2. Production, Use, Occurrence and Analysis

The early history of chromium compounds, including synthetic methods used in their preparation, has been reviewed (Mellor, 1931).

2.1 Production

Chromium was first isolated and identified as a metal by the French chemist, Vauquelin, in 1798, working with a rare mineral, Siberian red lead (crocoite, $PbCrO_4$).

A generalized flow diagram for the production processes used now to lead from chromite ore to the major products containing chromium is shown in Figure 1.

(*a*) *Chromite ore*

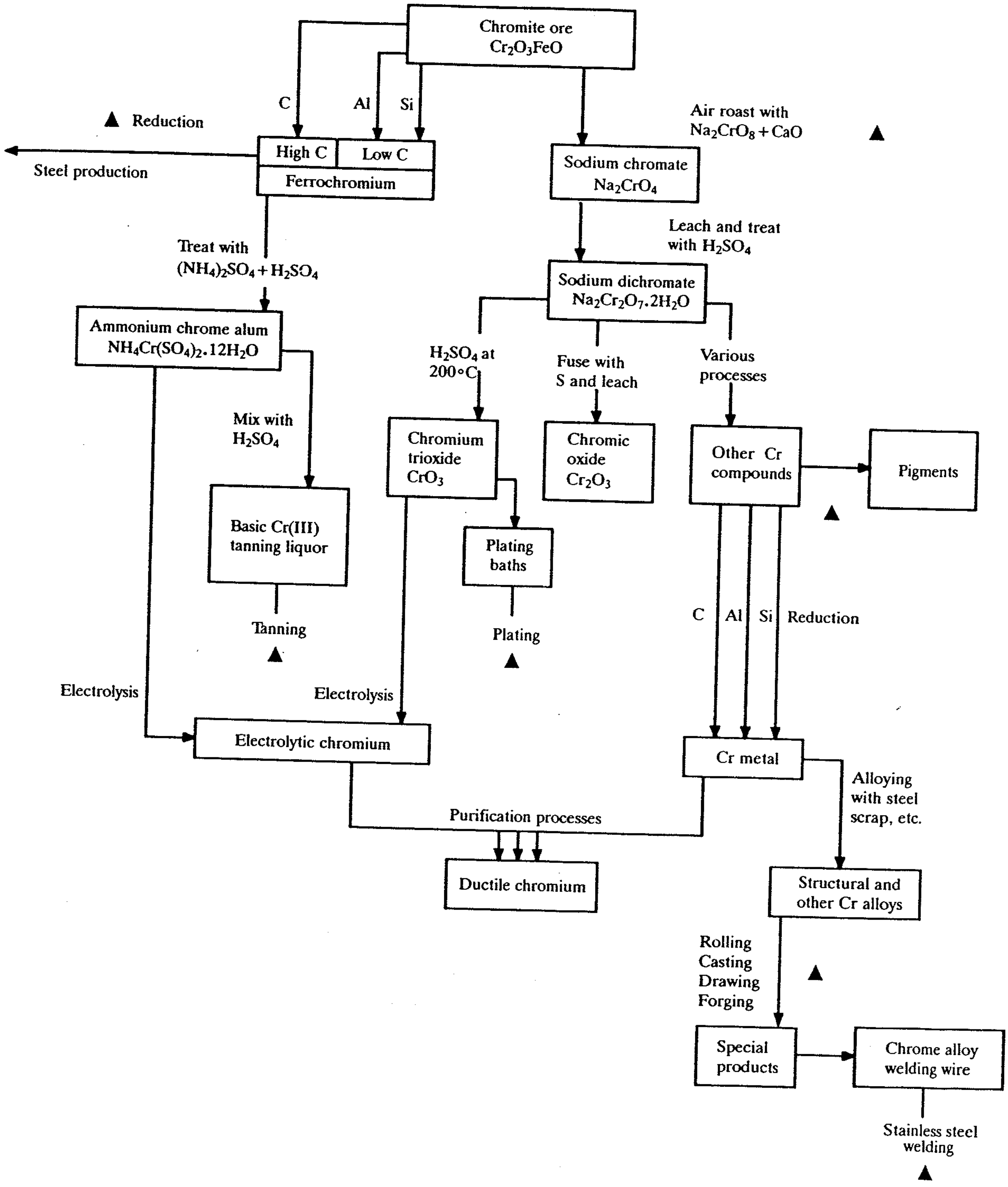
Although chromium is found in various minerals, chromite is the sole source of chromium used commercially (Stern, 1982). From 1797 until 1827, chromite from the Ural Mountains of Russia was the principal source of world supply, primarily for chemical use. After chromite ore was discovered in the USA in 1827, that country became the principal source for the limited world demand; it no longer produces it. Large Turkish deposits were developed in 1860 to supply the world market. Table 7 presents world production figures by region in 1976, 1982 and 1987.

(*b*) *Metallic chromium and chromium alloys*

Chromium metal is made commercially in the USA by two processes: (i) an electrolytic method in which a chromium-containing electrolyte, prepared by dissolving a high-carbon ferrochromium in a solution of sulfuric acid and chromium potassium sulfate, is subjected to electrolysis; and (ii) an aluminothermic reduction method in which chromic oxide is reduced with finely divided aluminium (Bacon, 1964; Papp, 1983).

