AIR POLLUTION ASPECTS

OF

BARIUM AND ITS COMPOUNDS

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FOREWORD

As the concern for air quality grows, so does the concern over the less ubiquitous but potentially harmful contaminants that are in our atmosphere. Thirty such pollutants have been identified, and available information has been summarized in a series of reports describing their sources, distribution, effects, and control technology for their abatement.

A total of 27 reports have been prepared covering the 30 pollutants. These reports were developed under contract for the National Air Pollution Control Administration (NAPCA) by Litton Systems, Inc. The complete listing is as follows:

Aeroallergens (pollens) Aldehydes (includes acrolein Hydrochloric Acid and formaldehyde) Ammonia Arsenic and Its Compounds Asbestos Barium and Its Compounds Beryllium and Its Compounds Biological Aerosols (microorganisms) Boron and Its Compounds Cadmium and Its Compounds Chlorine Gas Chromium and Its Compounds (includes chromic acid)

Ethylene Hydrogen Sulfide Iron and Its Compounds Manganese and Its Compounds Mercury and Its Compounds Nickel and Its Compounds Odorous Compounds Organic Carcinogens Pesticides Phosphorus and Its Compounds Radioactive Substances Selenium and Its Compounds Vanadium and Its Compounds Zinc and Its Compounds

These reports represent current state-of-the-art literature reviews supplemented by discussions with selected knowledgeable individuals both within and outside the Federal They do not however presume to be a synthesis of Government. available information but rather a summary without an attempt to interpret or reconcile conflicting data. The reports are

necessarily limited in their discussion of health effects for some pollutants to descriptions of occupational health exposures and animal laboratory studies since only a few epidemiologic studies were available.

Initially these reports were generally intended as internal documents within NAPCA to provide a basis for sound decision-making on program guidance for future research activities and to allow ranking of future activities relating to the development of criteria and control technology docu-However, it is apparent that these reports may also be of significant value to many others in air pollution control such as State or local air pollution control officials, as a library of information on which to base informed decisions on pollutants to be controlled in their geographic areas. tionally, these reports may stimulate scientific investigators to pursue research in needed areas. They also provide for the interested citizen readily available information about a given pollutant. Therefore, they are being given wide distribution with the assumption that they will be used with full knowledge of their value and limitations.

This series of reports was compiled and prepared by the Litton personnel listed below:

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Appreciation is expressed to the many individuals both outside and within NAPCA who provided information and reviewed draft copies of these reports. Appreciation is also expressed to the NAPCA Office of Technical Information and Publications for their support in providing a significant portion of the technical literature.

ABSTRACT

Soluble barium compounds are highly toxic when ingested, while insoluble compounds, such as the most common barium compound, barium sulfate, are generally nontoxic. Inhaled barium compounds cause a benign pneumoconiosis, called baritosis.

Ingestion of soluble barium compounds results in strong stimulation of the muscles, including the heart; irritation of the intestinal tract; and irritation of the central nervous system.

The major sources of barium compounds emitted into the atmosphere are the industrial processes involved in the mining, refining, and production of barium and barium-base chemicals, and the use of barium compounds as a fuel additive for the reduction of smoke emissions from diesel engines. Data have not been found on the quantity of emissions from industrial processes. Some limited data on barium emissions from diesel engine exhaust were estimated to be a maximum of $48,000~\mu\text{g/m}^3$ (25 percent soluble barium) at full load. No information is currently available on the concentration of barium or its compounds in ambient air.

No information has been found on the abatement of barium air pollution, or on the costs of its abatement or of damages resulting from barium air pollution. Methods are available for the determination of barium concentrations in the atmosphere.

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1. INTRODUCTION

Very little information is available on the air pollution aspects of barium and its compounds; however, the introduction of barium compounds into diesel fuels as a means of reducing black smoke emissions has focused interest on the effects of barium in the environmental air. While it is generally accepted that the insoluble compounds, such as barium sulfate, are nontoxic, the soluble compounds are known to be highly toxic when ingested, and inhalation of barium compounds can produce a benign pneumoconiosis, known as baritosis. ever, the effects of barium air pollution cannot be stated with certainty because of insufficient knowledge of the effects of atmospheric concentrations of barium compounds, particularly in the micron-particle size emitted from exhausts of diesel engines fueled with smoke-suppressant additives. A summary of some of the properties, toxicity, and uses of selected barium compounds are listed in Table 2 in the Appendix.

2. EFFECTS

2.1 Effects on Humans

The soluble salts of barium are highly toxic when ingested; barium chloride and barium carbonate, two of the soluble compounds, have been reported^{5,19} to cause toxic symptoms of a severe but usually nonfatal degree. One case is reported⁵ in which 7 grams of barium chloride taken orally produced severe abdominal pain and near-collapse, but not death. However, Patty¹⁹ indicates 0.8 to 0.9 grams to be a lethal dose. Few cases of industrial poisoning from soluble barium salts have been reported; most of these have been cases of accidental ingestion.

Ingested soluble barium compounds produce a strong stimulating effect on all muscles of the body. The effect on the heart muscle is manifested by irregular contractions followed by arrest of systolic action. Effects on the gastrointestinal tract cause vomiting and diarrhea, and on the central nervous system, violent tonic and clonic spasms followed in some cases by paralysis. 5,19

The symptoms of barium poisoning are excessive salivation, vomiting, colic, diarrhea, convulsive tremors, slow hard pulse, and increased blood pressure. The stomach, intestines, and kidney may hemorrhage, and muscular paralyses may follow.

Depending on the dose and solubility of the barium compound, death may occur in a few hours or a few days. 19 A death attributed to barium oxide poisoning was reported; 21 however, the usual effect of exposure to dusts and fumes of barium sulfide, barium oxide, and barium carbonate is irritation of eyes, nose and throat, and the skin. 21

The insoluble barium compounds are generally nontoxic when ingested. For example, barium sulfate, the most common of the insoluble barium compounds, is widely used as an opaque liquid, administered orally, in X-ray examination of the gastrointestinal tract.²¹

Inhalation of barium compounds is known to cause a benign respiratory affliction (pneumoconiosis) called baritosis, 21 which has been reported in workers exposed to finely divided barium sulfate in Italy, and in barite miners in the United States, Germany, and Czechoslovakia. 21 It has also been reported in workers producing lithopone, 20,21 and among workers exposed to barium oxide. 19 Generally, baritosis produces no symptoms of emphysema or bronchitis, and lung function tests show no respiratory incapacity, although some afflicted workers complain of dyspnea upon exertion. 19 The radiological appearances are very fine nodules on a reticulated background evenly distributed through the lung fields. 5,19 In the

majority of cases nodulation disappears if exposure to the barium compound is stopped. 19

Soluble barium is retained by muscle tissue for about 30 hours, and then the amount of retained barium decreases slowly. 5 Small amounts of barium become irreversibly deposited in the skeleton. However, the acceptance level must be limited as quantitative analysis of human bone reveal no accumulation above 7 ppm (ashed tissue) throughout a lifetime. Very little barium is retained by the liver, kidneys, or spleen, and practically none by the brain, heart, or hair. 5

Information on the properties, toxicity, and uses of barium and selected barium compounds is presented in Table 2 in the Appendix.

2.2 Effects on Animals

2.2.1 Commercial and Domestic Animals

No information was found on the effects of barium or barium compounds on commercial or domestic animals.

2.2.2 Experimental Animals

Miller¹⁵ reported on the toxicity of exhaust solids emitted from a laboratory diesel engine which was using fuel with a barium-base smoke-suppressant additive. The solids contained carbon, barium sulfate, and smaller amounts of barium carbonate. The LD_{50} for these solids was reported in

excess of 10 grams per kilogram of body weight. The type and number of animals used in this experiment were not reported. In a companion experiment, Miller exposed white rats (number not reported) to 10 times the concentration of airborne exhaust solids that would be emitted from a bus burning fuel with a barium-base smoke-suppressant additive. After a series of 10 exposures and fresh-air cycles, the animals were examined for lung damage. No unusual conditions were found.

Guinea pigs were used to test the effects of inhalation of barite dust. Nodular granulation of the lungs characteristic of baritosis was reported.⁵ Subcutaneous injection of 5,000 $\mu g/m^3$ of barium chloride caused acute toxicity and death in rabbits after 2 to $2\frac{1}{2}$ hours. Chronic poisoning resulted from repeated injection of 10,000; 5,000; and 2,000 $\mu g/kg.^{19}$

Bronchogenic carcinoma developed in rats injected with radioactive barium sulfate. Study of metabolism in rats showed 24-hour urinary and fecal excretions to be 7 and 20 percent respectively. Trace amounts of barium were irreversibly deposited in the skeleton. Nadel injected 0.2 ml/kg of a 30 percent suspension into the hearts of cats and subsequently found increased pulmonary resistance, decreased pulmonary compliance and functional residual capacity, increased end-expiratory transpulmonary pressure, and increased anatomic dead space.

