electron microscope), but also in the chloride-to-bromide ratios of the $PbBr_xCl_y$ aerosols. This behavior is shown in table 1-1. It has been demonstrated by Calingaert et al. [13] that lead bromide and lead chloride form a complete series of solid solutions with a preferential formation of the isomorphous 50-mole-percent compound lead bromochloride. The interplanar spacings of pure $PbBr_2$, $PbCl_2$, and stoichiometric $PbBrCl$ are plotted in figures 1-3 and 1-4; a definite change of slope occurs at the 50-mole-percent composition of $PbBrCl$. The additional points plotted represent interplanar spacings of aerosols generated at different temperatures. These points indicate that nonstoichiometric Pb-Br-Cl ratios can be obtained in essentially stable aerosols from $PbBrCl$ heated either above or below its melting point. The evolution of gaseous bromine from $PbBrCl$ melts has been reported by Zimdahl. [14]

In low-speed stop-and-go city driving the exhaust system is relatively cool; under such conditions $PbBrCl$ could be deposited in the exhaust system. In high-speed freeway driving this deposited $PbBrCl$ is subjected to higher temperatures, and nonstoichiometric bromide-rich compounds could be selectively volatilized from the exhaust system. At least one recent study by Moran and Manary [15] has reported unidentified bromide- and chloride-rich species in exhaust lead-containing particulates. The results depicted in figures 1-3 and 1-4 suggest, according to Boyer and Laitenen, that previous reports dealing with the existence of stoichiometric $PbBrCl$ could, with minor errors in interplanar spacing measurements, be interpreted in terms of nonstoichiometric compounds.

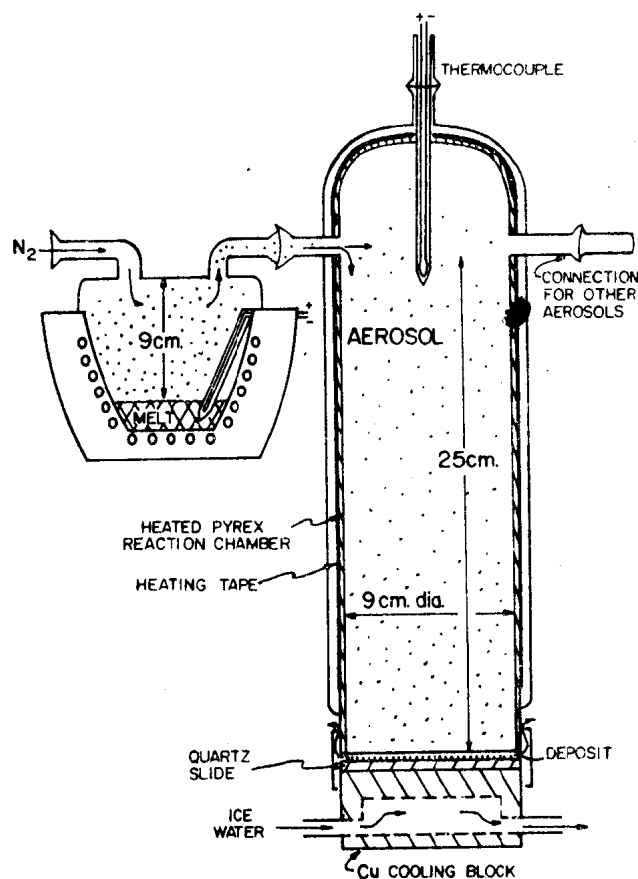


FIGURE 1-2.—Apparatus for the reaction of lead halide aerosols with other aerosols.

Figures 1-5 through 1-9 show progressive changes in morphology and geometric particle size of the aerosols with increasing Br/Cl ratios and decreasing generation temperatures. Thus at $510^\circ C$, well above the melting point of $PbBrCl$, the aerosols are well-defined spheres with a mean particle diameter of about $3 \mu m$. As the generation temperature is lowered to a few degrees above the melting point, the particles become progressively more elongated, with a cross-sectional diameter of about $1.5 \mu m$. Needlelike crystals with a cross-sectional diameter of $0.5 \mu m$ or less result when the generation temperature is well below the melting point.