In 1970, US production of chromium metal and metal alloys, other than ferrochromium alloys, was 14 thousand tonnes (about 75% by the electrolytic method; IARC, 1980a); this had increased to 18 thousand tonnes by 1976 (Morning, 1978). Production included chromium briquets, exothermic chromium additives and miscellaneous chromium alloys, in addition to chromium metal. By 1987, US production of chromium metal and ferrochromium-silicon (including exothermic chro-

Fig. 1. Simplified flow chart for the production of metallic chromium, chromium compounds and selected products from chromite ore. Processes for which occupational exposure levels to chromium are available are indicated by ▲[a]



[a] From Stern (1982)

mium additives and other miscellaneous chromium alloys) had dropped to 1900 tonnes (Papp, 1988).

Table 7. World mine production of chromite ore by region (thousand tonnes)[a]

Region[b]	1976	1982	1987
Albania	794	675	830
Brazil	172	276	227
Cuba	32	27	122
Cyprus	9	3	0
Egypt	1	0	0
Finland	414	345	712
France (New Caledonia)	10	50	62
Greece	27	29	64
India	401	364	522
Iran	160	41	56
Japan	22	11	12
Madagascar	221	44	100
Oman	0	0	6
Pakistan	11	4	8
Philippines	427	322	172
South Africa	2409	2431[c]	3787[c]
Sudan	22	19	8
Turkey	740	453	599
USSR	2120	2939	3148
Viet Nam	9	16	15
Yugoslavia	2	0	0
Zimbabwe	608	432	540
Total	8611	8481	10 990

[a] From Morning (1978); Papp (1987, 1988)

[b] In addition to the regions listed, Argentina, Bulgaria, China, Colombia, the Democratic Republic of Korea and Thailand may also have produced chromite ore, but output was not reported quantitatively and available general information was inadequate for formulation of reliable estimates of production.

[c] Includes production by Bophuthatswana

Chromium metal has been produced in Japan since 1956, where it is manufactured by two companies by electrolysis of an ammonium chromic sulfate solution. About 9000 tonnes were produced in 1977; there were no reported imports or exports (IARC, 1980a).

Ferrochromium is produced by treatment of chromite ore in electric furnaces using coke as a reducing agent. Worldwide production figures for all grades of ferrochromium are summarized in Table 8.

Table 8. World production of ferrochromium (all grades, in thousands of metric tonnes)[a]

Country	1983	1985	1987
Albania	35	13	35
Brazil	80	136.2	113.5
Finland	58.7	133	143
France	18.1	0	0
Germany, Federal Republic of	45	70	23
Greece	18.5	45	45
India	53.5	78.5	122.1
Italy	45.4	57.6	59
Japan	329.1	379.7	291
Philippines	27	51	59
South Africa	699.5	851	948
Spain	18	30	17.6
Sweden	119.4	135	110
Turkey	30.1	53.3	54
USA[b]	33	99.7	106.7
USSR	634	415	NA
Yugoslavia	68	73	80
Zimbabwe	140	180	185

[a] From Chromium Association (1989)

[b] Includes L and HC ferrochromium, FeSiCr, Cr metal and other miscellaneous alloys

NA, not available

Chromium-containing steels (stainless steels and others) are produced by melting cast iron and adding ferrochromium and/or steel scraps in large electric furnaces. The melt is transferred to a refining vessel to adjust the carbon content and impurity levels and is then cast into ingots or continuously into casting shapes. Defects in the cast steel are repaired by cutting or scarfing or by chipping or grinding. The desired shapes are produced primarily by rolling, and their surfaces are conditioned by a variety of operations, including grinding, polishing and pickling (Warner, 1984).

Production figures are given in Table 9.

Chromium alloys are produced by technology very similar to that used for steel production, except that the melting and decarburizing units are generally smaller and greater use is made of vacuum melting and remelting (Warner, 1984). No data were available on production volumes of these alloys.

Table 9. Stainless-steel production in selected countries[a] (in thousands of metric tonnes)

Country	1987	1988
Austria	54	67
Belgium	182	254
Finland	189	206
France	720	784
Germany, Federal Republic of	957	1186
Italy	550	623
Japan	2722	3161
Spain	327	426
Sweden	457	482
UK	393	427
USA	1840	1995
Yugoslavia	30	30

[a] From ERAMET-SLN (1989)

Cobalt-chromium alloys were first made in 1907 by fusion of cobalt with 10-60% chromium (Haynes, 1907). Commercial production began shortly thereafter, and since 1920 more than 75% of the cobalt used in the USA has been for the manufacture of alloys with chromium (Sibley, 1976).

Eight US companies produced chromium alloys in 1975, but separate data on the quantity of cobalt-chromium alloys produced were not available (Morning, 1978). Stellite (usually 53% Co, 35% Cr and the remainder tungsten) has been produced by one company in the UK (Roskill Information Services, 1974).

(*c*) *Chromium [III] compounds*

Solutions of *chromic acetate* are produced by dissolving freshly prepared hydrous chromic oxide in acetic acid (IARC, 1980a). Commercial mixtures of chromic acetate with sodium acetate have been prepared by reduction of sodium dichromate with glucose or corn sugar in the presence of acetic acid (Copson, 1956).