Examination of the lungs showed that the barium sulfate caused constriction of the peripheral airways, principally in the alveolar ducts.

Information on the toxicity of selected barium compounds to certain experimental animals, as presented by Spector, ²⁴ is contained in Table 3 in the Appendix.

2.3 Effects on Plants

No data have been found on the effect of environmental concentrations of barium on plants. Browning⁵ indicated that barium is toxic to plant life but gave no information on the chemical form or concentration, or the type of plant life involved.

2.4 Effects on Materials

No information has been found on the effect of environmental concentrations of barium on materials.

2.5 Environmental Air Standards

The American Conference of Governmental Industrial Hygienists at their 29th annual meeting in 1967 recommended an 8-hour threshold limit of 500 $\mu g/m^3$ for occupational exposure to the soluble compounds of barium in air. No ambient air quality standards for barium and its compounds are known to exist for either the United States or any other country.

3. SOURCES

3.1 Natural Occurrence

Barium is a soft, silvery metallic element found in nature only in combination with other elements. It frequently appears as gangue in lead and zinc ore deposits, although it also occurs in veins. The two main minerals are barite (barium sulfate, BaSO₄) and witherite (barium carbonate, BaCO₃).

Barite is by far the most important commercial barium ore.

It occurs in beds or masses in limestone, dolomite, shales, and other sedimentary formations; as residual nodules resulting from weathering of barite-bearing dolomite or limestone; and as gangue in veins or beds together with fluorspar, metallic sulfides, and other minerals. The chief barite-producing areas in the United States are located in Missouri, Arkansas, Georgia, and Nevada. The deposits of impure barite ores found in Kentucky and Tennessee are not worked extensively.

Witherite, which consists of 77.7 percent barium oxide and 22.3 percent carbon dioxide, is usually found associated with galena in veins.^{2,13} The mineral witherite is less common than barite and is found only in small quantities in the United States. The largest deposit in this country is in El Portal, Calif. This ore is not mined commercially in the United States and very little is imported.

Small quantities of barium are found in most igneous rocks, and it is a minor constituent of feldspar and mica.³

Trace quantities of barium are also found in coal.¹ The percentage of barium found in coal ash from various coal sources is shown in Table 1.

TABLE 1 ${\tt BARIUM\ CONTENT\ IN\ COAL\ ASH}^{1}$

Source of Coal	Percentage of Barium in Ash
West Virginia North Dakota	0.05 to 0.44 0.15
Alaska (Nenana field) England	0.4 to 0.8 0.0 to 4.3
Nova Scotia	0.0018 to 0.22
Germany (Newrode) Germany, brown coal	0.22 0.0001
Germany	<0.1
Portugal, anthracite Norway (Spitsbergen)	0.01 to 0.1 0.1 to 0.2

3.2 Production Sources

3.2.1 Mining and Milling of Barite

The methods used in mining barite ore vary widely with the type and size of the deposit and the desired end-product. Ladoo and Meyers¹³ list the following mining methods employed in the United States:

(1) Hydraulic mining of residual barite in clay or use of power shovels in open pits.

- (2) Blasting barite-bearing shale from open pits.
- (3) Underground mining of barite veins or beds.
- (4) Blasting of massive barite from open quarries.

Domestic production of barite, by State, is shown in Table 4 in the Appendix.

The methods for milling of barite depend upon the nature of the ore and the desired end-product. Approximately 90 percent of the barite being produced is ground and crushed for use in oil-well drilling; the remainder is used principally for the production of barium chemicals and lithopone. For use as a well-drilling mud--for which the only requirements are fine-grind, nonreactivity, and high specific gravity 13--the barite is only ground and bagged. For chemical industrial use, it is ground, then washed to remove impurities; in some cases it is passed through a magnetic separator to remove iron impurities.

Barite is marketed in the following grades: crude, handselect lump, jig and table concentrates, granular, fine-ground,
fine-ground bleached, and fine-ground off-color.

No information has been found on emission of barium from mining or milling facilities.

3.2.2 Barium Metal

Barium metal is produced by the reduction of barium oxide with aluminum, in retorts. The barium oxide and aluminum powder

are heated in the retort to 1,100 to 1,200°C, at low pressures (0.1 mm of mercury); the metallic barium distills as a vapor and is condensed and collected.

Barium metal is difficult and expensive to produce. It is highly reactive in normal atmospheres and combines rapidly, forming a barium salt. The major uses for metallic barium are as a getter (to remove residual gases) in radio tubes and as an alloying agent in the production of barium-nickel alloys and frarry metal, which is a bearing alloy of lead, barium, and calcium.^{2,3}

No data have been found on atmospheric emissions of barium during the production or use of this metal.

3.3 Product Sources

Barium is used in mineral form (barite) in the oildrilling industry and in the manufacture of certain chemicals,
including the white paint pigment lithopone. Barium is also
used as an additive to diesel fuels to suppress black smoke
emissions. The domestic consumption of crude barite in the
manufacture of barium products is indicated in Table 5 in the
Appendix.

3.3.1 Ground Barite

The largest use for ground barite is for oil-drilling mud. Approximately 5 tons of barite are used for the drilling

of each 1,000 feet of high-pressure well. 13 Other uses are as a filler in paper, rubber, cloth, linoleum, oilcloth, etc. 13 Bleached barite, prime white, is used as a pigment and extender in white paint. 16

Granular barite is used in the manufacture of glass and in ceramic glazes and enamels.^{2,13} The amount of ground and crushed barite sold to the consuming industries is shown in Table 6 in the Appendix.

No information has been found on the emissions of barite to the atmosphere from the barite-using plants.

3.3.2 Principal Barium Compounds

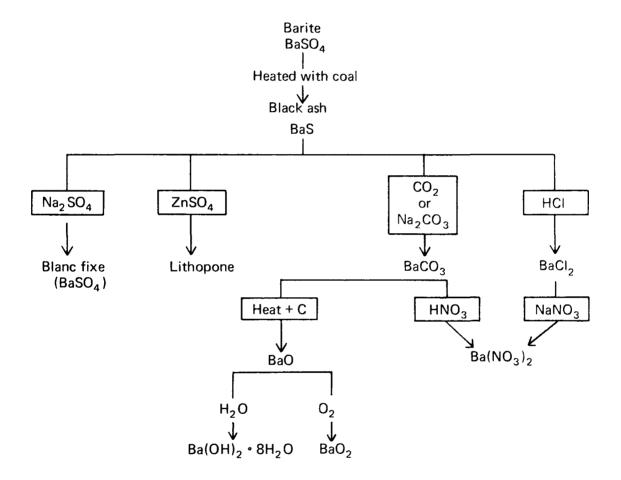
Barium chemicals are normally produced from ground or crushed barite, which is mixed with pulverized coal and roasted in a kiln, reducing the barite (barium sulfate) to barium sulfide (or black ash). The barium sulfide is then converted into commercial chemicals as shown in Figure 1.

The major barium compounds and their primary uses are as follows:

(1) <u>Lithopone</u> is a white powder consisting of approximately 70 percent barium sulfate and 30 percent zinc sulfide.

It is widely used in the manufacture of white pigment and is also mixed with other pigments as a substitute for white lead.

It is nonpoisonous, and is not blackened by exposure to hydrogen



sulfide gases. Lithopone is also used in the manufacture of automobile tires, rubber matting, rubber tubing, and other high-grade rubber products; as a filler in oilcloth, linoleum, and window-shade cloth; and in production of printer's ink and cosmetics.

(2) <u>Barium sulfate</u>, or blanc fixe (BaSO₄), is a white, insoluble, amorphous powder chemically precipitated from barium sulfate. It is used in the manufacture of coloring compounds and high-grade paint pigments. It also serves as a filler for rubber goods, linoleum, oilcloth, and glaze powders, and as a base for lithographic inks. Blanc fixe is also utilized in the manufacture of photographic paper, leather, and cloth.

