AIR POLLUTION ASPECTS

OF

CHROMIUM 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 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
- Hydrochloric Acid
- 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 Government. They do not however presume to be a synthesis of 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 documents. 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. Additionally, 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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ABSTRACT

Both hexavalent and trivalent compounds of chromium are toxic air pollutants to humans. Inhalation of chromium compounds may produce cancer of the respiratory tract. Workers in the chromate-producing industry have experienced deaths caused by cancer of the respiratory tract at a rate 28 times greater than the normal expected death rate. Exposure to airborne chromium compounds may also produce dermatitis and ulcers on the skin. Hypersensitive people react to hexavalent chromium compounds in very low concentrations (0.0001 percent potassium dichromate solution). The hexavalent chromium compounds are more toxic than trivalent compounds. The effects of low concentrations of these compounds on commercial animals and plants were not found. Chromic acid mists have been observed to discolor automobile and building paints.

The uses of chromium in the metallurgical and chemical industries and in products employing chromate compounds, as well as its presence in cement and asbestos,are believed to be the most likely sources of atmospheric pollution. In 1964 urban air concentrations averaged 0.015 $\mu g/m^3$ and ranged as high as 0.350 $\mu g/m^3$.

No information has been found on the economic costs of chromium air pollution or on the costs of its abatement. Analytical methods for the determination of chromium at the concentrations found in the atmosphere are available.

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1. INTRODUCTION

Chromium (Cr) is commonly known for its use as a decorative finish in chrome plating. Most of the chromium ore produced is used in the production of stainless and austenite steels. However, chromium chemicals* appear to be more important than chromium or chromium ore in relation to air pollution.

Chromium concentrations in the urban air average 0.015 $\mu g/m^3$ and range as high as 0.350 $\mu g/m^3$. Although the exact sources of chromium air pollution are not known, some possible sources are the metallurgical industry, chromate-producing industry, chrome plating, the burning of coal, and the use of chromium chemicals as fuel additives, corrosion inhibitors, pigments, tanning agents, etc. Industrial workers, especially in the chromate-producing industry and chrome-plating works, have been observed to develop a variety of health problems attributed to chromium. These problems include dermatitis, ulcers on the skin and in the upper respiratory tract, perforation of the nasal septum, and cancer of the respiratory tract.

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*Chromium forms a series of compounds corresponding to the oxidation states +2, +3, and +6. The chromous compounds, in which the chromium exhibits the +2 oxidation state, are so readily oxidized on standing in air or in aqueous solution that they are seldom encountered. Chromic compounds are trivalent and amphoteric. The oxides, Cr_2O_3 or CrO_2^-, are referred to as chromites, and the term chromite is easily confused with chromite ore, $FeOCr_2O_3$. Chromates, which are hexavalent, are acidic. They are usually water soluble and form the chromate ion ($CrO_4^=$) or dichromate ion ($Cr_2O_7^=$).

2. EFFECTS

The effects of chromium and its compounds on humans, animals, plants, and materials depend upon the chemical state of the chromium. Chromium metal and trivalent chromium are thought to be relatively nontoxic.[10] Hexavalent chromium may produce a variety of effects. Therefore, the chemical state of chromium in the atmosphere is important.

The oxidation potentials of chromium and its compounds indicate that trivalent chromium is most stable. The chemical potential favors oxidation of chromium metal and chromous ions to the trivalent state, and reduction of hexavalent chromium to the same state. However, a thin oxide layer is believed to protect the metallic chromium from further oxidation.[100]

Chromium trioxide (CrO_3) is perhaps the most important hexavalent chromium compound in the air. When it is added to water or acid, it forms chromic acid (H_2CrO_4) or one of its condensation products:

$$2H_2CrO_4 = H_2Cr_2O_7 + H_2O$$

$$3H_2CrO_4 = H_2Cr_3O_{10} + 2H_2O$$

$$nH_2CrO_4 = H_2Cr_nO_{3n+1} + (n-1)H_2O$$

The formation of the dichromate ion is instantaneous, while the formation of the higher condensation products is slower.[100] These hexavalent oxides are only variations in the hydration of chromium trioxide ($nCrO_3 \cdot H_2O$), and it is common to express the concentration of hexavalent chromium as CrO_3.

Chromite ore ($FeOCr_2O_3$), usually impure, is very inert. It is insoluble in water and acids and resists reactions with most chemicals.[101]

Chromic(III) compounds, being amphoteric, are insoluble in water but soluble in acids.[100] However, chromic compounds are readily complexed to form soluble coordination compounds.

Chromous(II) compounds are so easily oxidized that they are not normally found in mammals.[10]

The properties, toxicity, and uses of chromium compounds are listed in Table 7 in the Appendix.

2.1 Effects on Humans

2.1.1 Chromium Metal and Trivalent Chromium

Until 1956 it was believed that pure metallic chromium was biologically inert and exerted no harmful effects on the body. Moreover, trivalent chromium was considered to exert little or no harmful effects. These conclusions were substantiated by the failure at that time to produce toxic effects in animals[10,75] and the failure to observe a higher morbidity among workers in the chromium-manufacturing industry when compared to other ferroalloy workers.[15] However, more recent evidence indicates that at least the trivalent chromium can produce harmful effects. Sluis-Cremer and Du Toit[91] report that chrome-ore miners develop a benign pneumoconiosis after inhaling chromite dust, but they find no evidence of fibrosis. Worth and Schiller[104] indicate that bronchitis and emphysema may occur in chromite workers. There is mounting evidence

that animals too may suffer toxic effects. They have been made hypersensitive to both chromium(III) and chromium(IV). (See Section 2.2.2.) Some instances of hypersensitivity in humans to chrome-tanned leather have been described.[34] Moreover, dermal sensitivity to trivalent chromium has been observed in people who are epidermally sensitive to hexavalent chromium.[22,36]

2.1.2 Chromates

In contrast to the trivalent compounds, the hexavalent compounds are extremely irritative, corrosive, and toxic to body tissues, and, under some circumstances, exert a carcinogenic action on them.[10,37,73]

The more potent effects of the chromate compounds have been attributed by some investigators[45,75,76,83] to the differences in solubility of the chromium compounds. Most chromium(VI) compounds (except barium chromate and lead chromate) are very soluble in water and body fluids, while chromium(III) is soluble only in acid solution or when complexed with organic or other ligands. Chromite ore, on the other hand, is extremely insoluble. Pierce and Scheel[75] suggest that the toxicity of chromium is a function of its solubility in protein solution. In a subsequent study, Pierce and Stemmer[76] showed that chromium(III) reacted with human serum at the carboxylate groups. The interaction was dependent on pH level of serum, concentration of chromium, and amount of time allowed for the reaction.

It has been suggested that the highly soluble hexavalent compounds may penetrate some tissues before reacting with the tissue.[45,83] Studies[61,80,81,83] of the interaction of chromates with skin indicate that the chromates are reduced to trivalent chromium before binding with the skin. Samitz and his co-workers[80,81,84] have been investigating ascorbic acid as a means of chemically reducing the hexavalent chromium and complexing the resulting trivalent chromium with the ascorbic acid.

In contrast to these studies, Mancuso and Hueper[63] suggest that insoluble chromium compounds may play a causal role in the production of lung cancer because dust of insoluble chromium compounds is retained over long periods of time in the lungs.

Experimental studies were carried out in the U.S.S.R.[23] with hexavalent chromate. In this study 250 men were exposed to 12 different chromium aerosols, ranging in concentration from 1.5 to 40 $\mu g/m^3$. Results indicated that inhalation of air containing 10 to 24 $\mu g/m^3$ of chromium, even for a brief period of time, elicited a sensation of sharp irritation of the upper respiratory tract. For the volunteers most sensitive to the effects of chromium, 2.5 $\mu g/m^3$ of chromium represented the concentration of threshold perception; 1.5 $\mu g/m^3$ was below the perception threshold of the entire group. At these low levels (2.5 $\mu g/m^3$), eye sensitivity to light was

enhanced and adaption to the dark was inhibited. Rats also indicated similar responses.

2.1.2.1 Respiratory Tract

One of the most common effects of inhalation of chromate dust or chromic acid mist among chromite-producing industrial workers and chrome-plating workers is the perforation of the nasal septum.[10,55] This characteristic lesion appears as a painless hole. Often ulcers exist on the nasal septum without the subject's awareness of their presence. Samitz and Katz[82] in their review of the literature cite Edmundson,[29] who reported that 61.4 percent (175 out of 285) of the male workers in the production areas of a large chromate-producing plant exhibited perforation of the nasal septum. Hanslian *et al.*[41] examined 77 persons exposed to chromic acid mist during chrome plating: 19.3 percent had perforation of the nasal septum; 47.7 percent had nasal mucosa irritation; 34.8 percent had atrophy, of whom 9.0 percent had atrophy of the nasal skeleton; 34.8 percent had rhinitis sicca anterior; and 23.1 percent had a lesion of the sensory epithelium. Papillomas of the oral cavity and larynx in 14 persons were found to contain 9.25 μg of chromium. These workers were exposed an average of 6.6 years to a mist containing 4,000 $\mu g/m^3$ of chromium.