Chromic acetate was produced by five companies in the USA, but no data on volumes were available (IARC, 1980a); it is now produced by one company (Chemical Information Services Ltd, 1988). Annual production in Japan has been about 30 tonnes (IARC, 1980a). Chromic acetate is currently produced by two companies each in Japan and the UK and one each in Australia, Canada and Italy (Chemical Information Services Ltd, 1988).

Chromic chloride hexahydrate is prepared by dissolving freshly prepared chromium hydroxide in hydrochloric acid. Anhydrous chromic chloride can be produced by passing chlorine over a mixture of chromic oxide and carbon (Sax & Lewis, 1987). Chromic chloride has been produced by two companies in the USA, but no data on volumes were available.

In Japan, chromic chloride has been produced from chromic sulfate by converting it to purified chromic carbonate, which is treated with hydrochloric acid. About 100 tonnes of chromic chloride were produced by one Japanese company in 1977; there were no reported imports or exports. Four companies currently produce chromic chloride in Japan (Chemical Information Services Ltd, 1988).

Chromic chloride is also produced by three companies in the UK, two in the Federal Republic of Germany and one each in Australia and the German Democratic Republic (Chemical Information Services Ltd, 1988).

Chromic hydroxide is produced by adding a solution of ammonium hydroxide to the solution of a chromium salt (Sax & Lewis, 1987). It is produced by one company each in Argentina, Brazil, France, Japan and Turkey, two each in Austria, Spain, the UK and the USA and four in India (Chemical Information Services Ltd, 1988).

Chromic nitrate may be produced by the action of nitric acid on chromium hydroxide (Sax & Lewis, 1987). It is produced by three companies each in Japan, the UK and the USA, two each in Italy and Spain and one in the Federal Republic of Germany (Chemical Information Services Ltd, 1988).

Anhydrous *chromic oxide* is produced commercially by heating chromic hydroxide, by heating dry ammonium dichromate, or by heating sodium dichromate with sulfur and washing out the sodium sulfate (Sax & Lewis, 1987). The hydrated material is made commercially by calcining sodium dichromate with boric acid and hydrolysing chromic borate (IARC, 1980a).

Chromic oxide was produced by six companies in the USA in 1977. US production of the most important type of chromic oxide, chromic oxide green, was reported to be about 6000 tonnes in 1971 (IARC, 1980a), about 3700 tonnes in 1976 and 2700 tonnes in 1977 (Hartford, 1979). It is now produced by one company in the USA (Chemical Information Services Ltd, 1988). Chromic oxide has been produced in Japan by two companies, either by heating hydrous chromic oxide or chromium trioxide or by reducing sodium dichromate with carbon. An estimated 2700 tonnes were produced in 1977 (IARC, 1980a). It is also produced by two companies each in the Federal Republic of Germany and the UK and one each in France, India, Italy, Spain and Switzerland (Chemical Information Services Ltd, 1988).

A violet hexahydrate form of *chromic phosphate* is formed by mixing cold solutions of potassium chromium sulfate (chrome alum) with disodium phosphate. A green crystalline dihydrate is obtained by boiling the violet hexahydrate with acetic anhydride or by heating it in dry air (Udy, 1956).

Chromic phosphate is produced by two companies in the USA and one each in Australia, Austria, the Federal Republic of Germany, India, Japan and the UK (Chemical Information Services Ltd, 1988).

Solutions of mixed hydrated *chromic sulfates* are obtained by dissolving chromic oxide in concentrated sulfuric acid and allowing it to stand until crystals of the hydrated chromic sulfate separate. The anhydrous form is produced by heating any of the hydrates to 400°C in air or to 280°C in a stream of carbon dioxide (IARC, 1980a). Mixtures of *basic chromic sulfates* (containing mainly $Cr(OH)SO_4$) with sodium sulfate are produced commercially by the organic reduction (with such substances as molasses) of a solution of sodium dichromate in the presence of sulfuric acid or by reduction of dichromate solutions with sulfur dioxide (Copson, 1956).

Two companies in the USA produce chromium sulfate and one produces basic chromic sulfate, but no data on volumes were available (Chemical Information Services Ltd, 1988).

Both chromium sulfate and basic chromic sulfate have been produced in Japan since about 1950, by reduction of sodium dichromate with glucose. The combined production of the two producers in 1977 (which are still operating) was about 2000 tonnes basic chromic sulfate and about 120 tonnes chromium sulfate (IARC, 1980a).

Chromium sulfate is also produced by one company each in Brazil, France, India and New Zealand, two each in the Federal Republic of Germany and Spain and three in the UK. Basic chromic sulfate is also produced by one company each in Australia, Brazil, Colombia, Italy, Mexico, Pakistan, Turkey and the USSR, two each in China and India and three in the UK (Chemical Information Services Ltd, 1988).