Table 1-1.—Composition of lead halide aerosols produced at several temperatures

Aerosol No.	Generation temperatures ($^\circ C$)		Aerosol composition (Mole ratio $PbBr_xCl_y$)		
	Crucible	Chamber	x	y	x + y
1	370	318	1.78	0.35	2.13
2	366	370	1.64	0.48	2.12
3	412	403	1.58	0.47	2.05
4	450	450	1.23	0.83	2.06
5	505	365	1.28	0.75	2.03
6	510	370	1.25	0.74	1.99
7	500	450	1.24	0.80	2.04
8	505	450	1.21	0.85	2.06

LEAD HALIDE AEROSOLS
d-SPACINGS vs HALIDE COMPOSITION

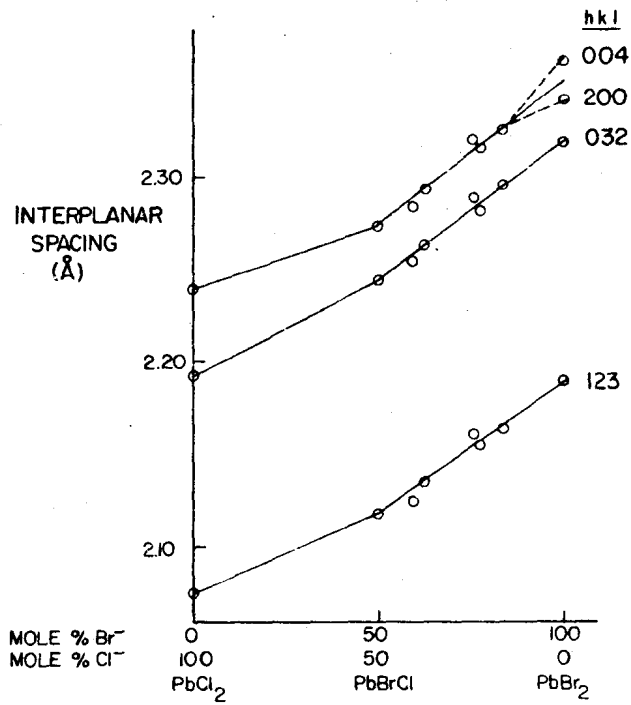


FIGURE 1-3.

LEAD HALIDE AEROSOLS
d-SPACINGS vs HALIDE COMPOSITION

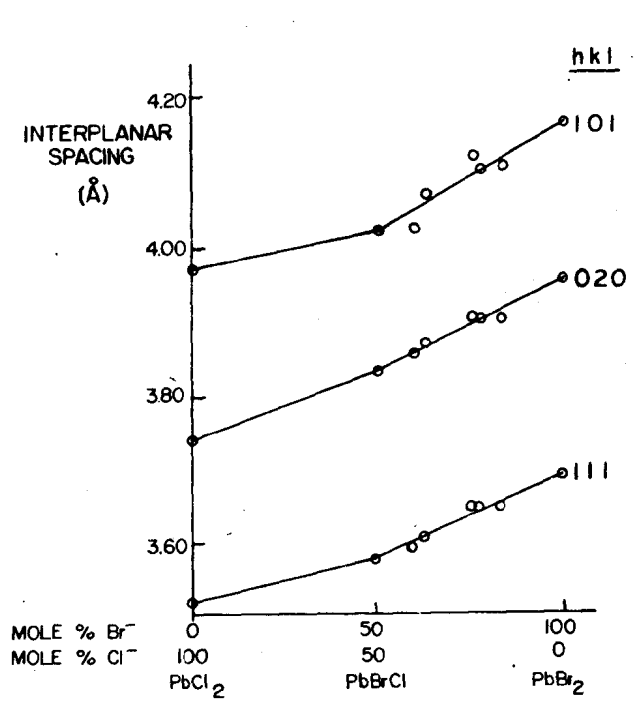


FIGURE 1-4.