Other effects of chromates on the respiratory tract include congestion and hyperemia, chronic catarrh, congestion of the larynx, polyps in the upper respiratory tract, chronic inflammation of the lung, emphysema, tracheitis, chronic

bronchitis, chronic pharyngitis, bronchopneumonia, and cancer of the respiratory tract.[10] (Cancer is discussed in detail in a following section.) These effects were not all observed in a U.S. Public Health Service examination of 897 chromate-producing workers.[37] The Public Health Service in 1953 reported finding a high incidence of severely red throats and a frequent history of pneumonia among these workers. Mikov[66] investigated 85 employees of a chrome-magnesite works and found 5 cases (5.9 percent) of early pneumoconiosis and 15 cases (18.8 percent) of chronic bronchitis. These workers were exposed to dust concentrations of 176,000 $\mu g/m^3$ (3.8 to 5.6 X 10^3 particles/cm^3) containing 4,500 to 9,200 $\mu g/m^3$ of chromium. Chronic bronchitis was observed only in workers with exposures longer than 5 years and pneumoconiosis only in those exposed more than 9 years.

2.1.2.2 Skin

One of the important effects of chromates on individuals is the development of hypersensitivity to these compounds with a resulting dermatitis.[10,37] This eczematoid dermatitis may cause inflammation of intact skin, usually on the hands and forearms, and occasionally on the feet, ankles, face, and back. If the contact with chromates is severe enough, these reactions will appear on normal healthy workers. However, on a few workers who are apparently hypersensitive to chromates, the dermatitis appears to be an allergy. The sensitization usually requires 3 to 6 months to develop, but in some instances several years of exposure have elapsed before sensitization.

Cairns and Colman[18] reported two cases of cement dermatitis on individuals with "green tattoos." Although chromium(III) had been used in tattooing, both subjects were sensitive to the chromate dust in the cement. Newhouse[72] tested 230 assemblers from an automobile factory with potassium dichromate and found that 36 percent reacted compared with 7.6 percent of 66 men in a control group. The cause of the hypersensitivity was traced to a chromate dip used on nuts, bolts, washers, and screws used by the assemblers. Similarly, Engel and Colman[31] found that 65 of 250 workers engaged in wet sanding of primer paint on car bodies developed dermatitis. Investigation revealed zinc chromate in the paint as the cause. An engraving foreman[54] at a Washington, D.C., daily newspaper reported that a worker became so sensitive to a residue of sodium dichromate on engraving plates that he contracted a dermatitis. The sodium dichromate solution had been washed from the plates before the worker handled them. Unfortunately, none of these studies indicates the concentration of chromates necessary to cause dermatitis. Nevertheless, it appears that even small amounts of chromates in air may cause dermatitis in some hypersensitive persons.

The hypersensitivity of individuals may be determined by patch tests.[28] The suggested concentration of potassium dichromate in the test solution is 0.1 to 0.5 percent. A patient with a strong hypersensitivity has reacted to a 0.005 percent potassium dichromate solution and 0.0001 to 0.0004 percent potassium

dichromate solution obtained as a filtrate solution extracted from cement. The original cement contained 0.03 to 6.9 μg of chromium(VI) per gram of cement; expressed as potassium dichromate, this would be 0.08 to 20 μg/g.

Epidermal hypersensitivity, as a result of industrial contact with chromates, has occurred in workers in woolen mills; automobile plants and garages; aircraft plants; locomotive maintenance shops; air-conditioning equipment maintenance shops; plants that manufacture or use chromate compounds; and tanning, photographic, and lithographic plants.[103]

In addition to dermatitis, skin contamination with chromates has been observed to produce ulcers--"chrome holes"--on industrial workers.[10,37,73] These ulcers have even on occasion penetrated to the bone. Over 50 percent of a group of chromate workers showed signs of either active or healed chrome ulcers (scars).[73] The ulcers appear most commonly on the hands, arms, and feet or, in fact, in any area where dust can accumulate, such as the knuckles and roots of the nails. Once the ulcer is formed, it is difficult to heal and, without proper treatment, may persist for long periods of time.

2.1.3 Carcinogenesis

Chromium compounds have been shown to produce cancer in the respiratory tract, especially among workers in the chromate-producing industry.[9,10,16,62,63] The U.S. Public Health Service[37] reported in 1953 that the death rate due to cancer of the respiratory tract of chromate workers was greater than 28

times the expected death rate: 470.8 deaths/100,000 compared with 16.7/100,000 males of the same age group in the United States. The large majority of cancers of the respiratory tract were bronchogenic carcinomas, but a few cancers were located in the upper respiratory tract, such as in the sinus, pharynx, and oral region. There is no evidence to suggest that chromium causes cancer of any organs other than those of the respiratory tract.

The time-concentration relationship between chromium exposure and cancer induction is not known. The average duration of exposure to chromium before death by cancer is 18 years.[10,37] The average time from initial exposure to the diagnosis of cancer is 21 years. The period between the onset of symptoms and death is less than 6 months, in some cases only a few weeks. Cancer that is apparently induced by chromate exposure may develop years after the exposure has ceased. Intervals of as long as 20 to 30 years between the end of exposure and appearance of cancer are on record. The concentration of chromium in the inhaled air that is necessary to produce lung cancer is not known. In most cases, the concentration was seldom measured, especially prior to 1940. In a U.S. Public Health Service study, the average chromium concentrations were measured in six chromate-producing plants. The results of these surveys are summarized in Table 1. The ore processors were exposed primarily to chromite ore, the typical composition of which is given in Table 2. Table 3 shows that

TABLE 1

MEAN CHROMIUM EXPOSURES FOR WORKERS IN CHROMATE-PRODUCING PLANTS[37]

Occupational Groups	Chromium Exposure Total Cr ($\mu g/m^3$)	CrO_3 ($\mu g/m^3$)
Ore processors	420	10
Soda ash-lime handlers	210	10
Mill room laborers	160	30
Mix operators (ore)	770	20
Mix operators (residue)	390	130
Kiln operators	210	90
Kiln building laborers	230	90
Crane operators	260	130
Leach operators	190	120
Mud operators	50	50
Residue drier operators	160	60
Residue mill operators	390	50
Alumina recovery operators	130	50
Evaporator operators	30	20
Chemical treat operators	120	50
Sulfate recovery operators	280	110
Liquor concentration operators	60	40
Centrifuge operators	200	130
Soda drying-bagging operators	110	100
Shippers	160	20
Chromic acid cookers-packers	30	20
Potash production operators	170	170
Chromate operators	30	30
Tanning compound operators	460	10

TABLE 2

TYPICAL COMPOSITION OF CHROMITE ORE[37]

Compound	Weight, percent
Cr_2O_3	14.2
Fe_2O_3	51.1
Al_2O_3	9.2
SiO_2	6.8
MgO	11.3
CaO	3.0
Loss on ignition	4.0

TABLE 3

CHROMIUM IN BODY TISSUES[10]
(μg/100g wet tissue)

Origin of Specimen	Range of Concentrations in People Without Known Exposure to Chromium	Range of Concentrations in Chromate Workers
Abdominal lymph nodes	1	4- 80
Adrenal glands	0-41	5- 76
Aorta		3
Bile		1
Bladder		3- 226
Bone	5	0- 292
Brain	0- 4	0- 5
Bronchus		95- 386
Cartilage		6
Hair		31
Heart		0- 20
Intestines	10	4- 5
Kidney	0- 9.6	0- 211
Larynx		21
Liver	1-11	0- 159
Lungs	0-33	130-9,887
Lung tumor		0-1,658
Metastatic tumors		2- 100
Muscle	0- 8	0- 19
Nasal septum		287
Pancreas	21	8- 36
Skin		5
Spleen	0-98	0- 91
Stomach	0- 5	4- 11
Thyroid	43	24- 53
Trachea		0- 32
Tracheobronchial lymph nodes	0- 1	12-7,590

chromate workers had accumulated appreciably higher concentrations of chromium in the body than the general population. However, examination of the lung tissues indicated that cancers were not always associated with the highest concentrations, nor were the cancers found in the area of the lungs containing the highest concentration of chromium.[10] Undoubtedly, individual susceptibility plays an important role in cancer induced by chromium compounds.

Which chromium compounds can produce cancer is unknown. However, since no cases of lung cancer have been reported among chrome-ore miners[10] or chromite workers,[37] it is generally presumed that cancer is induced by hexavalent compounds, chromates, dichromates, or chromic acid.[10] Acid-soluble, water-insoluble chromium compounds (probably trivalent) have also been suggested as carcinogens.[37]

Animal experiments have also indicated that chromium compounds are carcinogenic. Hueper and Payne[45] state that the high and early yield of tumors in mice implanted with chromium compounds leaves no doubt that chromium is a carcinogenic agent. Moreover, solubility plays an important role in the production of tumors. Calcium chromate, which has a high solubility, produced a high incidence of tumors, whereas barium chromate, which has a low solubility, produced a very low incidence of tumors after a long period of observation.[46]

2.1.4 Nutrition

Recently, chromium has been found to be an essential

element in the diet of rats, which infers that it may be essential to man.[65,85,86] Chromium deficiency in rats produces a syndrome that simulates diabetes: the normal glucose metabolism is inhibited.[85] Mertz[65] believes that chromium is an essential trace element for the normal function of carbohydrate metabolism. Schroeder et al.[86] have shown that chromium exists in all human tissue and is highest at the time of birth (Table 8, Appendix). The chromium content then decreases to a lower plateau. Only the chromium content in the lungs is observed to increase again significantly. Because of the ubiquitous nature of chromium, it has not been possible to find a group of people without chromium in their diet.

2.2 Effects on Animals

2.2.1 Commercial and Domestic Animals

No cases of animal poisoning due to airborne chromium were found in the literature. However, chromite (Cr_2O_3) has been used as an additive in feed for pigs,[10] dogs,[10] and beef cattle[77] to study the digestion of certain foods. In these studies approximately 100 percent of chromite (Cr_2O_3) was recovered unchanged in the feces.