Potassium chromic sulfate dodecahydrate (potassium chrome alum) is produced commercially by the reduction of potassium dichromate with sulfur dioxide (Copson, 1956). One company in the USA currently produces potassium chromic sulfate, but no data on volumes were available (Chemical Information Services Ltd, 1988). It was produced commercially in Japan before 1940. Production reached about 20-30 tonnes in 1970; subsequently, the annual quantity produced decreased rapidly, and only about one tonne was produced in 1977 (IARC, 1980a).

Potassium chromic sulfate is also produced by one company in Brazil and one company in Czechoslovakia (Chemical Information Services Ltd, 1988).

(*d*) *Chromium[VI] compounds*

Hexavalent chromium compounds that are commonly manufactured include sodium chromate, potassium chromate, potassium dichromate, ammonium dichromate and chromium trioxide. Other materials that contain chromium[VI] are paint and primer pigments, graphic art supplies, fungicides, wood preservatives and corrosion inhibitors (National Institute for Occupational Safety and Health, 1975). Each chromate-producing process involves the roasting of chromite ore with soda and lime at about 1100°C in a furnace or rotary kiln (Gafafer, 1953). Water-soluble hexavalent chromium compounds do not occur in the ore but comprise part of roast, residue and product materials (Kuschner & Laskin, 1971). The presence of lime ensures that aluminium and silicon oxides in the ore are converted to insoluble compounds, the soluble sodium chromate being recovered by a leaching and crystallization process (National Institute for Occupational Safety and Health, 1975). Chromium trioxide is produced by acidifying the leachate solution with sulfuric acid (Gafafer, 1953). In the manufacture of pigments, chromium trioxide or alkali chromates are reacted with soluble compounds of zinc, lead, iron, molybdenum, strontium and other metals (Stern, 1982). The insoluble precipitates are washed, filtered and dried in the wet department of the processing plant and then ground, blended and packed in the dry departments, where conditions are often dustiest (Gafafer, 1953).

Ammonium dichromate is produced by a crystallization process involving equivalent amounts of sodium dichromate and ammonium sulfate. When low alkali salt content is required, it can be prepared by the reaction of ammonia with chromium trioxide (Hartford, 1979).

Ammonium dichromate is produced by one company each in Argentina, Australia, Brazil, France, Japan, Spain and Switzerland, by two each in the Federal Republic of Germany and India, by four in the USA, and by five in the UK (Chemical Information Services Ltd, 1988).

Calcium chromate is produced commercially by the reaction of calcium chloride with sodium chromate. Hydrated forms can be made, but the anhydrous salt is the only product of commercial significance (IARC, 1980a).

Calcium chromate is currently produced by three companies in the USA, but no data on volumes were available (Chemical Information Services Ltd, 1988). Calcium chromate was formerly produced in Japan at an annual rate of about 100 tonnes, but it has been produced recently in only small amounts for reagent use (IARC, 1980a). It is also produced by one company each in Australia and the UK and two in France (Chemical Information Services Ltd, 1988).

Chromium trioxide is produced commercially by the reaction of sodium dichromate with concentrated sulfuric acid (Hartford, 1979). In 1978, there were two US producers of chromium trioxide, each with a capacity to produce 18 thousand tonnes per year (Anon., 1978). Annual US production in 1977 was in the range of 26 thousand tonnes (Hartford, 1979). In 1988, there were six US producers (Chemical

Information Services Ltd, 1988) with a combined capacity of 52 thousand tonnes per year (Anon., 1988a).

Commercial production in Japan was started before 1940. In 1977, three companies produced a total of 8300 tonnes, of which 1200 tonnes were exported; there were no reported imports (IARC, 1980a). Four companies currently produce chromium trioxide in Japan (Chemical Information Services Ltd, 1988).

Chromium trioxide is also produced by four companies each in the Federal Republic of Germany, India and the UK, three in China, two each in Argentina, Brazil and Mexico and one each in France, Italy, Pakistan, Poland and the USSR (Chemical Information Services Ltd, 1988).

Potassium chromate is produced by the reaction of potassium dichromate with potassium hydroxide or potassium carbonate (Hartford, 1979).

There was one US producer in 1977, but no data on volumes were available; combined US imports of potassium chromate and potassium dichromate in that year were 2.7 tonnes (US Department of Commerce, 1978). There are currently two US producers, but no data on volumes were available (Chemical Information Services Ltd, 1988). Combined US imports of the two compounds in 1985, 1986 and 1987, respectively, were 580, 750 and 1000 tonnes from the UK (52%), the USSR (22%), the Federal Republic of Germany (13%) and Canada (11%); combined US exports for the same years were 64, 19 and 9 tonnes to the Philippines (40%), the Republic of Korea (30%) and Panama (30%) (Papp, 1988).

The two Japanese producers made about one tonne in 1977 for reagent uses; there were no reported imports or exports (IARC, 1980a). One company currently produces potassium chromate in Japan (Chemical Information Services Ltd, 1988). It is also produced by five companies in the UK, four in Brazil, three each in India and Italy, and one each in Argentina, Canada, the Federal Republic of Germany, Spain and Switzerland (Chemical Information Services Ltd, 1988).

Potassium dichromate is produced industrially by roasting chrome ore with potassium carbonate (IARC, 1980a), or, preferably, by reacting sodium dichromate with potassium chloride (Hartford, 1979). Combined US production of potassium dichromate and potassium chromate in 1966 was estimated to be 2600-3800 tonnes, the potassium dichromate believed to be the more important industrially (IARC, 1980a).