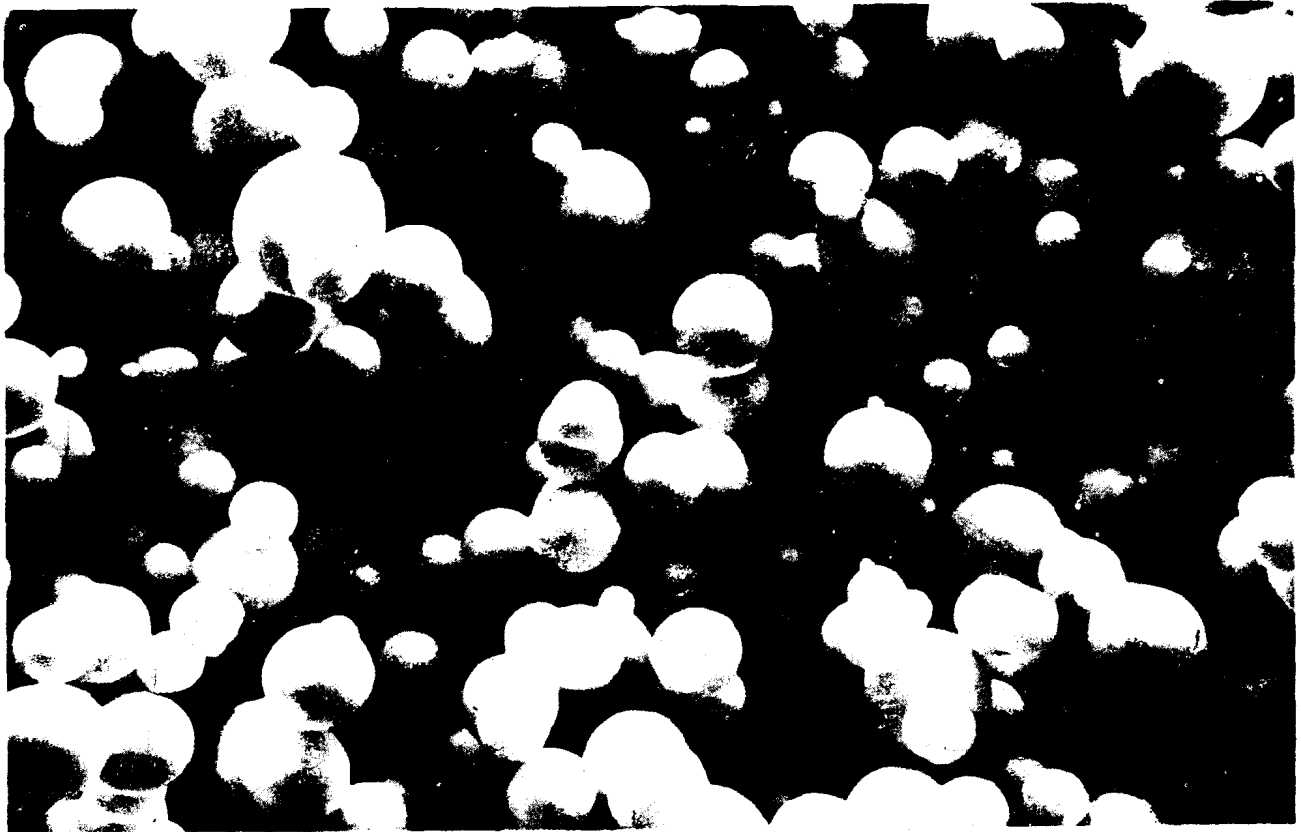


FIGURE 1-5.—Scanning electron micrograph of PbBr_{1.25}Cl_{0.74} aerosol particulates. Crucible temperature is 510° C; chamber temperature is 370° C.