An important medical use of barium sulfate, which is insoluble and nontoxic, is as a contrast emulsion in X-ray examination of the gastrointestinal tract. Because of its high X-ray absorption capacity, it clearly delineates the intestinal passages. It is also used medically as an anti-diarrheal powder. 2,3,13

(3) <u>Barium carbonate</u> (BaCO₃) serves as a raw material from which other barium compounds are produced. It is also used in the ceramic industry to prevent efflorescence, in claywares such as brick and tile, as an ingredient in optical glasses

and fine glassware, in case-hardening of steel, in the manufacture of photographic paper, and as a rat poison.^{2,3}

- (4) <u>Barium chloride</u> (BaCl₂) is used as a raw material in producing blanc fixe, in manufacturing barium colors, as a sodium hydroxide, and as a water softener. It also serves as an ingredient in case-hardened steels, and in medicinal preparations. 2,3,13
- (5) <u>Barium nitrate</u> $(Ba(NO_3)_2)$ is used primarily in green signal flares in pyrotechnics, and to a lesser extent in medicinal preparations.
- (6) <u>Barium oxide</u> (BaO) is used as a raw material in the preparation of barium peroxide, barium hydroxide, and barium methoxide. It is also utilized in the manufacture of lubricating oil detergent, ³ as an industrial drying agent, and in case-hardening of steels. ²
- (7) Miscellaneous barium chemicals include <u>barium</u>

 <u>hydroxide</u> (Ba(OH)₂), <u>barium chromate</u> (BaCrO₄), <u>barium chlorate</u>

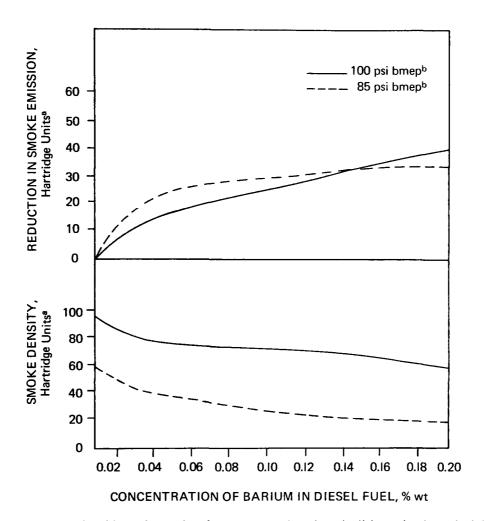
 (Ba(CLO₃)₂), and <u>barium cyanide</u> (Ba(CN)₂). The uses of these, and other barium compounds, are listed in Table 2 in the Appendix.

3.3.3 Diesel Fuel Additives

Barium-base organometallic compounds have been found effective in reducing black smoke emissions from diesel engines. 11,25

There are a number of such barium-base additives, the exact chemical compositions of which are considered proprietary information by the companies producing them. Concentrations of 0.075 to 0.200 percent by weight of additive in fuel have been found effective, with the lower figure of 0.075 percent weight generally used.

 $Miller^{15}$ reported that the smoke-suppressing effect of the barium-base additive has been evaluated in diesel engines manufactured by 21 European and 5 American companies. was substantially reduced in all cases. The additive decreases the amount of the black smoke by reducing the carbon concentration in diesel exhaust. The mechanism of carbon reduction is postulated to be inhibition of dehydrogenation of the hydro-In addition to its smoke-suppressant function, carbon fuel. the additive is claimed to reduce carbon deposits and provide wear-protection for injectors and piston rings, while producing no apparent effect on fuel consumption. 7,15 The effect of a barium-base additive in reducing smoke emission from a singlecylinder, direct-injection, 1.4-liter diesel engine operated at a high load of 100 psi brake mean effective pressure (bmep) and a moderately high load of 85 psi bmep is shown in Figure 2. The effect of fuel additive on full-load exhaust smoke from a 4½-inch bore x 6-inch stroke direct-injection engine is shown in Figure 3. According to Miller, 15 analysis of exhaust gases



^a Hartridge units: units of measurement based on the light-extinction principle, comparing exhaust gases with clean air.

FIGURE 2

Effect of Smoke-Suppressant Additive on Diesel Exhaust Emissions (1.4-liter engine) 11,12

^bpsi bmep: pounds per square inch brake mean effective pressure.

X____X Diesel Fuel
O----O Diesel Fuel + 0.1% Additive

△ ___ △ Diesel Fuel + 0.2% Additive

□ — □ Diesel Fuel + 0.3% Additive

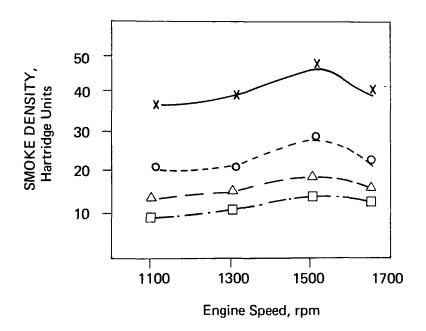


FIGURE 3

Effect of Smoke-Suppressant Additive on Diesel Exhaust Emissions (Direct-injection engine) 12

from a commercial 2-cycle engine and a 4-cycle engine (both operated at idle and at rated power and speed), using treated fuel in one case and untreated fuel in the other case, revealed no significant differences in the percentage of oxygen, carbon dioxide, or carbon monoxide. However, in two instances a reduction of 30 percent in unburned hydrocarbons was noted. The exhaust solids from the tests were also collected and analyzed. Although little change was noted in the average size of the particles, the total number of particles was reduced. The size of particles ranged from 1.5 microns to 74 microns in diameter with the average size being 16.6 microns. The results of the chemical analysis varied with type of engine, mode of operation, and chemical content of the fuel. Solids scraped from the vehicle muffler after the engine operated at high speed showed the presence of carbon and barium sulfate. 15

Golothan¹¹ reported similar results on tests run on a 5.8-liter, direct-injection engine. The additive had no significant effect on carbon monoxide or nitrogen oxide emissions. Golothan¹¹ also ran tests on the effect of the additive on the emissions of polynuclear aromatic hydrocarbons. Tests were run using diesel fuel both with and without the smokesuppressant additives in a single-cylinder direct-injection engine, a multicylinder direct-injection engine, and a

multicylinder precombustion chamber engine. The results are shown in Table 7 in the Appendix. The data showed that the influence of the additive on the amount of polynuclear aromatic hydrocarbon (PAH) depended on the engine type—the decrease in PAH was greater for the multicylinder engines than for the single—cylinder engine. The multicylinder engines are representative of the engines in use today, and therefore Golothan concluded that the use of barium antismoke additives in diesel fuel for modern engines will not increase the health hazard due to emission of polynuclear aromatic hydrocarbons.

The U.S. Navy ran smoke-suppressant tests on gas turbine engines using an organometallic material containing barium and found the material effective in reducing smoke. However, during the tests intolerable amounts of barium carbonate deposit adhered to the turbine and other flow passages. 9,22

Golothan¹¹ collected and analyzed the solids emitted from a number of test diesel engines and some operating diesel vehicles. The results from various test engines running on test beds are shown in Tables 8, 9, and 10 in the Appendix. The results from various vehicles running on road tests or a chassis dynamometer are shown in Table 11 in the Appendix. Golothan¹¹ summarized the results of his solid emission testing as follows:

(1) Up to about 25 percent of the barium compounds

consisted of soluble barium at a sampling point 10 feet from the engine, and upstream from the muffler. In certain engines, however, there was substantial conversion of the insoluble barium to barium sulfate within the exhaust system itself. In the 1.5-liter engine operated on the bench with fuel A, for example, the soluble barium at the end of the pipe was only 0.5 percent of the total barium, whereas before passing through the muffler, it was 11.5 percent under the same operating conditions. This conversion did not appear to occur in all engines, as indicated by the soluble barium content of 10 percent at the end of the exhaust pipe of the minibus engine operated on the motorway.

- (2) Under certain conditions, especially with fuel containing 0.3 percent by weight of sulfur, the proportion of soluble barium in the exhaust was very small, even when samples were taken upstream from the muffler.
- (3) In most of the engines examined, engine operating conditions within the range examined had only a minor effect on the ratio of soluble to insoluble barium.
- (4) The ratio of fuel sulfur to barium, even at ratios much above stoichiometric, has a pronounced effect on the soluble/insoluble barium ratio, with fuel containing 0.3 percent sulfur, and 0.075 percent by weight of barium antismoke additive. Doubling the amount of additive not only doubled the total barium,

but also increased the soluble/insoluble barium ratio. Similarly, reduction of the fuel sulfur content from 0.3 to 0.15 percent increased this ratio markedly.

From the data, Golothan¹¹ estimated that the maximum amount of soluble barium in exhaust gases that would be emitted at full load would be 12,000 $\mu g/m^3$. This was based on having an additive concentration in the diesel fuel of 0.075 percent by weight of barium and on 25 percent of the total barium in the exhaust solids being soluble.