2.2.2 Experimental Animals

A number of animal experiments have been conducted. The early experiments were summarized by Baetjer[10] and are listed in Table 9 in the Appendix. There is evidence that animals can be made hypersensitive to both chromium(III) and chromium(IV). Gross, Katz, and Samitz[39] produced hypersen-

sitive reactions in guinea pigs with potassium dichromate(VI) and chromic(III) chloride. They observed cross-reactions with chromic acetate, chromic nitrate, and chromic sulfate, and no reaction with chromic oxalate. Similar results were obtained by Jansen and Berrens.[50]

Hueper and Payne[45] have shown that cancer can be produced in experimental animals by implantation. However, Baetjer and her co-workers[11,12,92] have been unable in several attempts to produce more than a benign tumor in the lungs of mice and rats inhaling various chromium-containing dusts.

2.3 Effects on Plants

Chromium has been observed both to stimulate plant growth and to be toxic to plants. The effect depends largely on plant type, chromium concentration in the soil, and more importantly, availability of the chromium to plants. In soils less acidic than pH 4 very little chromium is available to plants. When small amounts (0.01 percent) of chromium are available, the growth of oats and barley is stimulated. However, even a smaller amount (0.005 percent) is toxic to wheat. Toxic effects may be expected in plants when the levels of available chromium in the soil exceed 10^{-7} μg/g of soil.[100] Nevertheless, some plants may tolerate as much as 100,000 μg/g.

No evidence of plant damage by airborne chromium was found in the literature.

2.4 Effects on Materials

Chromic acid is not only a strong acid but also a strong oxidizing agent. Therefore, it will cause corrosion of metals, discoloration of paints and building materials, and damage to paper and textiles. For example, damage to paints and building materials caused by the evolution of chromic acid mists from plating operations has been observed.[10]

The exposure of auto finishes to chromic acid mists in Detroit resulted in brown stains on light-colored cars and a blushing on darker shades of paint. Repainting was required because the color change in the paint could not be corrected by washing or polishing.[105]

2.5 Environmental Air Standards

The American Conference of Governmental Industrial Hygienists[97] and the American Industrial Hygiene Association[8,20] have recommended an 8-hour tolerance level of 100 $\mu g/m^3$ for chromic acid and chromates (as CrO_3). This is a reduction from a value of 1,000 $\mu g/m^3$ of chromate (as CrO_3), recommended in 1943 by the American Standard Association.[8]

In the U.S.S.R. a value for chromates (as CrO_3) of 1.5 $\mu g/m^3$ has been recommended as both the maximum permissible single dose and the maximum permissible average daily concentration.[23,52,56,79,94] The U.S.S.R. has also recommended as maximum allowable concentrations for trivalent chromium and its compounds (as Cr_2O_3) 250 $\mu g/m^3$ for a single exposure and 80 $\mu g/m^3$ for an average 24-hour exposure.[51]

3. SOURCES

The pollution of air by chromium and its compounds comes primarily from industrial use and end-product use. There has been no mining of chromite ore in the United States since 1961 because higher-grade ore can be purchased from foreign countries at a cheaper price.[69] Approximately 57 percent of the imported chromite ore ($FeOCr_2O_3$) is used in the metallurgical industry, 30 percent in refractory materials, and 13 percent in the chemical industry (see Table 10, Appendix).

3.1 Natural Occurrence

Elemental chromium is not found in nature. The only important commercial chromium mineral is chromite ($FeOCr_2O_3$), which is also never found in the pure form. (Some of the FeO is replaced with MgO or the Cr_2O_3 is replaced by Al_2O_3. Silica is also present.) Most soils and rocks contain small amounts of chromium, usually as chromic oxide (Cr_2O_3). The continental crust averages 0.037 percent by weight of chromium. In addition, most animal and plant tissues contain small amounts of chromium.

Soils have been observed to contain from a trace to 2.4 percent chromium. Vegetables of 25 botanical families were found to contain 10 to 1,000 μg of chromium per kilogram of dry matter, with most plants falling within the range of 100 to 500 μg/kg.

As stated above, chromite is no longer mined in this country. However, low-grade ore deposits do occur in California, Montana, Oregon, and Alaska.[67]

3.2 Production Sources

3.2.1 Metallurgical Industry

Use of chromite ore in the metallurgical industries is almost all confined to chrome alloys or chromium metal. The U.S. consumers of chrome ore are listed in Table 11 in the Appendix. The metallurgical chromite is usually converted into one of several types of ferrochromium or chromium metal that are alloyed with iron or other elements (usually nickel and cobalt). From these alloys are produced a great variety of useful steels. Over 60 percent of the chromium used in the metallurgical industry is used in making stainless steel; the remainder is used in austenite steels, high-speed steels, other alloy steels, high-temperature steels, and nonferrous alloys.[21,43] Chromium compounds polluting the air from metallurgical uses are likely to be in the trivalent or zero state.

3.2.2 Refractory Materials

Chromite ore is used in the manufacture of refractory bricks to line the inside of metallurgical furnaces because chromite has a high melting point (3,700^{o}F) and is chemically inert. In addition to their use as chromite bricks or magnesia-chrome bricks, chrome refractory materials may be used as coatings to close pores and for joining bricks within the furnace.[101] Studies of chromium air pollution from this source have not been found.

3.3 Product Sources

3.3.1 Chemical Industry

Sodium chromate and dichromate are produced directly from the chromite ore, and are the primary products from which other chromium compounds are manufactured. Table 12 in the Appendix lists the production of chromium chemicals in the United States. Basically, the manufacturing process for chromate chemicals is the same in all plants. Briefly, it consists of roasting the finely ground chromite ore with soda ash or with soda ash and lime. A water-soluble chromate, sodium chromate, is formed and is then converted by acidification into crystalline sodium dichromate (see Figure 1, Appendix):

$$2Cr_2O_3 + 4Na_2CO_3 + 3O_2 \longrightarrow 4Na_2CrO_4 + 4CO_2$$

Gafafer *et al.*[37] report a study in which the dust content of air in six chromate-producing plants was measured. The data show that trivalent chromium dusts are emitted from dry ores at the start of the process, and, after the chromite has been oxidized to chromate, chromate dusts are emitted throughout the remainder of the process (see Table 1, Page 11). The average dust content inside the six plants was 170 $\mu g/m^3$ of chromium(VI). No data were reported on concentration measurements of chromium outside the plants, but the concentration was thought to be much lower. However, analysis of samples

from a comparison paper plant, which was located only one-quarter mile from a chromate-producing plant, showed the presence of chromium in the settled dust. The authors comment that the contamination must have come from the chromate-producing plant. Several dust-controlled working areas in which the dust was exhausted from the plant were mentioned, but no mention of dust-control equipment on the exhaust system was made. Air samples at the mouth of some of these exhaust systems ranged as high as 148,000 $\mu g/m^3$ of chromate. From these data it may be concluded that chromate-producing plants can be a source of chromium air pollution.[37]

A substantial amount of chromium chemicals, estimated in 1956 at 2.8 million pounds of dichromate equivalent, are used in the manufacture of catalysts.[13,14,21,32,38,44,57,93,98]

Chromates are used for the oxidation of organic materials in production of synthetic dyes, saccharin, benzoic acid, anthraquinone, hydraquinone, camphor, and synthetic fibers. The oxidizing properties of chromates have led to their wide use as cleaning agents, in the purification of chemicals, and in inorganic oxidation.

3.3.2 Chrome Plating

A major percentage of the chromic acid that is consumed is used for chrome plating. This plating may be a decorative

finish or "hard" plating. The hydrogen bubbles that evolve from the electrolytic solution carry with them an aerosol of chromic acid. It is now common practice to exhaust these fumes to the atmosphere.[17] Small chrome-plating facilities are almost a neighborhood occurrence.

3.3.3 Other Uses

Chrome-tanning industries use more than 15 million pounds of chromic oxide (Cr_2O_3) annually. The chrome-tanning solution, containing chromium(III) sulfate ($(Cr(H_2O)_5OH)SO_4$), is made from sodium dichromate and may be prepared in a chemical plant or at the tannery.[21,37,100]

Primer paints and dips contain chromates and are used to prepare metal surfaces for painting. Automobile parts are usually dipped in the solution, whereas construction steels are normally sprayed.[21,32,100]

Pigments consume approximately 30,000 tons of sodium dichromate per year. Chromates and chromic oxide are combined with various other metals such as zinc, lead, iron, barium, molybdenum, and strontium to produce a variety of colors.[100]

Chromium mordants find a diversified usage in the textile industry.[100]

Graphic arts industries use approximately 200,000 pounds of dichromates. A photosensitive dichromate-colloid suspension

is used in preparing plates in many printing and reproducing processes.[21]

Fungicides and wood preservatives consume approximately 2.9 million pounds of chromium chemicals annually. The major fungicide use is for potato and tomato blight control, seed sterilization, and lawn fungicide control. The use of chromate wood preservatives in wooden cooling towers may be of particular interest in relation to air pollution.[21,100]

Chromate chemicals are used widely in cooling-tower recirculating water systems as rust inhibitors as well as wood preservatives. The most favored inhibitors are sodium chromate and complex chromate salts.[95] Such systems continuously discharge about 1 percent of their flow to waste (blowdown to waste water), and some water is lost to the atmosphere. Fresh water and chromate are then added to replace the lost water and chromate. The circulating water usually contains 15 to 300 ppm chromate ion. The lower concentrations are more common because synergistic ingredients are frequently used with chromates now.