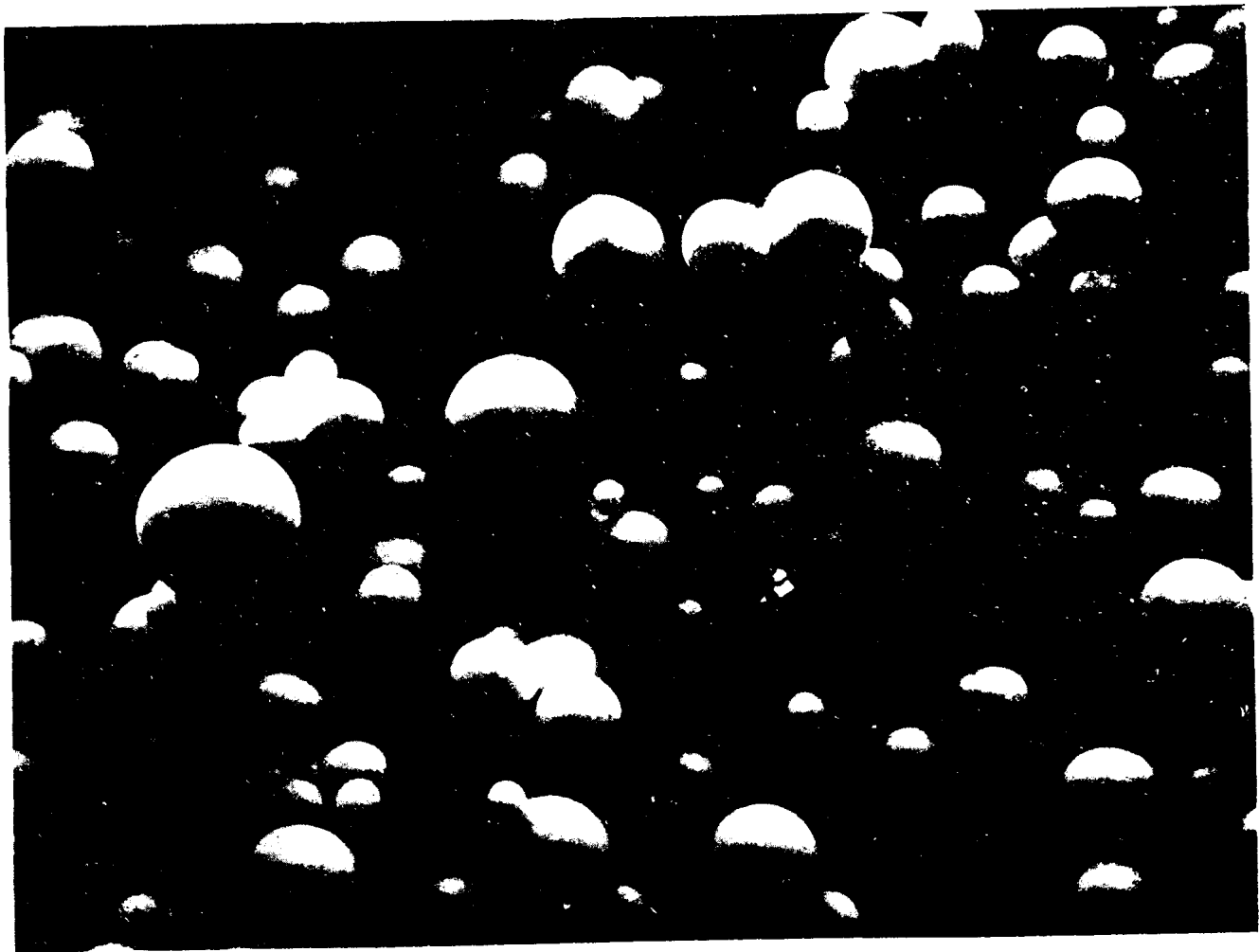


FIGURE 1-6.—Scanning electron micrograph of aerosol particulates. $\text{PbBr}_{1.28}\text{C}_{1.75}$. Crucible temperature is 505 °C; chamber temperature is 365 °C.



FIGURE 1-7.—Scanning electron micrograph of aerosol particulates. $\text{PbBr}_{1.55}\text{C}_{1.50}$. Crucible temperature is 412 °C; chamber temperature is 403°C.