The references quoted above gave only a limited amount of information on the composition of the exhaust gases and solids from diesel engines using barium-base additives. No information has been found which provides a complete analysis of the chemical or physical nature of automobile exhausts, or on the physiological effects of exhaust gases containing compounds of fuel additives.

3.4 Environmental Air Concentrations

No quantitative data have been found on the concentrations of barium or its compounds in the atmosphere. However, the National Air Sampling Network is currently collecting air samples for barium analysis. 17

Samples of the environmental air were taken from moving vehicles in downtown New York, Cincinnati, Washington, Chicago,

and Los Angeles in 1967 and 1968, under the auspices of the Division of Air Quality and Emissions Data, National Air Pol-lution Control Administration. On the basis of these samples, the presence of barium in the air was established; however, according to Morgan, the present techniques for sampling from moving vehicles are inadequate for quantitative analysis.

4. ABATEMENT

No information has been found on the abatement of barium or its compounds in the environmental atmosphere. Since most of the barium processed by industry is in solid form, the conventional methods for removal of solids, such as bag filters, electrostatic precipitators, and wet scrubbers, should prove effective in preventing their escape to the atmosphere. No information has been found on the control of emission of barium-containing exhaust solids from diesel engines operating with fuel containing barium-base smoke-suppressant additives.

5. ECONOMICS

No information has been found on the economic costs of barium air pollution or on the costs of its abatement.

Data on the production and consumption of barium and its compounds are presented in Section 3.

METHODS OF ANALYSIS

6.

6.1 Sampling Methods

Dusts and fumes of barium compounds may be collected by any of the usual methods for collection of particulate matter. For concentrations of barium encountered in ambient air, sampling has to be done with membrane filters. Barium solids from diesel engine exhaust samples have been collected on analytical-grade filter paper.

6.2 Quantitative Methods

Any barium sample soluble in hydrochloric acid can be analyzed by spectrographic methods. Low concentrations of barium can be quantitatively determined by emission spectrography or atomic absorption. Thompson et al. 27 reported that when barium is analyzed by atomic absorption, the minimum detectable limit is 0.02 $\mu g/m^3$ based on an air sample of 2,000 m^3 .

To convert all the barium collected on a filter to a soluble form for spectrographic analysis, the filter is ashed and the ash is dissolved in a hydrochloric acid and nitric acid mixture. To Golothan separated the soluble and insoluble barium compounds by digesting the solids on the filter paper with hydrochloric acid. This acid solution was analyzed directly for the soluble barium compounds. The solid residue

(remaining after the acid treatment) was asked and treated with acid and subsequently analyzed to determine the amount of insoluble barium compounds in the original sample.

Industrially, barium is usually determined by precipitating it as insoluble barium sulfate, separating the precipitate, and weighing it.^{2,3} When barium is associated with other alkaline earths such as calcium and strontium, the calcium is separated as calcium nitrate by dissolving it in a mixture of alcohol and absolute ether. The barium is then precipitated as barium chromate from the slightly acidified (acetic acid) mixture.³

7. SUMMARY AND CONCLUSIONS

Metallic barium is highly reactive, and if released to the atmosphere, quickly becomes converted to a barium salt. Soluble barium salts are very toxic, and if ingested, have a strong stimulating effect on all muscles, including the heart. Symptoms of barium poisoning are excessive salivation; vomiting; colic; diarrhea; convulsive tremors; slow, hard pulse; and increased blood pressure. There have been very few reported deaths due to barium poisoning. Insoluble barium compounds, such as common barium sulfate, are generally nontoxic. Inhaled barium compounds are known to cause a benign pneumoconiosis called baritosis, which does not cause symptoms of emphysema, bronchitis, or reduced respiratory capacity.

Tests on animals with exhaust solids from a diesel engine using fuels with barium-base smoke-suppressant additives indicated that the LD_{50} of these exhaust solids was in excess of 10 grams per kilogram of body weight. Very limited animal studies with these exhaust solids do not appear to have demonstrated any acute health effects from the concentrations used; no information is available on chronic effects. No information was found on the effect of barium and its compounds on plants or materials.

Barium occurs naturally mainly as barite (barium sulfate)

and witherite (barium carbonate). Approximately 90 percent of the barite produced is used as well-drilling mud. Lithopone and other barium compounds are produced with the remainder. No environmental emission data were found for the mines or refineries producing barite, lithopone, or any of the other barium compounds.

A number of proprietary barium-base organometallic compounds used as additives in diesel fuel have been found to be very effective in reducing smoke emissions from diesel engines. Tests with diesel engines with and without the smoke-suppressant additives showed very little change in gaseous emissions. Analysis of solids emitted from these engines revealed the presence of barium sulfate and barium carbonate. The soluble barium carbonate content varied from under 1 percent to about 25 percent of the total barium content of the exhaust solids. Based on the 25 percent soluble salt content, it was estimated that the maximum emission of barium from a diesel engine would be on the order of 48,000 μ g/m³ of exhaust. Sufficient data are not available to give detailed physical and chemical properties of these barium-containing diesel engine exhaust solids.

Although no quantitative measurements have been made of the environmental air concentrations of barium, qualitative measurements in some major U.S. cities have shown the presence of barium. Samples for quantitative measurements are being collected at the present time.

No information has been found on techniques for control of emissions of barium and its compounds. However, for industrial processes, control equipment such as filters, electrostatic precipitators, and wet scrubbers could be used.

No information has been found on the economic costs of barium air pollution or on the costs of its abatement.

The barium concentration in the atmosphere can be measured by collecting atmospheric samples on a filter, dissolving the barium compound, and analyzing the solution by spectrographic methods.

Based on the material presented in this report, further studies are suggested in the following areas:

- (1) Expansion of research on characterization and analysis of exhausts from motor vehicles. Special emphasis should be given to the various fuel additives, including barium and its compounds.
- (2) Additional research on acute and chronic health effects related to atmospheric barium and its compounds.
- (3) Measurement of ambient air concentrations of barium, especially in urban areas.

REFERENCES

- 1. Abernethy, R. F., and F. H. Gibson, Rare Elements in Coal, U.S. Bur. Mines, Inform. Circ. 8163 (1963).
- 2. "Barium," in <u>Encyclopedia of Science and Technology</u>, vol. 2 (New York: McGraw-Hill, p. 94, 1960).
- 3. "Barium" and "Barium Compounds," in <u>Kirk-Othmer Encyclo-pedia of Chemical Technology</u>, vol. 3 (New York: Wiley, pp. 77,80, 1964).
- 4. Brandt, A. D., <u>Industrial Health Engineering</u> (New York: Wiley, 1947).
- 5. Browning, E., <u>Toxicity of Industrial Metals</u> (London: Butterworths, pp. 53-56, 1961).
- 6. DeCorso, S. M., et al., Smokeless Combustion in Oil Burning Gas Turbines, Presented at the ASME-IEEE Joint Power Generation Conference, Detroit, 1967, Am. Soc. Mech. Engrs. Publication 67 PWR-5.
- 7. Deeter, W. F., California's Program to Reduce Diesel Smoke (Discussion of Paper), Preprint (1966).
- 8. Elkins, H. B., <u>The Chemistry of Industrial Toxicology</u> (New York: Wiley, 1959).
- 9. Fiorello, S. C., The Navy's Smoke Abatement Program, Society of Automotive Engineers, <u>S.A.E.-680345</u> (1968).
- 10. Glover, I., The Fuel Additive Approach Towards the Alleviation of the Nuisance of Diesel Smoke, <u>J. Inst. Petrol. 52</u> (509):137 (1966).
- 11. Golothan, D. W., Diesel Engine Exhaust Smoke. The Influence of Fuel Properties and the Effects of Using Barium-Containing Fuel Additive, Society of Automotive Engineers, S.A.E.-670092 (1967).
- 12. Influence of Fuel Properties and Effect of Anti-Smoke Additives on Diesel Exhaust Smoke, <u>S.A.E. Journal</u> <u>76(3):</u> 36 (1968).
- 13. Ladoo, R. B., and W. M. Meyers, <u>Non-Metallic Minerals</u> (New York: McGraw-Hill, 1951).