Corrosion inhibitors for a variety of applications contain chromates. Soluble chromates are effective inhibitors for the corrosion of iron, steel, zinc, aluminum, copper, brass, lead, and related alloys. These inhibitors have found practical

use in cooling towers (mentioned above), air conditioning equipment, automobile radiators, diesel locomotives, marine diesels, stationary diesels, refrigerating brines, ammonia condensers, ammonia absorption systems, stand-by boilers, operating boilers, steam-heating boilers, hot-water heating, salt for melting ice and snow, oil-well-drilling mud, gasoline pipelines, industrial coolers, hydroblasting make-up water, and hydraulic lifts.[100]

Paper matches contain a small amount of potassium dichromate as a burning-rate catalyst. Approximately 400 billion "lights" are manufactured per year.[21]

Fireworks contain some chromium chemicals.[100]

Gasoline antiknock chromium compounds have been tested, but have not been used because of deposition in the engine.[21] However, antistatic additives produced by the Shell Oil Company contain a chromium salt of alkylated salicylic acid. They are recommended for use in aviation or other fuels.[60]

Dry-cell batteries contain a small amount of lithium chromate.[87]

3.4 Other Sources

3.4.1 Asbestos

Some investigators[24,25,27,40,42] have suggested that the small amounts of chromium or other trace substances found

in asbestos may be the cause of cancer associated with asbestos. The chromium concentration found in the most common asbestos mineral, chrysolite, was approximately 1,500 μg/g.[25]

3.4.2 Coal

The concentration of chromium in coal ranges from 7 to 20 μg/g, and the ash contains 1 to 270 μg/g, depending on the origin of the coal.[1] The chromium emissions of six different types of coal-fired power plants are given in Table 4.

3.4.3 Cement

Cement contains chromium[28] sufficient to cause a dermatitis in some hypersensitive people when they come in contact with it.[17] Keenan and Perone[53] have shown that cement contains 0.03 to 7.8 μg of chromium(VI) per gram of cement and 28 to 60 μg of total chromium per gram, depending on the origin of the cement (see Table 13, Appendix). Chromates are thought to be produced during the kiln processing in the manufacture of cements.

The fact that chromates are produced in the heat treating of chromic oxide (Cr_2O_3) under alkaline conditions--as in the production of both chromate and cement--raises the question of production of chromates in other materials, e.g., asbestos.

3.4.4 Welding Rods

Fregert and Ovrum[35] and Shelley[88] have found hexavalent chromium in welding-rod fumes.

TABLE 4

CHROMIUM EMISSIONS FROM COAL-FIRED POWER PLANTS[26]

Type of Boiler Firing	Coal Rate ton/hr	Ash in Coal (as fired) %	Flue Gas Volume, scfm x 10^3		Chromium Emissions					
					$\mu g/m^3$		g/min		g/ton	
			B	A	B	A	B	A	B	A
Vertical	65.6	20.2	397.4	409.9	220	18	2.5	0.21	2.3	0.19
Corner	56.1	14.9	362.9	351.0	1,900	130	19	1.3	20	1.4
Front-wall	52.2	10.3	329.0	328.0	1,100	160	10	1.5	11	1.7
Spreader-stoker	9.2	8.4	53.9	59.6	450	350	.069	.059	.45	.39
Cyclone	64.4	7.7	553.6	500.8	1,900	500	30	7.1	31	6.6
Horizontally opposed	9.6	8.2	62.2	62.2	2,200	410	3.9	.72	24	4.5

A: After fly ash collection.

B: Before fly ash collection.

3.5 Environmental Air Concentrations

Air quality data obtained from the National Air Sampling Network are shown in Table 14 in the Appendix. The national average concentration of chromium in 1964 was 0.015 $\mu g/m^3$ and the national maximum was 0.350 $\mu g/m^3$.[2,4-6]

Schroeder *et al.*[86] investigated the chromium content of the kidneys, livers, lungs, and hearts of people living in various parts of the country. Their data, shown in Table 5, indicate that the environmental exposure to chromium varied significantly. Similar findings were obtained by Tipton and Shafer,[99] who concluded that lungs of subjects from Baltimore have significantly higher chromium concentrations than those from Dallas, Denver, Miami, and San Francisco.

Lee *et al.*[58,59] have measured the particle-size distribution of chromium in ambient air. These data are presented in Table 6.

TABLE 5

CHROMIUM CONCENTRATION IN HUMAN TISSUES BY CITY, U.S.[86]
(μg/g)

City	Kidney	Liver	Lung	Heart
Baltimore	.06	.038	.41	.03
Dallas	.022	.023	.11	.021
Denver	.04	.03	.14	.03
Miami	.015	.012	.14	.014
New York and Chicago	.09	.27	.72	.13
Richmond, Va.	.033	.024	.24	.051
Seattle and Tacoma	.029	.026	.34	.04

TABLE 6

PARTICLE SIZE OF CHROMIUM PARTICULATES IN THE AMBIENT AIR[58,59]

	Concentration ($\mu g/m^3$)				Mass Median Diameter (μ)			
	max	min	avg	max/min ratio	max	min	avg	max/min ratio
Cincinnati[a]	0.91	<0.01	0.16	>91.0	>10	<0.1	1.7	>100
Cincinnati[b]			0.31				1.5	
Fairfax[c]			0.28				1.9	
Indian Creek[d]	0.39	<0.01	0.11	>39	>10	<0.1	2.0	>100

[a]Samples collected in downtown Cincinnati, Ohio, May 24-June 3, 1967.

[b]Samples collected in downtown Cincinnati, Ohio, Sept. 8-23, 1966.

[c]Samples collected in Fairfax, Ohio, a suburb of Cincinnati, Ohio, Feb. 3-16, 1967.

[d]Samples collected at the Indian Creek Wild Life Preserve, Ohio, May 24-June 3, 1967.

4. ABATEMENT

Chromium air pollution usually occurs as particulate emissions, which may be controlled by the usual dust-handling equipment, such as bag filters, precipitators, and scrubbers. Chromium poses no peculiar control problems except when it is emitted as aerosols (e.g., sprays and chromic acid mists).

Some chrome-plating facilities have installed methods of preventing air pollution. Moisture-extractor vanes in the hood-duct system have been used to break up bubbles in the exhaust gases.[101] Most exhaust systems use slot hoods to capture the mists discharged from the plating solutions. The device most commonly used to remove air contaminants from exhaust gases in the hard-chrome-plating facilities is a wet collector. The scrubber water becomes contaminated with the acid; therefore, efficient mist eliminators must be used in the scrubber to prevent a contaminated mist from being discharged to the atmosphere.

The mist emissions from a decorative-chrome-plating tank with lesser mist problems can be substantially eliminated by adding a suitable surface-active agent to the plating solutions. The action of the surface-active agent reduces the surface tension, which in turn reduces the size of the hydrogen bubbles. Several of these mist inhibitors are commercially available.

In a new plating facility, there will be an attempt to replace the hood system with a coating of synthetic material that will float on the electrolyte. The coating is expected to suppress the chromic acid mist to prevent it from leaving the bath.[19]

5. ECONOMICS

No information has been found on the economic costs of chromium air pollution or on the costs of its abatement. However, chromic acid mists have caused some material damage to building and auto paints (see Section 2.4).

Data on the production and consumption of chromium are presented in Section 3.

6. METHODS OF ANALYSIS

6.1 Sampling Methods

Dusts and fumes of chromium compounds may be collected by any method suitable for collection of other dusts and fumes; the impinger, electrostatic precipitator, and filters are commonly used. The National Air Sampling Network uses a high-volume filtration sampler.[96] Chromic acid mists may be collected in an impinger using water or caustic solutions.[102]

6.2 Quantitative Methods

Emission spectroscopy has been used by the National Air Pollution Control Administration for chromium analysis of samples from the National Air Sampling Network.[3,96] The samples are ashed and extracted to eliminate interfering elements. The minimum detectable chromium concentration by emission spectroscopy is 0.0064 $\mu g/m^3$ for urban samples and 0.002 $\mu g/m^3$ for nonurban samples. The different sensitivities result from different extraction procedures required for urban samples.[7]

Thompson *et al.*[96] have reported that the National Air Pollution Control Administration uses atomic absorption to supplement results obtained by emission spectroscopy. The method has a minimum detectable limit of 0.002 $\mu g/m^3$ based on a 2,000 m^3 air sample.

West[102] indicates that the ring oven technique for the

determination of chromium is sensitive to 0.15 μg and has a normal range of 0.3 to 1.0 μg. The chromium is oxidized to the hexavalent state, and the method, therefore, measures total chromium. Diphenylcarbazide is used as the indicator.

A multichannel flame spectrometer has been used by Iida and Fuwa[47,48] to measure magnesium, calcium, copper, manganese, and chromium simultaneously in biological materials. Their initial work indicated a sensitivity of 1.0 μg/ml; however, phosphates seriously interfered with the application of the analysis.[47] In subsequent studies,[48] they added 8-hydroxyquinoline and perchloric acid, which not only eliminated the interference, but increased the sensitivity of the test to two of the elements, calcium and manganese (0.1 μg/ml).

The concentration of chromic acid mists in air can be estimated by a direct field method described by Ege and Silverman.[30,89,90] This is a spot-test method using phthalic anhydride and S-diphenylcarbazide.

A coulometric method for determination of chromium in biological materials is described by Feldman _et al_.[33] The method is sensitive to 0.2 μg of chromium.

Pierce and Cholak[74] have described an atomic absorption method for the determination of chromium in biological systems. The sample must be ashed. The method is sensitive to 0.1 μg of chromium or 0.05 μg/g.