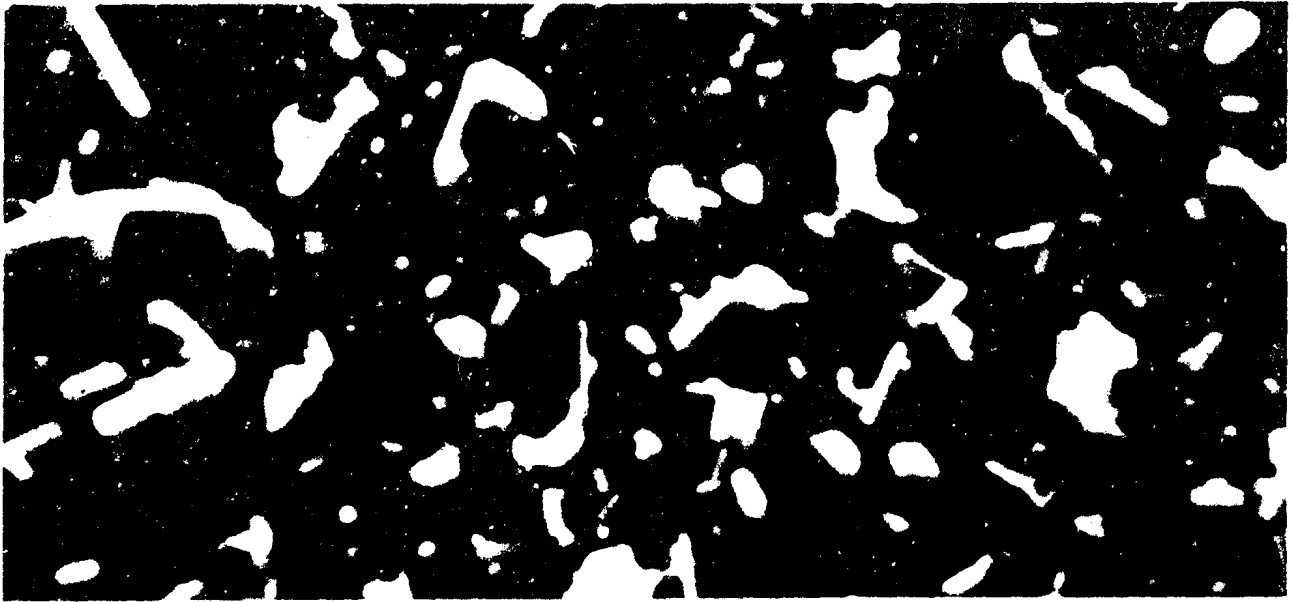


FIGURE 1-8.—Scanning electron micrograph of aerosol particulates. $\text{PbBr}_{1.64}\text{Cl}_{1.48}$. Crucible temperature is 366 °C; chamber temperature is 370 °C.