Three companies in the USA produce potassium dichromate (Chemical Information Services Ltd, 1988). Current information on imports/exports is given above. Potassium dichromate was first produced commercially in Japan before 1940. Production by two companies in 1978 amounted to about 1000 tonnes, well below the 3200 tonnes level of 1972 and below the 1977 level of 1400 tonnes. Exports are believed to be minor (IARC, 1980a).

Potassium dichromate is also produced by six companies in India, five in the UK, four in Brazil, two each in the Federal Republic of Germany and Italy, and one each in Argentina, Romania, Spain, Switzerland, Turkey, Yugoslavia and the USSR (Chemical Information Services Ltd, 1988).

Sodium chromate is produced commercially by roasting chromite ore with sodium carbonate, or with sodium carbonate and calcium oxide, and leaching to dissolve the sodium chromate. After treatment to remove hydrated alumina, the sodium chromate solution is either marketed directly or evaporated to produce hydrated or anhydrous crystals (Hartford & Copson, 1964). Sodium chromate may also be produced from sodium dichromate by treatment with sodium hydroxide.

Two companies produced sodium chromate in the USA in 1978. The combined US production of sodium chromate and sodium dichromate increased from 123 thousand tonnes in 1967 to 144 thousand tonnes in 1977 (Hartford, 1979), and was 159 thousand tonnes in 1978. Currently, three companies in the USA have been reported to produce sodium chromate, but data on production volumes were not available (Chemical Information Services Ltd, 1988).

Commercial production in Japan started before 1940. Production in 1977 by the two producing companies was less than 10 tonnes (IARC, 1980a); two companies currently produce this compound (Chemical Information Services Ltd, 1988). It is also produced by five companies in India, four in Brazil, three in the UK, two in the Federal Republic of Germany and one in Spain (Chemical Information Services Ltd, 1988).

Sodium dichromate is produced commercially by the reaction of sulfuric acid with sodium chromate (Hartford, 1979). Three companies in the USA produced this compound in 1976. In 1988, two of five companies that produced it (Chemical Information Sciences Ltd, 1988) had a combined capacity of 144 thousand tonnes per year (Anon., 1988b).

Sodium dichromate was first produced commercially in Japan in about 1908. In 1978, the combined production of two companies was estimated to be 20.7 thousand tonnes, slightly below the 1977 level of 21 thousand tonnes (IARC, 1980a). Three companies currently produce it in that country (Chemical Information Services Ltd, 1988).

Sodium dichromate is also produced by five companies in India, four each in Brazil and the UK, three in China, two each in the Federal Republic of Germany and Turkey, and one each in Argentina, Czechoslovakia, Italy, Mexico, Pakistan, Poland, Romania, Spain, Switzerland and the USSR (Chemical Information Services Ltd, 1988).

Barium chromate is produced commercially by the reaction of barium chloride with sodium chromate (Copson, 1956). Five companies in the USA produced this chemical in 1977 (IARC, 1980a), and now there are four (Chemical Information Services Ltd, 1988), but no data on volumes were available. Barium chromate is produced by one company in Japan (Chemical Information Services Ltd, 1988). Production in 1977 was estimated to have been less than 50 tonnes; there were no reported imports or exports (IARC, 1980a). It is also produced by four companies in France, two in the UK, and one each in Australia, Austria, Belgium, the Federal Republic of Germany, India, Italy and Spain (Chemical Information Services Ltd, 1988).

Basic lead chromate (Chrome Orange) is produced by the reaction of lead oxide with sodium dichromate in the presence of acetic acid or by the reaction of lead nitrate with sodium chromate in the presence of sodium carbonate (Chalupski, 1956). No information on production of this compound in the USA was available, but combined production of Chrome Yellow and Chrome Orange, containing various proportions of basic lead chromate, amounted to 32.1 thousand tonnes in 1976 and 28.2 thousand tonnes in 1977 (Hartford, 1979). Basic lead chromate is also produced by one company each in Argentina, Colombia, the Federal Republic of Germany, Italy, Japan, Poland and Spain (Chemical Information Services Ltd, 1988).

Lead chromate (Chrome Yellow) can be produced by reacting sodium chromate with lead nitrate, or by reacting lead monoxide with chromic acid solution. By varying the proportion of reactants, either lead chromate ($PbCrO_4$) or lead chromate oxide (basic lead chromate; $PbO.PbCrO_4$) can be produced. High lead chromate content is associated with yellow pigments; increasing the lead chromate oxide content gives orange colours; and mixing with lead molybdate gives red pigments (Chalupski, 1956).

No information on production of this compound in the USA was available, but combined production of Chrome Yellow and Chrome Orange pigments was 32.1 thousand tonnes in 1976 and 28.2 thousand tonnes in 1977 (Hartford, 1979). Assuming an average of 70% lead chromate in these pigments, about 20 thousand tonnes of lead chromate were produced in the USA or imported for use in these pigments in that year. Lead chromate is currently produced by five companies in the USA (Chemical Information Services Ltd, 1988).