- 14. The Merck Index, 8th ed. (Rahway, N.J.: Merck, 1968).
- 15. Miller, C. O., Diesel Smoke Suppression by Fuel Additive Treatment, Society of Automotive Engineers, <u>S.A.E.-670093</u> (1967).
- 16. <u>Minerals Yearbook</u>, Bureau of Mines, U.S. Govt. Printing Office, Washington, D.C. (1966).
- 17. Morgan, G., Director, Division of Air Quality and Emissions Data, National Air Pollution Control Administration, personal communication (May 1969).
- 18. Nadel, J. A., "Alveolar Duct Constriction After Barium Sulfate Microembolism," in <u>Pulmonary and Embolic Disease</u> (San Francisco: Calif. Univ. Dept. of Medicine, 1964).
- 19. Patty, F. A., <u>Industrial Hygiene and Toxicology</u>, vol. II (New York: Wiley, pp. 998-1002, 1962).
- 20. Report of the Medical Lectures and Discussion at the 5th International Silicosis Convention—Munster Westphalia, April 1967, Staub Rein. der Luft 27(9):42 (1967).
- 21. Sax, I. N., <u>Dangerous Properties of Industrial Materials</u> (New York: Reinhold Book Corp., 1968).
- 22. Shayeson, M. W., Reduction of Jet Engine Exhaust Smoke with Fuel Additives, Society of Automotive Engineers, <u>S.A.E.-</u> 670866 (1967).
- 23. Slade, D. H., Meteorology and Atomic Energy, U.S. Atomic Energy Commission, Division of Technical Information (July 1968).
- 24. Spector, W. S., <u>Handbook of Toxicology</u>, vol. 1 (Washington, D.C.: Division of Biology and Medicine, National Academy of Sciences-National Research Council, Apr. 1955).
- 25. Stern, A. C., <u>Air Pollution</u>, vol. III (New York: Academic Press, 1968).
- 26. Thomas, C. W., and N. A. Wayman, <u>Atmospheric Behavior of Airborne Radio Nuclides</u>, Pacific Northwest Lab Annual Report, BNWL 481, U.C. 48, vol. 11, part 2 (Dec. 1967).

- 27. Thompson, R. J., G. B. Morgan, and L. J. Purdue, Analyses of Selected Elements in Atmospheric Particulate Matter by Atomic Absorption, Preprint, presented at the Instrument Society of America Symposium, New Orleans, La. (May 5-7, 1969).
- 28. Threshold Limit Values for 1967—Recommended and Intended Values, 29th Annual Meeting of the American Conference of Governmental Industrial Hygienists, Chicago (May 1967).

OTHER REFERENCES

Ayre, J. E., Human Cell-Dysplasia Following Barium, <u>Ind. Med.</u> Surq. 35:393 (1966).

Barium Carbonate Poisoning, J. Am. Med. Assoc. 174:197 (1960).

Barium and Its Inorganic Compounds, Hygienic Guide Series, Am. Ind. Hyg. Assoc. J. (Nov.-Dec. 1962).

Bauer, G. C. H., et al., A Comparative Study of the Metabolism of ^{140}Ba and ^{45}Ca in Rats, Biochem. J. 63:535 (1956).

Bligh, P. H., and D. M. Taylor, Comparative Studies of the Metabolism of Strontium and Barium in the Rat, <u>Biochem. J.</u> 87:612 (1963).

Boekelman, W. A., Barium in Human and Animal Tissues, <u>Ned-Tijdischr. Geneesk</u> 105:2145 (1961); <u>Chem. Abstr. 56</u>:6519c (1962).

Boender, C. A., et al., Iron Absorption and Retention in Man, Nature 213:1236 (1967).

Boyd, E. M., and M. Abel, Acute Toxicity of Barium Sulfate Administered Intragastrically, <u>Can. Med. Assoc. J. 94</u>:849 (1966); <u>Abstr. J. Am. Med. Assoc.</u> 196(6):243 (1966).

Cember, H., et al., Pulmonary Penetration of Particles Administered by Intratracheal Insufflation, A.M.A. Arch. Ind. Hyg. Occup. Med. 10:124 (1954).

Cember, H., et al., Pulmonary Effects from Radioactive Barium Sulfate Dust, A.M.A. Arch. Ind. Health 12:628 (1955).

Cember, H., et al., The Elimination of Radioactive Barium Sulfate Particles from the Lung, A.M.A. Arch. Ind. Health 13:170 (1956).

Cember, H., et al., The Influence of Radioactivity and Lung Burden on the Pulmonary Clearance Rate of Barium Sulfate, Am. Ind. Hyq. Assoc. J. 22:27 (1961).

Christensen, H. E., et al., Experimental Barium Poisoning, Paper, 10th Annual Meeting, American Industrial Hygienists' Association, Detroit, Mich. (Apr. 7, 1949).

- Diengott, D., et al., Hypokalaemia in Barium Poisoning, Lancet 2:343 (1964).
- DiPalma, J. R. (Ed.), <u>Drill's Pharmacology in Medicine</u>, 3rd ed (New York: McGraw-Hill, pp. 709,987,1429-1430, 1965).
- DuBois, K. P., and E. M. K. Geiling, <u>Textbook of Toxicology</u> (New York: Oxford Univ. Press, p. 139, 1959).
- Fairhall, L. T., <u>Industrial Toxicology</u>, 2nd ed. (Baltimore: Williams & Wilkins, pp. 21-23, 1957).
- Fleming, A. J., and C. A. D'Alonzo (Eds.), Modern Occupational Medicine (Philadelphia: Lea & Febiger, pp. 81-82,386, 1954).
- Gleason, M. N., R. E. Gosselin, and H. C. Hodge (Eds.), <u>Clinical Toxicology of Commercial Products</u>, 2nd ed. (Baltimore: Williams & Wilkins, Section III, p. 31, 1963).
- Goodman, L. S., and A. Gilman (Eds.), <u>The Pharmacological</u>
 <u>Basis of Therapeutics</u>, 3rd ed. (New York: Macmillan, pp. 804-805, 1965).
- Huppertz, A., Barite Lung, Fortschr. Gebiete Röntgenstrahlem u. Nuklearmed. 89:146 (1958); Air Pollution Control Assoc. Abstr. 5:2755 (1959).
- Huston, J., Jr., et al., Pulmonary Reaction to Barium Sulfate in Rats, Arch. Pathol. 54:430 (1952).
- Johnson, D., Jr., et al., Tolerance of Chickens for Barium, Proc. Soc. Exptl. Biol. Med. 104:436 (1960).
- Johnson, F. B., and L. E. Zimmerman, Barium Sulfate and Zinc Sulfide Deposits Resulting from Golfball Injury to the Conjunctiva and Eyelid, <u>Am. J. Clin. Pathol</u>. <u>44</u>:533 (1965).
- Johnstone, R. T., and S. E. Miller, <u>Occupational Diseases and Industrial Medicine</u> (Philadelphia: Saunders, pp. 221,235,268, 1960).
- Lewi, Z., and Y. Bar-Khayim, Food-Poisoning from Barium Carbonate, <u>Lancet</u> 2:342 (1964).
- Morton, W., Poisoning by Barium Carbonate, Lancet 2:738 (1945)

Oettingen, W.F. von, "Poisoning," in <u>A Guide to Clinical</u>
<u>Diagnosis and Treatment</u>, 2nd ed. (Philadelphia: Saunders, pp. 255-256, 1958).

Osol, A., and G. E. Farrar, Jr. (Eds.), <u>The Dispensatory of the United States of America</u>, 25th ed. (Philadelphia: Lippincott, pp. 139-141, 1955).

Pendergrass, E. P., and R. R. Greening, Baritosis. Report of a Case, A.M.A. Arch. Ind. Hyg. Occup. Med. 7:44 (1953).

Poisoning with Barium Carbonate, <u>J. Am. Med. Assoc.</u> 101:625 (1933).

Rumiantsev, G. I., On the Problem of Baritosis, <u>Gigiena i Sanit</u>. 23:17 (1958); <u>Air Pollution Control Assoc. Abstr.</u> 6:3152 (1960).

Rumyantsev, G. I., Effect on the Organism of Rare, Dispersed, and Other Metals and Their Compounds Used in Industry: Barium, <u>Toksikol. Redkikh Metal.</u>, pp. 176-187 (1963); <u>Chem. Abstr. 60</u>:4682e (1964).