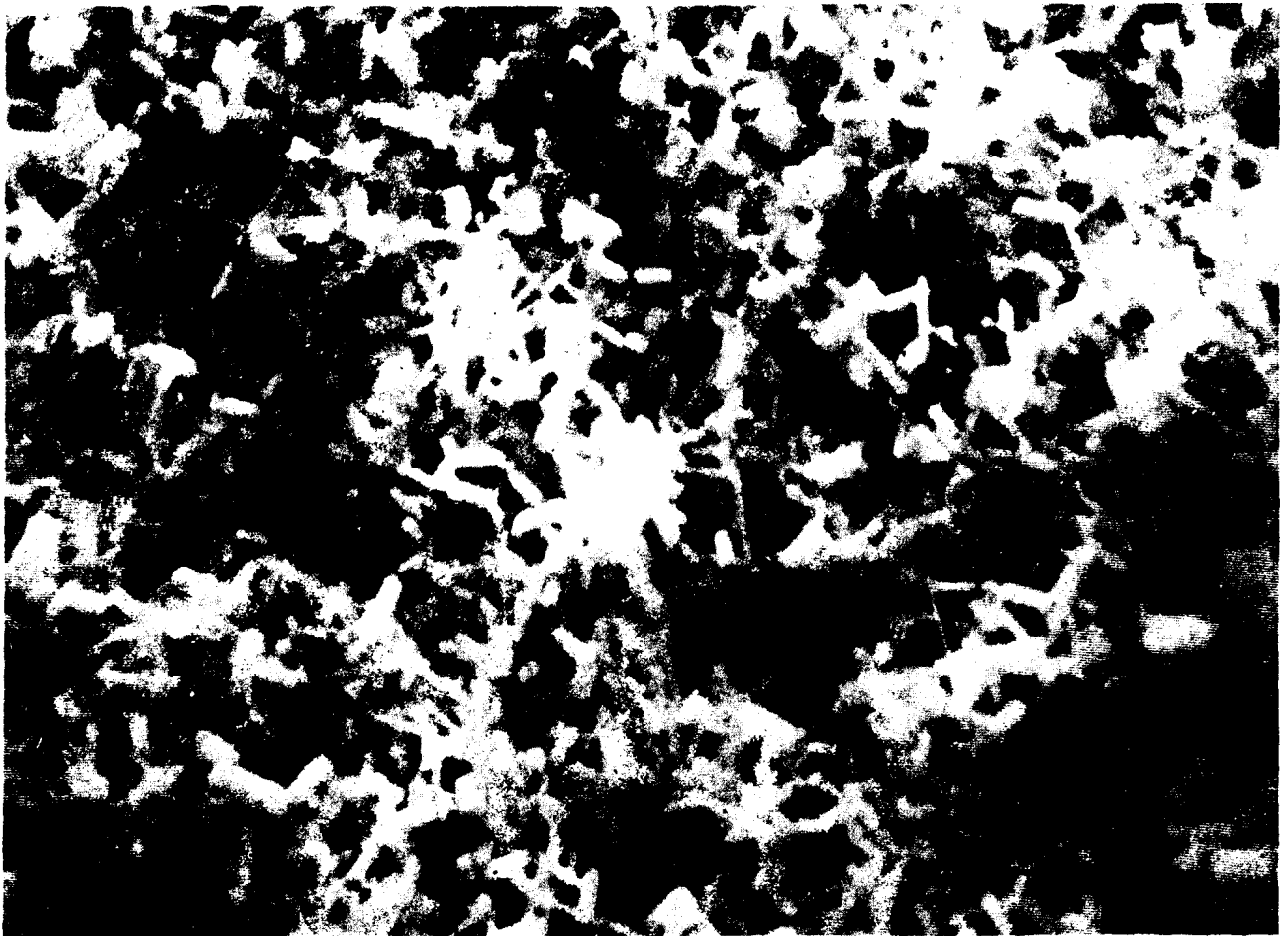


FIGURE 1-9.—Scanning electron micrograph of $\text{PbBr}_{1.78}\text{Cl}_{1.35}$ aerosol particulates. Crucible temperature is 370 °C; chamber temperature is 318 °C.

TABLE 1-2.—Exposure of lead halide aerosols to high humidity, high carbon dioxide atmospheres, and filtered automobile exhaust

Exposure conditions	Mole ratio $PbBr_xCl_y$				Halide remaining (percent)
	Before		After		
	x	y	x	y	
3 percent H_2O vapor, 7 percent CO_2 , 25°C, 24 h	(¹)	(¹)	1.33	0.68	—
12 percent H_2O vapor, 7 percent CO_2 , 50°C, 90 h	(¹)	(¹)	1.36	0.65	—
Filtered unleaded auto exhaust, 105°C, 1 h	1.24	0.85	1.24	0.79	99.5
Filtered leaded auto exhaust, ultraviolet (UV) light, 105°C, 2 h	1.21	0.85	1.20	0.84	99.0

¹ Not analyzed.

Although these results establish the character of the lead halide aerosols that have been artificially generated in the manner previously described, they do not necessarily imply that lead-containing exhaust particles behave similarly as a function of temperature. They do, however, indicate the feasibility of both compositional and morphological changes occurring in the exhaust system.

Further studies were conducted at the University of Illinois to determine the behavior of these model lead-containing aerosols on exposure to high humidity, to high carbon dioxide concentrations, and to automotive exhaust gases from which the particulate matter had been partially removed. Automobile ex-

haust gas was obtained by inserting a probe into the exhaust line of a 1966 six-cylinder Ford engine; the probe was placed about 1 ft. downstream from the exhaust manifold. This gas was then passed through heated copper tubing into a temperature-controlled enclosure containing a 3-ft. temperature equilization line, a stainless steel filter assembly fitted with glass fiber filters, and a reaction chamber (fig. 1-2) containing the lead halide aerosol. The gas flow rate was 1.7 l/min; the chamber temperature was maintained at 105° C to prevent condensation of water.

The results of these experiments are given in tables 1-2 and 1-3. It is clear that "laboratory pure" lead halide aerosols are quite stable toward hydroly-



FIGURE 1-10.—Scanning Electron Micrograph of Exhaust Particulates from Leaded Gasoline.



FIGURE 1-11.—Scanning Electron Micrograph of Exhaust Particulates from Unleaded Gasoline.