Commercial production in Japan was started in about 1910, and there were three major producers and one minor producer in 1977. Production in 1977 was 10.8 thousand tonnes and exports were 1800 tonnes. Six companies currently produce lead chromate in Japan (Chemical Information Services Ltd, 1988). Production of Chrome Yellow in 1984, 1985 and 1986, respectively, was 9900, 8500 and 7900 tonnes (Sasaki, 1985, 1986, 1987).

Lead chromate is also produced by six companies in Spain, five in Italy, three in Belgium, two each in Argentina, Austria, Canada, China, the Federal Republic of

Germany, France, the Netherlands and Turkey, and one each in Australia, Colombia, Mexico, Poland, Taiwan and the UK (Chemical Information Services Ltd, 1988).

Molybdenum orange pigments are variable complexes of lead sulfate, lead chromate and lead molybdate, made by pouring sodium dichromate, sulfuric acid and sodium molybdate into excess lead nitrate, preferably cold, at pH3. An ageing step is required in precipitation to permit development of the orange tetragonal form (Hartford, 1979).

Molybdenum orange is currently produced by four companies in the USA (Chemical Information Services Ltd, 1988). US imports for 1985, 1986 and 1987, respectively, were 980, 750 and 1100 tonnes from Canada (78%), the Federal Republic of Germany (16%) and Japan (6%) (Papp, 1988). Four companies currently produce molybdenum orange and molybdenum red in Japan (Chemical Information Services Ltd, 1988), and production of molybdenum red in 1984, 1985 and 1986, respectively, was 2900, 2600 and 2200 tonnes (Sasaki, 1985, 1986, 1987).

Molybdenum orange (including molybdenum red) is also produced by one company each in Australia, Austria, Canada, Colombia, India, Italy, Mexico and Taiwan, two each in Belgium, the Federal Republic of Germany, France and the Netherlands and four in Spain (Chemical Information Services Ltd, 1988).

Strontium chromate is prepared by adding a solution of a strontium salt to a solution of sodium chromate (Lalor, 1973).

Production of strontium chromate by three companies in the USA in 1970 was estimated to be 680 tonnes (Lalor, 1973). US imports in 1977 were 242 tonnes, mostly from Canada (US Department of Commerce, 1978). It is currently produced by five companies in the USA, but no data on volumes are available (Chemical Information Services Ltd, 1988). US imports for 1985, 1986 and 1987, respectively, were 390, 120 and 120 tonnes from France (61%), the Federal Republic of Germany (15%) and Canada (11%) (Papp, 1988).

Production in Japan began after 1940. The combined production of three companies in 1977 was about 600 tonnes, comparable with that of the previous seven years; there were no reported imports or exports (IARC, 1980a). Two companies currently produce strontium chromate in that country (Chemical Information Services Ltd, 1988).

Strontium chromate is also produced by four companies in France, two each in Australia, Italy, Spain and the UK and one each in Austria, Belgium, Brazil and the Federal Republic of Germany (Chemical Information Services Ltd, 1988).

Zinc chromates have been produced commercially since about 1940. Basic zinc chromates (including 'zinc chromates') are prepared by reaction between a solution of chromium trioxide and a slurry of zinc oxide. Zinc potassium chromates are prepared by a reaction between a solution of sodium dichromate, a slurry of zinc oxide and a solution of potassium chloride (Lalor, 1973).

Zinc chromate (zinc tetroxychromate) is currently produced by three companies each in Belgium, France, Italy, Japan, Spain and the USA, two each in Argentina and Austria, and one each in Australia, Canada, Colombia, India, the Netherlands, Norway, Poland, Taiwan, Turkey and the UK. Zinc potassium chromate is produced by two companies in Austria, one each in Belgium, France, Italy, Norway, Turkey and the USA (Chemical Information Services Ltd, 1988), and probably elsewhere. Production of 'zinc chromate' in Japan in 1984, 1985 and 1986 was 1530, 1280 and 1000 tonnes, respectively (Sasaki, 1985, 1986, 1987).

(*e*) *Other chromium compounds*

Chromium carbonyl is produced by the reaction of carbon monoxide with chromic chloride and aluminium metal (IARC, 1980a). Two companies in the USA produce this chemical, but no data on volumes are available. Chromium carbonyl is also produced by one company in the Federal Republic of Germany (Chemical Information Services Ltd, 1988).

2.2 Use

An early use of chromium compounds was as pigments, particularly chrome yellow. Basic chromic sulfate was used in tanning hides, as the reaction of chromium with collagen raises the hydrothermal stability of the leather and renders it resistant to bacterial attack. The most important use of chromium, namely as an alloying element, developed gradually during the nineteenth century and led to the introduction of chromium steels (Westbrook, 1979).

Chromium is currently used in such widely diversified products as stainless, tool and alloy steels, heat- and corrosion-resistant materials, special purpose alloys, alloy cast iron, pigments, metal plating, leather tanning, chemicals, and refractory materials for metallurgical furnaces. It is used in the metallurgical industry to enhance such properties as hardenability (response to quenching), creep (unit stress that will produce plastic deformation at a specified rate and temperature), strength and impact strength and resistance to corrosion, oxidation, wear and galling; its major use is in the production of stainless steel. Chromium pigments represent the largest use of chromium in the chemical industry (Papp, 1983).