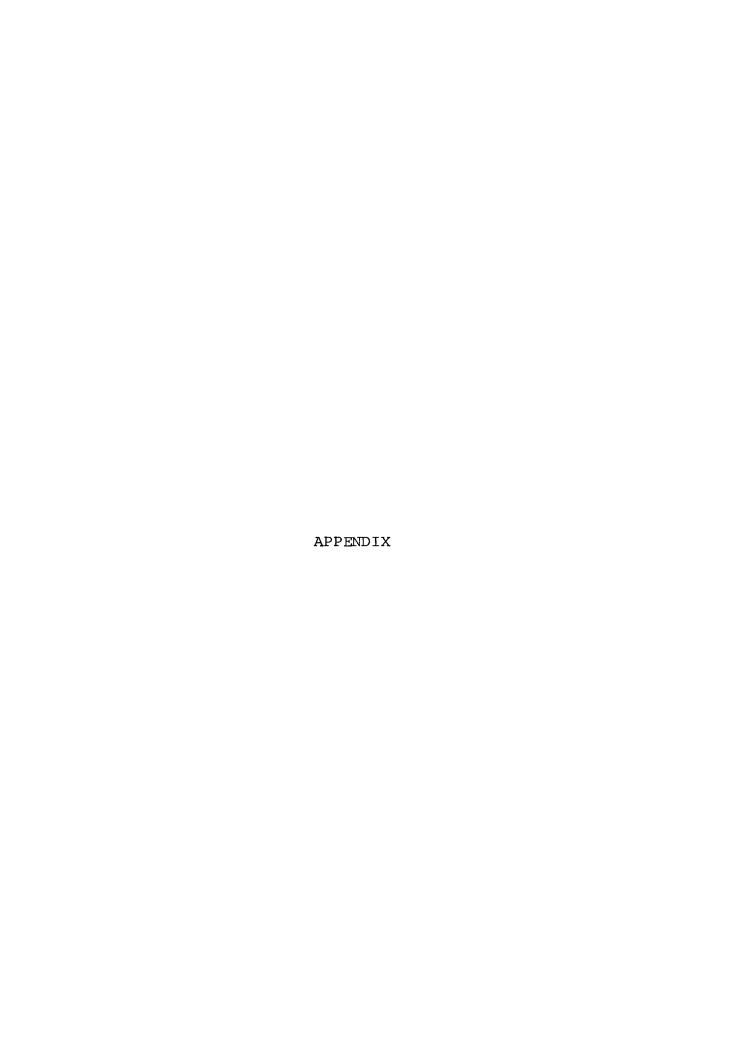
Sollmann, T., <u>A Manual of Pharmacology</u>, 8th ed. (Philadelphia: Saunders, pp. 665-667, 1957).

Spedini, F., and P. L. Valdini, Study of Barite Pneumoconiosis, Radiol. Med. 26:1 (1939); abstr., J. Ind. Hyg. Toxicol. 23:95 (1941).

Thienes, C. H., and T. J. Haley, <u>Clinical Toxicology</u>, 4th ed. (Philadelphia: Lea & Febiger, pp. 167-169, 1964).

Truhaut, R., and F. Berrod, Toxicology of Barium. II. Metabolism and Distribution in the Organs of the Guinea Pig Following Semi-Chronic Poisoning, Ann. Pharm. Franc. 20:637 (1962); Chem. Abstr. 58:10645f (1963).

U.K. Ministry of Labour, <u>Annual Report of H. M. Chief</u>
<u>Inspector of Factories on Industrial Health--1963</u> (London: Her Majesty's Stationery Office, pp. 39-40, 1964).



PROPERTIES, TOXICITY, AND USES OF BARIUM AND SOME BARIUM COMPOUNDS²,3,13,14,25

Compound	Properties	Toxicity	Uses
Barium Ba	Yellowish- white, slightly lus- trous lumps mp 850°C bp 1,140°C	The symptoms of barium poisoning are excessive salivation, vomiting, colic, violent diarrhea, convulsive tremors, increased blood pressure, hemorrhages in gastrointestinal tract and kidneys, muscular paralysis	Used as a getter in electronic tubes and as alloying agent with nickel for spark plug elements. Emissions from barium-133 and barium-137 are used as standards in spectrometry
Barium acetate Ba(C ₂ H ₃ O ₂) ₂ • H ₂ O	White crys- tals. Loses its H ₂ O of hydration at 110 ^O C	Poisonous	As mordant for printing fabrics; in lubricating oil and grease; as cata-lyst for organic reactions
Barium benzene sulfonate Ba(C ₆ H ₅ SO ₃) ₂ • H ₂ O	White, nacre- ous leaflets, fully soluble in water	Poisonous	In lubricating oil addi- tives
Barium binoxalate Ba(HC ₂ O ₄) ₂ • 2H ₂ O	Dihydrate, very slightly soluble in water	Poisonous	

TABLE 2 (Continued)

PROPERTIES, TOXICITY, AND USES OF BARIUM AND SOME BARIUM COMPOUNDS

Compound	Properties	Toxicity	Uses
Barium bromate Ba(BrO ₃) ₂ •H ₂ O	White crystals or crystalline powder. De- composes at 260°C	Poisonous	In preparation of rare earth bromates; as cor-rosion inhibitor for low-C steel
Barium bromide BaBr ₂	mp 847 ^O C Very soluble in water. Colorless crystals	Poisonous	In the manufacture of other bromides; in the preparation of phosphors
Barium carbonate BaCO ₃	White, heavy powder. Al-most insoluble in water. Decomposes at ~1,300°C into BaO and CO ₂ . Soluble in HCl	Poisonous	As rat poison; in ceramics, enamels; in manufacture of paper, barium salts, optical glasses; in case-hardening steels

TABLE 2 (Continued)

PROPERTIES, TOXICITY, AND USES OF BARIUM AND SOME BARIUM COMPOUNDS

Compound	Properties	Toxicity	Uses
Barium chlorate Ba(ClO ₃) ₂ H ₂ O	Hydrate. Monoclinic prismatic crystals. mp anhydrous 414 ^O C		In pyrotechnics (green fire); in manufacture of explosives and matches; as mordant in dyeing
Barium chloride BaCl ₂	Crystals or granules or powder. Very soluble in water	Poisonous	In manufacture of blanc fixe; as mordant for acid dyes; in weighting and dyeing textile fabrics; as boiler compounds for softening water; as purifying agent in brines; in manufacture of barium colors and of chlorine and sodium hydroxide; as flux for magnesium alloys; in case-hardened steel

TABLE 2 (Continued)

PROPERTIES, TOXICITY, AND USES OF BARIUM AND SOME BARIUM COMPOUNDS

Compound	Properties	Toxicity	Uses
Barium chromate BaCrO ₄	Yellow, heavy, monoclinic	Poisonous	As a pigment almost en- tirely in anticorrosion jointing pastes to pre- vent electrochemical cor- rosion at junctions of dissimilar metals; some use in artists' colors and in coloring glass, cera- mics, porcelain. Also used in metal primers, pyrotechnic compositions, safety matches
Barium cyanide Ba(CN) ₂	White crys- talline pow- der. Slowly decomposes in air. Very soluble in water	Very poisonous	In electroplating pro- cesses
Barium dithionate BaS ₂ O ₆ •2H ₂ O	Rhombic or monoclinic, colorless crystals	Poisonous	

TABLE 2 (Continued)
PROPERTIES, TOXICITY, AND USES OF BARIUM AND SOME BARIUM COMPOUNDS

Compound	Properties	Toxicity	Uses
Barium ferrocyanide BaFe(CN) ₆ •6H ₂ O	Yellow crys- tals. Decom- poses at 80°C		
Barium fluoride BaF ₂	White powder. mp 1,353 ^O C bp 2,260 ^O C	Poisonous	As a flux and opacifier in vitreous enamels; in the manufacture of carbon brushes for motors and generators; in heat-treating metals; in embalming; in glass manufacture
Barium formate Ba(HCOO) ₂	Crystals. Soluble in water	Poisonous	
Barium hexafluoro- silicate BaSiF _e	Decomposes at 300°C	Highly toxic, especially when brought into solution by alkali	In preparation of silicon tetrafluoride; as pesti-cide

TABLE 2 (Continued)

PROPERTIES, TOXICITY, AND USES OF BARIUM AND SOME BARIUM COMPOUNDS

Compound	Properties	Toxicity	Uses
Barium hydroxide Ba(OH) ₂ •8H ₂ O	White powder. Slightly solu- ble in water. mp 78°C Dehydrates at 780°C	Poisonous	In manufacture of alkali, glass; in synthetic rubber vulcanization; in corrosion inhibitors, drilling fluids, lubricants, pesticides, sugar industry; as boiler scale remedy; in refining animal and vegetable oils; in softening water; in frescopainting
Barium hypophosphite Ba(H ₂ PO ₂) ₂ 'H ₂ O	Monoclinic. Crystalline powder	Poisonous	In nickel plating
Barium iodate Ba(IO ₃) ₂	White crys- tals. Be- comes anhy- drous at 130 ⁰ C	Poisonous	
Barium iodide BaI ₂		Poisonous	In the manufacture of other iodides