TABLE 1-3.--Decomposition of lead halides subjected to various conditions

Sample and conditions	Halide left after decomposition (μeq)	Halide lost during decomposition (μeq)	Total halide recovered (μeq)	Theoretical Pb and halide available (μeq)	Pb found by atomic absorption (μeq)
"Pure" PbBr_2	—	—	69.2	65.8	68.4
PbBr_2 , 6.2 mW/cm^2 , dry CO_2 -free air, 32° C, 25 h	(¹)	7.94 (30.1 percent)	(¹)	(¹)	26.4
PbBr_2 , 9 percent CO_2 , moist air, 25° C, 24 h	18.0	<0.05 (<0.3 percent)	18.0	18.4	18.0
"Pure" PbBrCl	—	—	292	297	294
PbBrCl , 9 percent CO_2 , moist air, 50° C, 72 h	282	1.1 (0.4 percent)	283	288	288
PbBrCl , 6.2 mW/cm^2 , dry N_2 , 32° C, 51.5 h	176	9.6 (9.2 as Br_2 ; 0.4 as Cl_2 ; 5.1 percent of total)	186	194	190
PbBrCl , 6.2 mW/cm^2 , dry CO_2 -free air, 32° C, 50 h	116	5.8 (5.4 as Br_2 ; 0.4 as Cl_2 ; 4.8 percent of total)	122	124	121

¹ Not analyzed.

tic exchange with water or to reaction with carbon dioxide under these experimental conditions. Furthermore, although Robbins and Snitz [16] have reported that up to 75 percent of the bromine is lost from fresh automobile exhaust particles in the first 20 min. after emission, no evidence of such losses was obtained for these model lead halide aerosols in the simulated exhaust gas exposure.

Scanning electron microscope studies of the particulates collected on the glass fiber filters with the experimental setup previously described show quite dramatically the difference between particles collected under dynamic conditions from the exhaust of an automobile burning leaded and unleaded gasolines. (figs. 1-10 and 1-11). Figure 1-10 shows that instead of the filter collecting well-defined particles, the lead halides actually "grow" on the filter strands. Figure 1-11 for unleaded gasoline shows that the particles collected have a mean diameter considerably smaller than the 0.3 μm value normally quoted for automotive emissions.

Chemical Characterization: The lead halides (PbBr_2 , PbCl_2 , and PbBrCl) and the alpha and beta forms of the double salt lead bromochloride ammonium chloride ($2\text{PbBrCl}\cdot\text{NH}_4\text{Cl}$), account for 80 to 100 percent of the lead-containing compounds found in the exhaust of automobiles burning gasoline containing a lead antiknock additive, according to Habibi et al., [4] Hirschler et al., [6] and Bayard and Ter Haar. [17] The exact composition depends upon the fuel and driving conditions. Habibi [5] has noted that large particles (greater than 200 μm) in fresh exhaust contain PbBrCl , $2\text{PbO}\cdot\text{PbBrCl}$, and small amounts of PbSO_4 and $\text{Pb}_3(\text{PO}_4)_2$. These particles would fall out very rapidly. (The settling velocity is about 70 cm/s). In the 2- to 10- μm range the principal constituent is PbBrCl . The submicrometer particles contain

PbBrCl and $2\text{PbBrCl}\cdot\text{NH}_4\text{Cl}$; the latter is not a primary product but is formed as the exhaust is diluted and mixed with outside air.

Natusch and associates [18] at the University of Illinois have examined the dependence of elemental composition in automobile exhaust particles on depth into the individual particles. Relatively large particles (10 μm) were obtained from a cyclone collector attached to an automobile operated under test cycle conditions by Universal Oil Products Co. Two surface analysis techniques were employed. In the first, the particles were etched on one side with a stream of positively charged argon ions; both the etched and unetched sides were analyzed with an electron microprobe. The second technique utilized Auger electron microprobe spectroscopy with simultaneous ion etching.

Both techniques showed that lead, bromine, and chlorine occur at much higher levels on the particle surfaces than in their interior (fig. 1-12), indicating that surface deposition (perhaps condensation) takes place in the exhaust system. The particles studied all had small, submicrometer particles fused to their surfaces (fig. 1-13), and there is marginal evidence from these microprobe studies indicating that these attached particles may be highly enriched in lead, bromine, and chlorine.

These results suggest that lead bromochloride vapor may either condense directly from the vapor phase or be deposited as small particles onto large, partially molten particles that are rich in Al, Fe, Ca, Zn, P, and S (fig. 1-13). It is not clear whether particles of this composition are derived from the fuel itself, from engine or exhaust materials, or from the intake air. Essentially similar matrix compositions were found for particles obtained from unleaded fuel.