The Mine Safety Appliances Co.[70,71] has a lightweight sampler for estimating quickly the chromic acid mist concentrations in the atmosphere. The operating principle of this instrument is based on the method described above by Ege and Silverman.[30,89,90]

7. SUMMARY AND CONCLUSIONS

The exposure of industrial workers to airborne chromium compounds and chromic acid mists, particularly the hexavalent chromates, has been observed to produce irritation of the skin and respiratory tract, dermatitis, perforation of the nasal septum, ulcers, and cancer of the respiratory tract. Chromium metal is thought to be nontoxic. Hexavalent compounds appear to be much more harmful than trivalent compounds, with the toxic effects depending on solubility. Two effects that appear to be particularly important in relation to air pollution are hypersensitivity to chromium compounds and induction of cancers in the respiratory tract. Exposure of industrial workers in the chromate-producing industry has shown an incidence of deaths from cancer of the respiratory tract which is over 28 times greater than expected. Time-concentration relationships for induction of cancer are not known.

No evidence of damage by airborne chromium to animals or plants has been found. Chromic acid mists have discolored paints and building materials.

In 1964, atmospheric concentrations of total chromium averaged 0.015 $\mu g/m^3$ and ranged as high as 0.350 $\mu g/m^3$. Although the exact sources of chromium air pollution are not known some possible sources are the metallurgical, refractory,

and chemical industries that consume chromite ore; chemicals and paints containing chromium; and cement and asbestos dust. Particulate control methods should be adequate for chromium-containing particles.

No information has been found on the economic costs of chromium air pollution or on the costs of its abatement. Methods of analysis are available to determine the amount of chromium concentration in the ambient air.

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

(1) Resolution of the question of toxicity, hypersensitivity, and cancer induction with relation to the valence of chromium and solubility of chromium compounds.

(2) Determination of the concentration and time of exposure of chromium required to produce cancer.

(3) Determination of the concentration and time of exposure of chromium required to produce allergenic reactions in hypersensitive people of the general public.

(4) Determination of the concentration and valence of chromium adjacent to chrome steel plants, refractory fabricating plants, chromate-producing plants, chrome-plating operations, spray-painting operations, cement-making operations, etc.

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APPENDIX

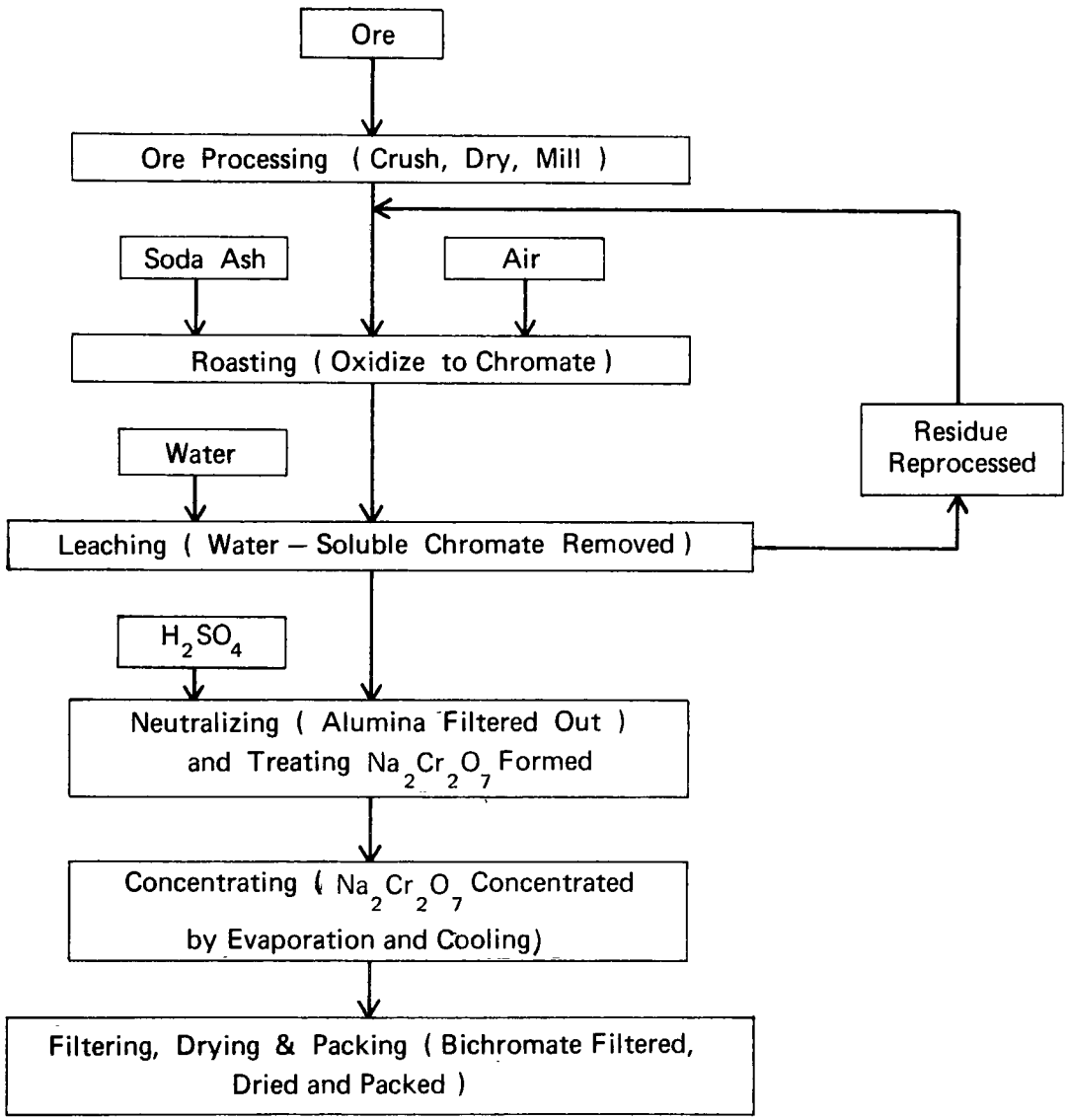

FIGURE 1

Typical Flow Diagram of Chromate-Producing Plant[21]

TABLE 7. PROPERTIES, TOXICITY, AND USES OF SOME CHROMIUM COMPOUNDS[64]

Compound	Properties	Toxicity	Uses
Chromium trioxide CrO_3	mp 197°C Decomposes at 250°C	Dermal contact can cause primary irritation and ulceration as well as allergic eczema. Inhalation can cause nasal irritation, septal perforation. Pulmonary irritation, bronchogenic carcinoma may result from breathing chromate dust. Ingestion causes violent gastrointestinal irritation with vomiting, diarrhea. Renal injury has been reported in experimental animals	In chromium plating, copper stripping, aluminum anodizing; as corrosion inhibitor; in photography, purifying oils and acetylene, hardening microscopical preparations. Med. and vet. use: 5% solution as topical antiseptic and astringent. 20% solution as caustic
Chromic acetate $Cr(C_2H_3O_2)_3$	Slightly soluble in water. Practically insoluble in alcohol		As a mordant in dyeing; in tanning; in hardening photographic emulsions; to improve light stability and dye affinity of textiles and polymers; in catalyst for polymerization of olefins
Chromic bromide $CrBr_3$	Soluble in boiling water Sublimes		In catalysts for polymerization of olefins

(continued)

TABLE 7. PROPERTIES, TOXICITY, AND USES OF SOME CHROMIUM COMPOUNDS (Continued)

Compound	Properties	Toxicity	Uses
Chromic carbonate $Cr_2O_3 \cdot xCO_2 \cdot yH_2O$	A basic carbonate of indefinite composition. Blue-gray amorphous powder		In preparation of chromic salts
Chromic chloride $CrCl_3$	Sublimes at 950°C	Keep tightly closed. MLD iv in mice 801,000 μg/kg See chromium trioxide	In chromizing; in manufacture of Cr metal and compounds; as catalyst for polymerization of olefins and other organic reactions; as textile mordant; in tanning; in corrosion inhibitors; as waterproofing agent
Chromic fluoride CrF_3	mp >1,000°C bp >1,100°C	See chromium trioxide	The hydrates are used in printing and dyeing woolens, coloring and hardening marble, mothproofing woolen fabrics, treating silk, polishing metals, and as halogenation catalyst
Chromic formate $Cr(HCOO)_3$	Decomposes above 300°C		In printing cotton skeins; in leather tanning and waterproofing

(continued)

TABLE 7. PROPERTIES, TOXICITY, AND USES OF SOME CHROMIUM COMPOUNDS (Continued)

Compound	Properties	Toxicity	Uses
Chromic hydroxide $Cr(OH)_3$	Practically insoluble in water		As pigment, e.g., Guignet's green; in tanning industry, as mordant; as catalyst for organic reactions
Chromic nitrate $Cr(NO_3)_3$	Decomposes above 60°C		In preparation of Cr catalyst; in textile printing; as corrosion inhibitor
Chromic oxide Cr_2O_3	mp 2,435°C bp ~3,000°C		In abrasives; as refractory materials, electric semiconductors; as pigment, particularly in coloring glass; in alloys, printing fabrics and banknotes; as catalyst for organic and inorganic reactions
Chromic phosphate $CrPO_4$	Does not melt by 1,800°C		As green pigment; in wash primers; in catalysts for dehydrogenation of hydrocarbons and polymerization of olefins
Chromic potassium oxalate $K_3[Cr(C_2O_4)_3]$	Freely soluble in water		In tanning industry; in dyeing chromate colors on wool

(continued)

TABLE 7. PROPERTIES, TOXICITY, AND USES OF SOME CHROMIUM COMPOUNDS (Continued)