(*a*) *Chromite ore*

Use of chromite ore in the USA decreased from 1.3 million tonnes in 1974 to 912 thousand tonnes in 1976, when utilization by the three consuming industries was as follows: metallurgical, 59.3%; refractory, 20.1%; and chemical, 20.6% (Morning, 1978). US consumption of chromite ore (and concentrate) was 504 thousand tonnes in 1987, 91% of which was used by the chemical and metallurgical industries and 9% by the refractory industry (Papp, 1988).

The metallurgical grade is used primarily to produce ferrochromium alloys, which are used in the production of stainless and other special steels (Bacon, 1964). The major use of chromite refractory materials in 1974 was in iron and steel processing, nonferrous alloy refining, glass making and cement processing (Morning, 1975); in 1987, the primary use was in refractory bricks to line metallurgical furnaces (Papp, 1988). Chemical-grade chromite ore is converted (by a series of operations involving roasting with soda ash and/or lime and leaching, with appropriate control of acidity) to sodium dichromate, used as such and in the production of many other chromium chemicals (Copson, 1956).

The major use of chromite ore in Japan has been in the production of ferrochromium (90%), the balance being used in the manufacture of refractory materials (6%), chromium compounds (3%) and chromium metal (1%) (IARC, 1980a).

(*b*) *Metallic chromium and chromium alloys*

Chromium metal (pure) is used to prepare alloys with high purity specifications. Chromium is thus an important and widely used alloying element in ferrous and nonferrous alloys, including those based on nickel, iron-nickel, cobalt, aluminium, titanium and copper. In alloys based on nickel, iron-nickel and cobalt, chromium is used primarily to confer oxidation and corrosion resistance. In alloys of aluminium, titanium and copper, chromium is used to control microstructure. Stainless steel contains at least 12% and may contain up to 36% chromium. Chromium-containing tool steels contain 1-12% chromium. Most full alloy steels contain 0.5-9% chromium, but some grades contain up to 28%. Cast irons contain 0.5-30% chromium (Papp, 1983).

In 1976, 70% (170 thousand tonnes) of all US chromium metal and metal alloys were used in the production of stainless steel. Of the total of chromium metal and alloys used in the production of commercial alloys, about 60% was in high-carbon ferrochromium, 11% in low-carbon ferrochromium, 21% in ferrochromium-silicon and 7.4% in other alloys, chromium briquets, exothermic additives and chromium metal (Morning, 1978). In 1987, 82% (330 thousand tonnes) of all US chromium ferroalloys, metal and other chromium-containing materials were used in the production of stainless steel. Of the total of chromium metal and alloys used in the production of commercial alloys, about 88% was in high-carbon ferrochromium, 6.5% in low-carbon ferrochromium, 4% in ferrochromium-silicon, 0.5% in other alloys and 1% in chromium metal (Papp, 1988).

Chromium-containing steels are widely used in, for instance, general engineering, architectural panels and fasteners, pollution control equipment, chemical equipment, cryogenic uses, hospital equipment, domestic equipment, automotive parts, engine components and food processing (Eurométaux, 1986).

Chromium alloys are used in a large variety of applications, including jet engine parts, nuclear plants, high-temperature reaction vessels, chemical industry equipment, high temperature-resistant equipments, coinage, desalinization plants, ships' propellers, acid-resistant equipment, cutting tools and implants (National Research Council, 1974).

Cobalt-chromium alloys were originally developed for use in cutting tools. Subsequently, because of their corrosion resistance, they were also used for equipment in contact with acids and other chemicals. They are used for facing valves and seats in internal combustion engines; wearing surfaces or cutting edges of hot shears, trimming dies, cam gauges, punches and turbine blades; pipeline linings; and pumps for corrosive liquids (Cobalt Development Institute, 1985). Stellite alloys are used in high-temperature applications. The superalloys are used for turbine discs and blades and nozzle vanes in jet engines; grates and quenching baskets in furnaces; and high-temperature springs and fasteners (Roskill Information Services, 1974). Vitallium alloy (27 wt% Cr, 5% Mo, 0.5% C, balance Co) is most commonly used as a denture alloy (Sullivan *et al.*, 1970).

(*c*) *Chromium[III] compounds*

Chromic acetate is used in printing and tanning, as a textile mordant, a polymerization and oxidation catalyst, and an emulsion hardener (Hartford, 1979; Sax & Lewis, 1987). Most of the chromic acetate produced in Japan has been used in dyeing processes (IARC, 1980a).

Chromic chloride is used for the production of commercial solutions of the basic chlorides ($Cr(OH)_2Cl$) by reaction with sodium hydroxide. These solutions have been reported to have minor special applications, such as use as a mordant for alizarin dyes on cotton yarn and certain cyamine dyes on silk. In Japan, they are also used for decorative chromium plating (IARC, 1980a).

Anhydrous chromic chloride has been used as a catalyst for polymerizing olefins, for chromium plating (including vapour plating), for preparing sponge chromium and other chromium salts, as an intermediate, and for waterproofing (Sax & Lewis, 1987).