TABLE 2 (Continued)

PROPERTIES, TOXICITY, AND USES OF BARIUM AND SOME BARIUM COMPOUNDS

Compound	Properties	Toxicity	Uses
Barium manganate(VI) BaMnO ₄		Poisonous	As pigment in fresco painting instead of Scheele's green because not so poisonous as latter.
Barium mercu- ric bromide BaHgBr ₄	Very deli- quescent, crystalline mass. Freely soluble in water	Poisonous	
Barium mercu- ric iodide BaHgI ₄	Yellow or reddish crys- tals	Poisonous. See Barium	As an aqueous solution known as Rohrbach's solution, for separating minerals of different density
Barium nitrate Ba(NO ₃) ₂	White crys- tals or pow- der. mp 592 ^O C	Poisonous	In manufacture of BaO ₂ ; as pyrotechnic for green fire; as green signal lights; in the vacuum tube industry

TABLE 2 (Continued)

PROPERTIES, TOXICITY, AND USES OF BARIUM AND SOME BARIUM COMPOUNDS

Compound	Properties	Toxicity	Uses
Barium nitrite Ba(NO ₂) ₂	White crystals. Soluble in water. Decom- poses at 217 ^O C	Poisonous	In diazotization reactions; for prevention of corrosion of steel bars; in explosives
Barium oxalate BaC ₂ O ₄	White crystal- line powder	Poisonous	
Barium oxide BaO	White to yel- lowish-white powder or lumps. mp 1,923°C	Poisonous	Porous grades are marketed especially for drying gases and solvents (particularly alcohols, aldehydes, and petroleum solvents). Swells but does not become sticky upon absorption of moisture. Also used for making barium methoxide, case-hardening steels, and lubricating oil detergents
Barium perchlorate Ba(ClO ₄) ₂ •3H ₂ O	Colorless crystals. Soluble in water. De- composes at 400° C	Poisonous	In the determination of ribonuclease; as absorbent for water in C and H analysis

TABLE 2 (Continued)

PROPERTIES, TOXICITY, AND USES OF BARIUM AND SOME BARIUM COMPOUNDS

Compound	Properties	Toxicity	Uses
Barium permanganate Ba(MnO ₄) ₂	Brownish- violet to black crys- tals	Poisonous	As dry cell depolarizer
Barium peroxide BaO ₂	White or grayish-white, heavy powder. mp 450 ⁰ C	Poisonous	In bleaching animal sub- stances, vegetable fibers, and straw; as glass de- colorizer; in manufacture of H ₂ O ₂ and oxygen; in dyeing and printing tex- tiles; with powdered alu- minum in welding; in cathodes; in igniter compo- sitions. As oxidizing agent in organic synthesis
Barium phos- phate dibasic BaHPO4	Crystals. Practically insoluble in water	Poisonouș	In fireproofing composi- tions; in preparation of phosphors
Barium phosphite BaHPO ₃	Crystalline powder	Poisonous	

TABLE 2 (Continued)

PROPERTIES, TOXICITY, AND USES OF BARIUM AND SOME BARIUM COMPOUNDS

Compound	Properties	Toxicity	Uses
Barium plati- nous cyanide BaPt(CN) ₄	Large dichroic crystals. Soluble in about 35 parts water	Poisonous	As aqueous solution mixed with some adhesive and painted on paper or wood, exhibits luminescence when exposed to the invisible ultraviolet rays of the spectrum or to roentgen, radium, or cathode rays; hence used in radiography for making X-ray screens
Barium selenate BaSeO ₄	Orthorhombic crystals. Decomposes by heat	Poisonous	
Barium selenide BaSe	Cubic micro- crystalline powder. De- composes in water		In photocells, semicon- ductors
Barium silicide BaSi ₂	Metal-like, gray lumps. Melts at white heat		For deoxidizing and desul- furizing steel and for oth- er metallurgical purposes

TABLE 2 (Continued)

PROPERTIES, TOXICITY, AND USES OF BARIUM AND SOME BARIUM COMPOUNDS

Compound	Properties	Toxicity	Uses
Barium sulfate (blanc fixe) BaSO ₄	Fine, heavy odorless powder. Decomposes above 1,600°C. Not soluble in water or diplute acids	Nontoxic. Inhalation produces a benign pneumoconiosis called baritosis with no symptoms of emphysema, bronchitis, or reduced respiratory capacity	In manufacture of photographic papers; as filler for rubber, linoleum, oilcloth, storage batteries, glazed powders, lithographic inks; as a watercolor pigment for colored paper; as a paper coating. Med. use: X-ray contrast medium. Antidiarrheal and demulcent powder. Vet. use: X-ray examination of gastrointestinal tract of dogs and cats
Barium sulfide BaS	Heavy white powder. mp >2,000°C	Poisonous	As depilatory; in luminous paints; in manufacture of lithopone; for vulcanizing rubber, generating H ₂ S. In commercial depilatory mixtures for preoperative preparation
Barium sulfide (black ash) BaS		Poisonous	As raw material for other barium compounds

TABLE 2 (Continued)

PROPERTIES, TOXICITY, AND USES OF BARIUM AND SOME BARIUM COMPOUNDS

Compound	Properties	Toxicity	Uses
Barium sulfite BaSO ₃	Odorless white crystals or powder	Poisonous	In paper manufacture
Barium tartrate CaH ₄ BaO ₆ •H ₂ O	White granular powder	Poisonous	
Barium thiocyanate Ba(SCN) ₂ •H ₂ O	Deliquescent white crystals. Very soluble in water	Poisonous	In dyeing; in photography; as dispersing agent for cellulose; in preparation of thiocyanates of other metals
Barium thiosulfate BaS ₂ O ₃	Crystalline powder. De- composes	Poisonous	In manufacture of explosives, matches; as an iodometry standard; in photographic diffusiontransfer process

TABLE 2 (Continued)

PROPERTIES, TOXICITY, AND USES OF BARIUM AND SOME BARIUM COMPOUNDS

Compound	Properties	Toxicity	Uses
Barium titanate BaTiO ₃	Light grey- buff powder or crystals. mp 1,625°C. Insoluble in water and alkalies. Slightly solu- ble in dilute acids	Animal experiments show low toxicity	In electronic devices, e.g., as voltage-sensitive dielectric in so-called dielectric amplifiers, in computer elements, magnetic amplifiers, memory devices.
Barium uranium oxide BaU ₂ O ₇	Orange or yel- low powder		For painting on porcelain

Compound	Animal	Route ^a	Dose ^b	Dosage mg/kg Value	Time of Death
Barium acetate	Rabbit	or	LD	236	24 hr
	Rabbit	or	LD	815	$1\frac{1}{2}$ hr
	Rabbit	sc	LD	96	•
	Rabbit	iv	LD	8-15	
Barium carbonate	Mouse	or	LD	200	
	Rat	or	LD ₅₀	1,480 <u>+</u> 340	1 - 8 days
	Rat	or	LD	50-200	
	Rabbit	or	LD	170-300	
	Pig	?	LD	1,000	
Barium chloride	Frog	sc	LD	60	
	Mouse	or	LD	7-14	
	Rat	or	LD	355 - 533	
	Rat	sc	LD	45- 89	
	Rat	iv	MLD	2 0	
	Guinea Pig	sc	${ m LD}$	50 - 60	
	Rabbit	or	LD	170	
	Rabbit	sc	LD	40-75	
	Rabbit	sc	LD	50	
	Rabbit	SC	LD	113	
	Rabbit	iv	LD	100-200	
	Rabbit	iv	LD	4 - 30	

TABLE 3 (Continued)

TOXICITY TO ANIMALS OF SELECTED BARIUM COMPOUNDS

Compound	Animal	Routea	Dose ^b	Dosage mg/kg Value	Time of Death
Barium chloride					
(Continued)	Cat	sc	LD	18-60	
	Cat	iv	LD	40-60	
	Dog	or	LD	90	
	Dog	sc	LD	10-20	
	Dog	sc	${ m LD}$	15 - 25	
	Dog	sc	LD	1	
	Dog	iv	LD	300 _s	
	Pigeon	or	LD	500	
	Pigeon	sc	LD	60 - 80	
	Chicken	sc	LD	60-80	
	Chicken	sc	LD	50 - 80	
	Chicken	sc	LD	55	
	Sheep	iv	${ m LD}$	5	
	Horse	or	LD	800-1,200	
	Horse	iv	LD	700	
	Hedgehog	or	LD	4,800-9,600	
	Hedgehog	sc	LD	50	

TABLE 3 (Continued)

TOXICITY TO ANIMALS OF SELECTED BARIUM COMPOUNDS

Compound	Animal	<u>Route^a</u>	Dos e ^b	Dosage mg/kg Value	Time of Death
Barium fluoride	Frog	sc	LD	1,375	
	Guinea pig	or	LD	350	
	Guinea pig	sc	LD	550	
Barium silicofluoride	Rat Rabbit	or or	LD ₅₀	175 175	

aRoute: or--oral.

sc--subcutaneous.
iv--intravenous.

b_{Dose:} LD

LD--lethal dose.