Compound	Properties	Toxicity	Uses
Chromic potassium sulfate $KCr(SO_4)_2$	mp 89°C		As mordant for dyeing fabrics uniformly; in tanning leather, printing calico; for rendering glue and gum insol; in manufacture of ink, other chromium salts; for waterproofing fabrics, hardening photographic emulsions
Chromic sulfate $Cr_2(SO_4)_3$	Peach-colored solid. Practically insoluble in water and acids	MLD iv in mice 247,000 μg/kg	For insolubilization of gelatin; in catalyst preparation; as mordant in textile industry; in tanning of leather; in chrome plating; in manufacture of Cr, CrO_3, and Cr alloys; to improve dispersibility of vinyl polymers in water; in manufacture of green varnishes, paints, inks, glazes for porcelain
Chromite $FeCr_2O_4$			As only important commercial ore
Chromium carbonyl $Cr(CO)_6$	Sinters at 90°C. Decomposes at 130°C. Explodes at 210°C. Sublimes at room temperature	LD_{50} iv in mice 100,000 μg/kg	In catalysts for olefin polymerization and isomerization; as gasoline additive to increase octane number; in preparation of chromous oxide, CrO

(continued)

TABLE 7. PROPERTIES, TOXICITY, AND USES OF SOME CHROMIUM COMPOUNDS (Continued)

Compound	Properties	Toxicity	Uses
Chromium Cr	mp 1,900°C bp 2,480°C	See chromium trioxide	In manufacture of chrome-steel or chrome-nickel-steel alloys (stainless steel); for greatly increasing resistance and durability of metals; for chrome plating of other metals. The man-made ^{51}Cr isotope is used as tracer in various blood diseases and in determination of blood volume (as the chloride or as Na chromate)
Chromium tetrafluoride CrF_4	mp 200°C bp 400°C	A strong irritant	
Chromous acetate $Cr(C_2H_3O_2)_2$	Slightly soluble in cold water; readily soluble in hot water	See chromium trioxide	In preparation of other chromous salts; as O_2 absorber in gas analyses
Chromous bromide $CrBr_2$	mp 842°C		In chromizing
Chromous chloride $CrCl_2$	mp 824°C	See chromium trioxide	In chromizing; in preparation of Cr metal; in catalysts for organic reactions; as O_2 absorbent; in analysis

(continued)

TABLE 7. PROPERTIES, TOXICITY, AND USES OF SOME CHROMIUM COMPOUNDS (Continued)

Compound	Properties	Toxicity	Uses
Chromous fluoride CrF_2	mp 1,100°C bp above 1,300°C	A strong irritant See chromium trioxide	In chromizing; in catalytic cracking of hydrocarbons; as alkylation catalyst; in nuclear reaction fuels
Chromous formate $Cr(HCOO)_2$	Soluble in water		In baths for Cr electroplating; in catalysts for organic reactions
Chromous oxalate CrC_2O_4			
Chromous sulfate $CrSO_4$	Soluble in water		As analytical reagent; for absorption of O_2 from gas mixtures; as dehydrohalogenating and reducing agent
Chromyl chloride CrO_2Cl_2	mp -96.5°C bp 117°C	Burns and blisters the skin. Handle only in well-ventilated hood	As catalyst for polymerization of olefins; in oxidation of hydrocarbons, in Etard reaction for production of aldehydes and ketones; in preparation of various coordination complexes of Cr
Chromyl fluoride CrO_2F_2	Sublimes at 29.6°C mp 31.6°C	See chromium trioxide	As fluorination catalyst; to increase olefin-polymer receptivity for dyes

(continued)

TABLE 7. PROPERTIES, TOXICITY, AND USES OF SOME CHROMIUM COMPOUNDS (Continued)

Compound	Properties	Toxicity	Uses
Lead chromate (chrome yellow) $PbCrO_4$	mp 844°C	LD_{50} ip in guinea pigs 400,000 μg/kg	As pigment in oil and water colors; in printing fabrics, decorating china and porcelain; in chemical analysis of organic substances. Basic lead chromates of colors from brown-yellow to red are used as pigments
Potassium chromate(VI) K_2CrO_4	mp 975°C	See chromium trioxide LD sc in rabbits 12,000 μg/kg	Has a limited application in enamels, finishing leather, rust-proofing of metals, being replaced by the sodium salt; as a reagent in analytical chemistry
Potassium dichromate(VI) $K_2Cr_2O_7$	mp 398°C Decomposes at ~500°C	Internally, a corrosive poison--30 g reported fatal within 35 min. Industrial contact may result in ulceration of hands, destruction of mucous membranes, and perforation of nasal septum. Chromates have been reported as causing cancer of the lung	In tanning leather, dyeing, painting, decorating porcelain, printing, photolithography, pigment prints, staining wood, pyrotechnics, safety matches; for bleaching palm oil, wax, and sponges; in waterproofing fabrics; as an oxidizer in the manufacture of organic chemicals; in electric batteries; as a depolarizer for dry cells. As corrosion inhibitor in preference to sodium dichromate where lower solubility is advantageous. Med. use: externally as astringent, antiseptic, caustic. Vet. use: as caustic for superficial growths

(continued)

TABLE 7. PROPERTIES, TOXICITY, AND USES OF SOME CHROMIUM COMPOUNDS (Continued)

Compound	Properties	Toxicity	Uses
Sodium chromate(VI) $Na_2CrO_4 \cdot 4H_2O$	mp 20°C	LD sc in rabbits 243,000 μg/kg	In protecting iron against corrosion and rusting
Sodium dichromate(VI) $Na_2Cr_2O_7 \cdot 2H_2O$	Anhydrous salt mp 356.7°C	Irritant and caustic to skin, mucous membranes. See chromium trioxide	As oxidizing agent in manufacture of dyes, many other synthetic organic chemicals, inks, etc.; in chrome-tanning of hides; in electric batteries; in bleaching fats, oils, resins, sponges; in refining petroleum; in manufacture of chromic acid, other chromates, and chrome pigments; in corrosion inhibitors, corrosion-inhibiting paints; in many metal treatments; in electroengraving of copper; as mordant in dyeing; for hardening gelatin; for defoliation of cotton plants and other plants and shrubs. Med. use: in solution as antiseptic, astringent, caustic
Ammonium dichromate(VI) $(NH_4)_2Cr_2O_7$	Decomposes at ~180°C Flammable	Causes skin irritation, ulceration, "chrome sores," perforation of nasal septum, pulmonary irritation	As source of pure nitrogen, especially in the laboratory; in pyrotechnics (Vesuvius fire); in lithography and photoengraving; in special mordants, catalysts, and porcelain finishes

(continued)

TABLE 7. PROPERTIES, TOXICITY, AND USES OF SOME CHROMIUM COMPOUNDS (Continued)

Compound	Properties	Toxicity	Uses
Ammonium chromic sulfate $NH_4Cr(SO_4)_2$	mp 94°C		As mordant in textile industry; in manufacture of electrolytic Cr metal
Zinc dichromate $ZnCr_2O_7 3H_2O$	Orange-yellow powder. Insoluble in water		
Ferric chromate(VI) $Fe_2(CrO_4)_3$	Practically insoluble in water		As pigment for ceramics, glass, and enamels
Cupric chromate(III) $CuCr_2O_4$	Practically insoluble in water. Grayish-black crystals		In fungicides, seed protectants, and wood preservatives; as mordant in dyeing textiles; in protecting textiles against insects and microorganisms. Copper-chromium oxide as a selective hydrogenation catalyst
Cupic chromate(VI) $CuCrO_4$	Practically insoluble in water. Yellowish-brown crystals		Same as Cupric chromate(III)

(continued)

TABLE 7. PROPERTIES, TOXICITY, AND USES OF SOME CHROMIUM COMPOUNDS (Continued)

Compound	Properties	Toxicity	Uses
Basic cupric chromate $CuCrO_4Cu(OH)_2$	Practically insoluble in water. Yellow, copper-red, or chocolate brown to lilac crystals		Same as Cupric chromate(III)
Basic cupric chromate $CuCrO_4 \cdot 2Cu(OH)_2$	Practically insoluble in water. Light-brown powder		Same as Cupric chromate(III)
Basic cupric chromate $CuCrO_4 \cdot 3Cu(OH)_2$	Practically insoluble in water. Yellow to yellowish-brown crystals		Same as Cupric chromate(III)
Copper chromium oxide A mixture of $CuCr_2O_4$ and CuO	Stable in atmospheric O_2. Practically insoluble in water		Same as Cupric chromate(III)

APPENDIX

TABLE 8

CHROMIUM IN HUMAN TISSUE BY AGE IN THE UNITED STATES[86]

Tissue	0-45 days	45 days-10 years	10-20 years	20-30 years	30-40 years	40-50 years	50-60 years	60-70 years	70-80 years	80+ years
Kidney	51.8	57.8	3.7	2.3	2.1	3.9	3.0	2.4	2.0*	10.0*
Liver	17.9	16.6	4.6	2.9	1.8	3.1	2.5	1.3	1.1*	1.3*
Lung	85.2	10.2	6.8	8.2	15.6	31.8	24.8	21.0	38.0*	1.1*
Aorta	19.5*	7.0*	7.0	4.2	9.1	4.9	4.2	4.4*	2.6*	0*
Heart	82.4	1.7	2.1	3.3	3.8	6.0	3.7	3.0	2.9*	0*
Pancreas	*	2.6*	3.4	2.5	6.5	2.5	3.6	3.7	2.9*	0.9*
Spleen	27.0	4.1*	1.6	1.1	1.7	1.5	1.8	3.0	1.9*	0.3*
Testis	*	*	2.1*	1.8	3.1	3.2	2.3	3.6	1.1*	1.0*

*Five or less samples.

TABLE 9
ANIMAL EXPOSURES TO CHROMATES[10]

Species	Type of Exposure	Material	Average Dose or Concentration	Duration	Effect
Rabbits and cats	Inhalation	Chromates	1,000-50,000 $\mu g/m^3$	14 hr/day 1-8 mo	Pathological changes in lungs
Rabbits	Inhalation	Dichromates	11,000-23,000 $\mu g/m^3$ as bichromate	2-3 hr for 5 days	No effect
Cats	Inhalation	Dichromate	11,000-23,000 $\mu g/m^3$ as bichromate	2-3 hr for 5 days	Bronchitis, pneumonia
Mice	Inhalation	Mixed dust containing chromates	1,500 $\mu g/m^3$ as CrO_3	4 hr/day 5 days/wk for 1 yr	No harmful effects
Mice	Inhalation	Mixed dust containing chromates	16,000-27,000 $\mu g/m^3$ as CrO_3	1/2 hr/day intermittently	Fatal to some strains
Mice	Inhalation	Mixed dust containing chromates	7,000 $\mu g/m^3$ as CrO_3	37 hr over 10 days	Fatal
Rats	Inhalation	Mixed dust containing chromates	7,000 $\mu g/m^3$ as CrO_3	37 hr over 10 days	Barely tolerated
Rabbits and guinea pigs	Inhalation	Mixed dust containing chromates	5,000 $\mu g/m^3$ as CrO_3	4 hr/day 5 days/wk 1 yr	No marked effects

(continued)

TABLE 9 (Continued)
ANIMAL EXPOSURES TO CHROMATES

Species	Type of Exposure	Material	Average Dose or Concentration	Duration	Effect
Rats	Ingestion	Potassium chromate added to drinking water	500 ppm	Daily	Maximum nontoxic level
Mature rats and mice	Ingestion	Zinc chromate in feed	1%	Daily	Maximum nontoxic level
Young rats	Ingestion	Zinc chromate in feed	0.12%	Daily	Maximum nontoxic level
Young rats	Ingestion	Potassium chromate in feed	0.12%	Daily	Maximum nontoxic level
Dogs, cats, and rabbits	Ingestion	Mono- or dichromates	1,900-5,500 μg chromium/kg body wt/day (1,000 μg chromium equivalent to 2,830 μg $K_2Cr_2O_7$ or 3,800 μg K_2CrO_4)	29-685 days	No harmful effects
Dogs	Ingestion	Potassium dichromate	1,000,000-2,000,000 μg as Cr	Daily	Fatal in 3 mo
Dogs	Stomach tube	Potassium dichromate	1,000,000-10,000,000 μg as Cr		Rapidly fatal

(continued)

TABLE 9 (Continued)
ANIMAL EXPOSURES TO CHROMATES

Species	Type of Exposure	Material	Average Dose or Concentration	Duration	Effect
Monkeys	Subcutaneous	Potassium dichromate	20,000-700,000 μg 2% solution		Fatal
Dog	Subcutaneous	Potassium dichromate	210,000 μg as Cr		Rapidly fatal
Guinea pigs	Subcutaneous	Potassium dichromate	10,000 μg		Lethal
Rabbits	Subcutaneous	Potassium dichromate	1.5 cc of 1% solution/ kg body wt		80% fatal
Rabbits	Subcutaneous	Potassium dichromate	20,000 μg		Lethal
Rabbits	Subcutaneous	Potassium dichromate	0.5-1 cc of 0.5% solution/kg body wt		Nephritis
Rabbits and guinea pigs	Subcutaneous or intra-venous	Sodium chromate	100,000-300,000 μg as CrO_3		Rapid death
Mice	Intravenous	Zinc chromate	100 μg/mo as zinc chromate	10 mo	Tolerated
Mice	Intravenous	Zinc chromate	750 μg	1 dose	Fatal
Mice	Intravenous	Barium chromate	2,500 μg/dose as barium chromate	9 doses at 6-wk intervals	Tolerated

(continued)

TABLE 9 (Continued)
ANIMAL EXPOSURES TO CHROMATES

Species	Type of Exposure	Material	Average Dose or Concentration	Duration	Effect
Rabbits	Intravenous	Potassium dichromate	0.7 cc of 2% solution/kg body wt		Fatal
Dogs	Intravenous	Potassium chromate	10,000,000 μg		Fatal
Dogs	Intravenous	Potassium chromate	23,000 μg		Survived
Dog	Intravenous	Potassium dichromate	210,000 μg as Cr		Rapidly fatal
Dog	Intravenous	Potassium dichromate	3,000 μg/100 cc blood/dose	2 doses	Marked kidney damage

TABLE 10

CONSUMPTION OF CHROMITE IN THE UNITED STATES[68]
(Thousand Short Tons)

Year	Metallurgical Industry		Refractory Industry		Chemical Industry		Total	
	Gross Weight	Average Cr_2O_3 %	Gross Weight	Average Cr_2O_3 %	Gross Weight	Average Cr_2O_3 %	Gross Weight	Average Cr_2O_3 %
1957-61 (Avg)	816	46.7	378	34.9	154	45.3	1,348	43.2
1962	590	46.6	365	35.0	176	45.3	1,131	42.7
1963	632	48.7	368	34.6	187	45.1	1,187	43.8
1964	832	49.0	430	33.8	189	45.1	1,451	44.0
1965	907	49.8	460*	34.7*	217*	45.0	1,584*	44.8*
1966	828	49.6	439	34.6	194	44.9	1,461	44.5

*Revised in 1966.

APPENDIX

TABLE 11

U.S. CONSUMERS OF CHROME ORE[43]

Metallurgical

Armco Steel Corp.
Baltimore Works
3400 East Chase St.
Baltimore, Md.

Chromium Mining & Smelting Co.
Riverdale, Ill.

Interlake Iron Corp.
1900 Union Commerce Building
Cleveland, Ohio

Keokuk Electro-Metals Co.
Keokuk, Iowa

Montana Ferroalloys, Inc.
P. O. Box 1400
Memphis, Tenn.

Ohio Ferro-Alloys Corp.
839 30th St., N.W.
Canton, Ohio

Pacific Northeast Alloys, Inc.
P. O. Box 6247, Hillyard Station
Spokane, Wash.

Pittsburgh Metallurgical Co.
Niagara Falls, N. Y.

Tennessee Products & Chemical Corp.
2611 West End Avenue
Nashville, Tenn.

Union Carbide Metals Co.
30 East 42nd Street
New York, N. Y.

Universal Cyclops Steel Corp.
Bridgeville, Pa.

Vanadium Corporation of America
420 Lexington Avenue
New York, N. Y.

Chemical

Columbia-Southern Chemical Corp.
902 Garfield Avenue
Jersey City, N. J.

Diamond Alkali Co.
300 Union Commerce Building
Cleveland, Ohio

Diamond Alkali Co.
Kearny Plant
Bellevue Turnpike
Kearny, N. J.

Foote Mineral Co., Inc.
10 East Chelton Avenue
Philadelphia, Pa.

Frank Samuel & Co., Inc.
Lincoln-Liberty Building
Broad & Chestnut Streets
Philadelphia, Pa.

Imperial Paper & Color Corp.
P. O. Box 231
Glen Falls, N. Y.

Solvay Process Division
Allied Chemical & Dye Corp.
P. O. Box 271
Syracuse, N. Y.

Refractory

Basic Refractories, Inc.
845 Hanna Building
Cleveland, Ohio

Eastern Stainless Steel Corp.
Box 1975
Baltimore, Md.

General Refractories Co.
1520 Locust St.
Philadelphia, Pa.

APPENDIX

TABLE 11 (Continued)

Refractory (Continued)

Harbison-Walker Refractories Co.
1800 Farmers Bank Building
Pittsburgh, Pa.

Kaiser Aluminum & Chemical Corp.
1924 Broadway
Oakland, Calif.

E. J. Lavino & Co.
3 Penn Center Plaza
Philadelphia, Pa.

Frank Samuel & Co., Inc.
Lincoln-Liberty Building
Broad & Chestnut Streets
Philadelphia, Pa.

U.S. Steel Corp.
525 William Penn Place
Pittsburgh 30, Pa.

APPENDIX

TABLE 12

PRODUCTION OF CHROMIUM CHEMICALS[49]

Type of Chemical	Short Tons 1967	Short Tons 1966
Chrome yellow and orange pigments	28,716	31,409
Molybdate chrome orange	9,903	10,858
Sodium bichromate and chromate (hydrous)	131,348	141,478

APPENDIX

TABLE 13

CHROMIUM CONTENT OF PORTLAND CEMENT[28]
(μg of Cr/g of Cement)

Source	Cr(VI) in Two Washings*	Total Cr in Two Washings*	Total Cr in Residue	Total Cr in Untreated Cement
Illinois	1.6	3.5	35.0	42.5
Michigan	1.3	3.3	26.0	28.0
Michigan	4.5	4.8	42.5	50.0
Michigan	7.8	8.8	35.0	45.0
Mississippi	3.7	4.3	43.0	52.0
Missouri	7.2	7.4	57.5	60.0
New York	3.4	5.6	36.0	38.9
Ohio	3.6	3.9	26.9	29.3
Pennsylvania	0.03	1.6	30.9	35.2
Pennsylvania	0.3	4.1	25.0	27.5
Tennessee	1.1	1.9	60.0	60.0
Texas	2.0	2.3	30.0	31.8
Texas	1.5	1.8	32.5	35.0
Mean	2.9	4.1	36.9	41.2
Range	0.03-7.8	1.6-8.8	25.0-60.0	27.5-60.0

*70-100% of soluble chromium was removed by first washing.