 $\text{LD}_{50}\text{--lethal}$ dose which kills 50 percent of the group of test animals

(usually 10 or more).

MLD--minimum lethal dose which kills one of the group of test animals.

TABLE 4

DOMESTIC PRODUCTION OF BARITE, UNITED STATES 16

(Thousand Short Tons)

	1057.61	· · · · · · · · · · · · · · · · · · ·				
State	1957 - 61 (avg)	1962	1963	1964	1965	1966
Arkansas	311	259	236	233	249	233
California	21	7	5	6	4	15
Georgia		109	117	109	*	*
Kentucky	*	*	6	6		
Missouri	244	304	287	267	32 9	337
Nevada	95	138	120	149	91	139
New Mexico	*	*	1	*		
South Carolina	122	16	*	39	31	2 9
Tennessee			24			
All Other	40	27	28	21	148	194
Total	833	860	824	830	852	947

^{*}withheld to avoid disclosing company confidential data, included with "All Other."

APPENDIX 54

TABLE 5

DOMESTIC CONSUMPTION OF BARITE 16

(Thousand Short Tons)

	In Man	ufacture of	
Year	Ground Barite	Barium Chemicals	Total
1957 - 61 (avg)	1,202	167	1,369
1962	1,043	168	1,211
1963	1,048	182	1,230
1964	1,103	174	1,277
1965	1,199	189	1,388
1966	1,215	202	1,417

TABLE 6

GROUND AND CRUSHED BARITE SOLD BY PRODUCERS TO CONSUMING INDUSTRIES 16

	1957 - 61 (avg)		1	962	1	1963	
Industry	Short Tons	Percent of Total	Short Tons	Percent of Total	Short Tons	Percent of Total	
Well drilling Glass Paint Rubber Undistributed	1,077,006 19,075 16,453 20,213 10,553	94 2 1 2 1	934,007 39,017 19,786 26,235 4,045	91 4 2 3	907,134 56,362 34,611 28,479 3,121	89 5 3 3	
	1	964	1	965	1966		
Well drilling Glass Paint Rubber Undistributed	930,965 56,866 58,396 26,675 3,787	87 5 6 2	986,889 70,158 68,827 29,992 12,718	84 6 6 3 1	1,022,106 73,660 69,805 38,249 4,605	85 6 6 3	

TABLE 7

EFFECT OF ADDITIVE ON EMISSIONS OF POLYNUCLEAR AROMATIC HYDROCARBONS*-
MEAN TOTAL CONTENTS11

(ppm)

	1.4	-Liter, Di Engine	rect-Injec , l cyl	tion	Injection	, Direct- Engine,	bustion	r, Precom- Chamber e, 4 cyl
	Load, 100 psi bmep			s Fuel ition	1,200 rpm, Full Load		2,000 rpm, Full Load	
Fuel	Total in Exhaust Solids	Total in Exhaust Gas						
Automotive gas-oil	823	2.08	727	5.69	440	0.43	605	0.72
Automotive plus .antismoke additive	1,775	2.71	813	4.8	620	0.24	563	0.35

^{*}Mainly penanthrene, pyrene, and fluoranthene (proportions not given).

TABLE 8

ANALYSIS OF SOLIDS EMITTED FROM 1.5-LITER AUTOMOTIVE DIESEL ENGINE^{all}

Engine Speed (rpm)	Engine Load (psi, bmep)	Fuel ^b	Exhaust Sampling Position	Fuel Consumption (lb/hr)	Soluble Barium in Exhaust Solids (% wt of total Ba)
1,500	30	А	10 ft from engine	3.2	8.5
1,500	90	A	10 ft from engine	7.2	11.5
3,500	70	A	10 ft from engine	16.7	10.5
1,500	90	A	End of pipe	7.25	0.5
1,500	30	В	10 ft from engine	3.2	15.0
1,500	90	В	10 ft from engine	7.5	25.0
3,500	70	В	10 ft from engine	16.25	18.0
1,500	90	С	10 ft from engine	7.3	5.5
1,500	90	С	End of pipe	7.2	0.8

^aEngine type: 4-cylinder, high-speed, four-stroke-unit prechamber engine, with Ricardo Mk V combustion chambers.

bFuels: A = automotive gas-oil (0.3% wt sulfur) + antismoke additive to 0.15% wt barium in fuel.

B = 0.15% wt sulfur fuel + antismoke additive to 0.15% barium in fuel.

C = automotive gas-oil (0.3% wt sulfur) + antismoke additive to 0.075% wt barium in fuel.

TABLE 9

ANALYSIS OF SOLIDS EMITTED FROM 5.8-LITER, TRUCK-TYPE DIESEL ENGINE^{all}

Engine Speed (rpm)	Engine Load (psi, bmep)	Fuel ^b	Exhaust Sampling Position	Fuel Consumption (lb/hr)	Soluble Barium in Exhaust Solids (% wt of total Ba)
1 000	20	70	10 65 5000	6.4	1.9
1,000	30	A	10 ft from engine	19.3	13.0
1,000	100	A	10 ft from engine		
2,600	30	A	10 ft from engine	21.5	8.0
2,600	80	A	10 ft from engine	41.3	9.5
1,000	100	Α	20 ft from engine		13.0
1,000	30	В	10 ft from engine	6.2	17.0
1,000	100	В	10 ft from engine	17.5	24.0
2,600	30	В	10 ft from engine	21.4	23.0
2,600	80	В	10 ft from engine	42.3	23.0
1,000	100	С	10 ft from engine	18.0	7.5
1,000	100	С	20 ft from engine		8.5

^aEngine type: 6-cylinder, direct-injection, four-stroke unit.

bFuels: A = automotive gas-oil (0.3% wt sulfur) + antismoke additive to 0.15% wt barium in fuel.

B = 0.15% wt sulfur fuel + antismoke additive to 0.15% wt barium in fuel.

C = automotive gas-oil (0.3% wt sulfur) + antismoke additive to 0.075%
 wt barium in fuel.

TABLE 10 $\label{table 10} \mbox{ANALYSIS OF SOLIDS EMITTED FROM TWO-STROKE AUTOMOTIVE DIESEL ENGINE$^{\mbox{all}} $}$

Engine Speed (rpm)	Engine Load (psi, bmep)	Fuel ^b	Exhaust Sampling Position	Fuel Consumption (lb/hr)	Soluble Barium in Exhaust Solids (% wt of total Ba)
1,200	93.5	A	10 ft from engine	23.0	6.5
2,000	83.0	Α	10 ft from engine	36.0	1.8
2,000	80.5	В	10 ft from engine	35.4	25.5

^aEngine type: 3-cylinder, opposed-piston, automotive two-stroke unit.

^bFuels: A = automotive gas-oil (0.3% wt sulfur) + antismoke additive to 0.15% wt barium in fuel.

B = 0.15% st sulfur fuel + antismoke additive to 0.15% wt barium in fuel.

TABLE 11 $\label{table 11} \mbox{ANALYSIS OF SOLIDS EMITTED FROM DIESEL VEHICLES} \mbox{\cite{thm 1}}$

<u>Vehicle</u>	Engine	Type of Test	Concentration of Antismoke Additive in Fuel (% wt Ba)*	Operating Condition	Sample Collection Technique	Soluble Ba in Exhaust (% wt of total Ba)
Tanker	8.4-liter, direct- injection	Driving on test track	0.075	Normal driving for 126 miles	Dismantlable silencer	1.4
7-ton truck	5.4-liter, direct- injection	Driving on test track	0.15	30 mph in third gear	Filtration, end of ex- haust pipe	5.5
Minibus	1.6-liter, prechamber	Driving on motorway	0.15	53 mph in top gear	Filtration, end of ex- haust pipe	10.0
Sedan	1.5-liter, prechamber	Chassis dynamometer operation	0.075	60 mph in top gear	Filtration end of ex- haust pipe	1.6

^{*}Fuel: automotive gas-oil, containing 0.3% wt sulfur.