TABLE 14
CONCENTRATION OF CHROMIUM IN THE AIR[2,4-6]
($\mu g/m^3$)

Location[a]	1954-59[b]		1960		1961		1962		1963		1964		1965	
	Max	Avg	Max	Avg	Max	Avg	Max	Avg	Max	Avg	Max	Avg	Max	Avg
Alabama														
Birmingham	.140	.038									.043	.016	.010	.005
Gadsden											.000	.000		
Huntsville									.000	.000				
Arizona														
Grand Canyon Pk.[a]													.0012	.0011
Maricopa Co.[a]													.0023	.0014
Paradise Valley											.000	.000	.002	.002
Phoenix			.190	.084			.015	.001			.023	.007		
Arkansas														
Montgomery Co.[a]													.0025	.0021
Texarkana											.005	.001		
California														
Bakersfield											.009	.008		
Burbank											.018	.009		
Humboldt Co.[a]													.0036	.0022
Los Angeles	.160	.037	.057	.030	.032	.018	.086	.026	.033	.015				
Monterey											.008	.005		
Pasadena	.006	.002					.038	.023						
San Bernardino									.036	.004				
San Francisco	.006	.001					.100	.020	.021	.006				
San Jose	.009	.001							.007	.002				
Santa Barbara							.016	.006						
Colorado														
Denver	.050	.019					.025	.009	.028	.007	.012	.005		
Montezuma Co.[a]													.0037	.0028
Pueblo									.000	.000				
Connecticut														
Bridgeport							.006	.003						
Hartford											.000	.000		
New Haven											.000	.000		
Norwich									.000	.000				
District Of Columbia														
Washington	.010	.004					.052	.016	.026	.006	.180	.016		

(continued)

TABLE 14 (Continued)

CONCENTRATION OF CHROMIUM IN THE AIR
($\mu g/m^3$)

Location[a]	1954-59[b]		1960		1961		1962		1963		1964		1965	
	Max	Avg	Max	Avg	Max	Avg	Max	Avg	Max	Avg	Max	Avg	Max	Avg
Florida														
St. Petersburg							.016	.008						
Tampa	.160	.032							.018	.004				
Georgia														
Atlanta	.081	.023							.028	.007			.006	.002
Idaho														
Boise			.031	.020			.022	.007			.025	.007	.005	.001
Illinois														
Chicago	.076	.028			.065	.039			.025	.013	.052	.014		
Cicero							.045	.018						
East St. Louis	.050	.007							.110	.029				
Joliet									.000	.000				
Moline											.009	.007		
North Chicago									.000	.000				
Rock Island											.009	.002		
Springfield							.026	.014						
Indiana														
Beverly Shore													.000	.000
East Chicago	.120	.013									.160	.033		
Evansville											.000	.000		
Fort Wayne											.000	.000		
Hammond									.031	.008				
Indianapolis	.081	.024			.100	.042	.068	.016			.020	.008		
Muncie									.008	.002				
Parke Co.[a]													.0038	.0027
Terre Haute									.007	.003				
West Lafayette											.006	.002		
Iowa														
Cedar Rapids									.000	.000				
Delaware Co.[a]													.0031	.0021
Des Moines	.047	.019	.058	.029			.017	.005			.009	.003		
Dubuque											.000	.000		

(continued)

TABLE 14 (Continued)

CONCENTRATION OF CHROMIUM IN THE AIR
($\mu g/m^3$)

Location[a]	1954-59[b]		1960		1961		1962		1963		1964		1965	
	Max	Avg	Max	Avg	Max	Avg	Max	Avg	Max	Avg	Max	Avg	Max	Avg
Kansas														
Wichita	.046	.017									.007	.001		
Kentucky														
Ashland											.010	.007		
Covington											.018	.012		
Louisiana														
Lake Charles							.000	.000						
New Orleans	.110	.025					.045	.010	.017	.011				
Maine														
Acadia Natl. Pk.[a]													.020	.0091
Maryland														
Baltimore	.290	.094			.430	.108					.350	.069	.028	.018
Calvert Co.[a]													.0016	.0010
Cumberland									.000	.000				
Massachusetts														
Boston	.350	.051									.013	.007		
Brockton													.000	.000
Lynn							.000							
Somerville							.000	.000						
Springfield											.000	.000		
Michigan														
Detroit	.082	.029					.038	.016	.033	.010	.049	.014		
Grand Rapids									.012	.010				
Kalamazoo			.029	.019										
Muskegon									.007	.003				
Minnesota														
Minneapolis	.070	.020									.022	.002		
Moorhead											.000	.000		
St. Paul							.020	.013						
Mississippi														
Jackson Co.[a]													.027	.012
Missouri														
Shannon Co.[a]													.0019	.0014
St. Louis	.130	.041					.065	.021	.063	.020	.026	.007		

(continued)

TABLE 14 (Continued)

CONCENTRATION OF CHROMIUM IN THE AIR
($\mu g/m^3$)

Location[a]	1954-59[b]		1960		1961		1962		1963		1964		1965	
	Max	Avg	Max	Avg	Max	Avg	Max	Avg	Max	Avg	Max	Avg	Max	Avg
Montana														
Glacier Natl. Pk.[a]													.0038	.0016
Helena											.007	.001		
Nebraska														
Lincoln							.000	.000						
Thomas Co.[a]													.0026	.0019
Nevada														
Las Vegas					.061	.031	.024	.014	.031	.008	.009	.001		
Reno									.000	.000				
White Pine Co.[a]													.0028	.0012
New Hampshire														
Coos Co.[a]													.0022	.0011
New Jersey														
Bayonne									.025	.015			.011	
Bridgeton													.005	.003
Camden	.008						.018	.014	.011	.010				
Newark					.130	.046	.069	.020			.063	.020		
Paterson									.011	.010				
New Mexico														
Albuquerque			.130	.057					.006				.006	.002
Rio Arriba Co.[a]													.0053	.0045
New York														
Buffalo							.059	.010						
Cape Vincent[a]													.021	.0069
Glen Cove							.027	.019						
Massena					.027	.019								
Mt. Vernon					.039	.035								
New Rochelle					.032	.022								
New York	.073	.021					.078	.027	.042	.016	.019	.006		
Rochester			.290	.055	.042	.036								
Troy							.024	.015						

(continued)

TABLE 14 (Continued)

CONCENTRATION OF CHROMIUM IN THE AIR

($\mu g/m^3$)

Location[a]	1954-59[b]		1960		1961		1962		1963		1964		1965	
	Max	Avg	Max	Avg	Max	Avg	Max	Avg	Max	Avg	Max	Avg	Max	Avg
North Carolina														
Asheville			.026	.020										
Cape Hatteras[a]													.0027	.0015
Charlotte	.071	.023									.016	.002		
Durham									.008	.007				
Winston-Salem							.030	.016						
Ohio														
Akron			.130	.041									.011	.009
Cincinnati	.039	.009	.200	.086	.140	.053	.260	.063	.100	.023	.240	.040		
Cleveland	.130	.043					.035	.017	.034	.020	.047	.014		
Youngstown	.075	.047	.170	.051			.030	.005	.054	.012				
Oklahoma														
Cherokee Co.[a]													.0017	.0010
Tulsa					.028	.016								
Oregon														
Curry Co.[a]													.0014	.00035
Portland	.071	.025							.041	.004	.023	.004		
Pennsylvania														
Allentown					.054	.036							.000	
Altoona	.006	.001							.009	.002			.007	.002
Bethlehem					.130	.048							.010	.005
Clarion Co.[a]													.0091	.0070
Johnstown									.060	.010				
Lancaster							.028	.016						
Philadelphia	.078	.026	.120	.049	.057	.024	.100	.018	.042	.013	.028	.011		
Pittsburgh	.200	.028	.380	.197			.120	.041	.090	.023	.097	.021		
Scranton					.052	.030								
Puerto Rico														
Bayamon													.000	.000
Rhode Island														
East Providence									.000	.000				
Washington Co.[a]													.0055	.0036

(continued)

TABLE 14 (Continued)

CONCENTRATION OF CHROMIUM IN THE AIR

($\mu g/m^3$)

Location[a]	1954-59[b]		1960		1961		1962		1963		1964		1965	
	Max	Avg	Max	Avg	Max	Avg	Max	Avg	Max	Avg	Max	Avg	Max	Avg
South Carolina														
Richland Co.[a]													.0040	.0020
South Dakota														
Black Hills Frst[a]													.0011	.00055
Tennessee														
Chattanooga	.002				.130	.041					.053	.015		
Memphis											.006			
Nashville	.076	.029									.069	.011		
Texas														
El Paso							.015	.006			.000			
Houston	.140	.025									.015	.004		
Matagorda Co.[a]													.0032	.0026
Odessa									.000	.000				
Tyler									.007	.002				
Utah														
Salt Lake City	.009	.019									.007	.001		
Vermont														
Orange Co.[a]													.0044	.0026
Virginia														
Portsmouth													.006	.004
Richmond													.000	.000
Shenandoah Pk.[a]													.0029	.0018
Washington														
Seattle	.200	.047					.330	.039	.100	.015				
Spokane					.092	.041								
Tacoma	.120	.018					.024	.002			.022	.001		
West Virginia														
Charleston	.290	.097			.360	.132					.180	.044		
Huntington			.042	.021										
Wisconsin														
Door Co.[a]													.0024	.0018
Milwaukee	.088	.029									.039	.010		

(continued)

TABLE 14 (Continued)

CONCENTRATION OF CHROMIUM IN THE AIR
($\mu g/m^3$)

Location[a]	1954-59[b]		1960		1961		1962		1963		1964		1965	
	Max	Avg	Max	Avg	Max	Avg	Max	Avg	Max	Avg	Max	Avg	Max	Avg
Wyoming														
Cheyenne	.030	.011									.000			
Yellowstone Natl. Pk.													.0027	.00068

[a] All locations are urban unless indicated with an * which indicates nonurban.

[b] The data in this column may include only one year or the average of all measurements made during these years.