Chromic hydroxide has been used as a catalyst, a tanning agent, a mordant, and in the preparation of Guignet's green (hydrated chromic oxide green) (Sax & Lewis, 1987).

Chromic nitrate has been used as a catalyst and a corrosion inhibitor (Sax & Lewis, 1987). It has also been used in textiles and in the manufacture of chromium dioxide (Hartford, 1979).

Most *chromic oxide* (anhydrous and hydrated) is used as a pigment. A substantial portion is also used in metallurgy in the manufacture of chromium metal and aluminium-chromium master alloys and, to a lesser extent, as a catalyst, in refractory brick, and as a chemical intermediate (IARC, 1980a; Sax & Lewis, 1987).

Anhydrous chromic oxide is the most stable green pigment known and is used in applications requiring resistance to heat, light and chemicals (e.g., in glass and ceramics). It is used in dyeing polymers, and its resistance to alkali makes it a valuable colourant for latex paints. It has special use in colouring cement and granules for asphalt roofing and in camouflage paints. Metallurgical-grade anhydrous chromic oxide is used in the manufacture of chromium metal and aluminium-chromium master alloys. It is used as a catalyst in the preparation of methanol, butadiene and high-density polyethylene. Chromic oxide is also used in refractory brick as a minor component to improve performance. When used as a mild abrasive for polishing jewellery and fine metal parts, it is known as 'green rouge' (IARC, 1980a).

Hydrated chromic oxide is also used as a green pigment, especially for automotive finishes (IARC, 1980a).

In Japan, chromic oxide has been used for the production of refractory materials (36%), pigments (35%), abrasives (15%) and other uses, such as glaze for glass (14%) (IARC, 1980a).

Chromic phosphate is used in pigments, phosphate coatings and wash primers, and as a catalyst (Hartford, 1979; Sax & Lewis, 1987).

Chromic sulfate is used in chrome plating, chromium alloys, green paints and varnishes, green inks, ceramic glazes, and as a mordant for textile dyeing. Basic chromic sulfate is the principal chemical used in leather tanning (Sax & Lewis, 1987).

Potassium chromic sulfate (chrome alum) has been reported to be used as a mordant prior to application of mordant dyes. It is also used to treat cotton that has been dyed with certain direct cotton dyes and sulfur dyes, rendering the dyed textile faster to washing. Another important application is in the preparation of hydrous chromic oxide, which, in turn, is used to make many of the trivalent chromium mordants (Howarth, 1956). It has also been used in chrome-tan liquors for tanning, in photographic fixing baths, and in ceramics (Sax & Lewis, 1987).

(*d*) *Chromium[VI] compounds*

Ammonium dichromate has a variety of uses, including a mordant for dyeing; in pigments; in the manufacture of alizarin, potassium chromic sulfate and catalysts; in oil purification; in pickling; in leather tanning; in synthetic perfumes; in photography; in process engraving and lithography; and in pyrotechnics (Sax & Lewis, 1987).

Calcium chromate is largely used as a corrosion inhibitor and as a depolarizer in batteries (Hartford, 1979). Its addition to protective coatings for steel and light metals is sometimes reported as a pigment use, but its primary function in these products is to inhibit corrosion. It is also used in ceramics and in paint pigments (Barium & Chemicals, undated). The use of calcium chromate as a pigment was discontinued in Japan some years ago (IARC, 1980a).

A major use of *chromium trioxide* has been in chromium plating, particularly in the production of automobiles. Uses in other metal-finishing operations include aluminium anodizing, particularly on military aircraft; chemical conversion coatings, which provide both decoration and corrosion protection; and the production of phosphate films on galvanized iron or steel (IARC, 1980a). Other uses of chromium trioxide are as a wood preservative (Anon., 1988a), as a corrosion inhibitor for ferrous alloys in recirculating water systems, as an oxidant in organic synthesis and in catalyst manufacture. Small amounts are used to modify the properties of basic magnesite refractories (IARC, 1980a).

US demand for chromium trioxide was 31.5 thousand tonnes in 1978 (Anon., 1978) and 57 thousand tonnes in 1988 (Anon., 1988a). The pattern of use in the USA in 1978 was as follows: metal treating and plating, 80%; wood treatment, 10%; chemical manufacturing, 5%; and other, 5% (Anon., 1978). The pattern of use in the USA in 1988 was: wood treatment, 63%; metal finishing, 22%; other (including water treatment, magnetic particles and catalysts), 7% (Anon., 1988a).

In Japan, the major use of chromium trioxide (90%) has been in chromium plating; 3% is used in pigments and 7% in other uses such as abrasives. The total used in Japan dropped from 11 800 tonnes in 1972 to 8300 tonnes in 1977 (IARC, 1980a).

Potassium chromate has limited applications in the textile industry — when a potassium rather than a sodium salt is essential or when differences in solubility or other physical properties make its use desirable (Howarth, 1956). Among these uses are as a mordant for wool, in dyeing nylon and wool with mordant acid dyes, in oxidizing vat dyes and indigosol dyes on wool, in dyeing with chromate colours, in treating direct dyes and some sulfur dyes on cotton to render them faster to washing, in oxidizing aniline black, and in stripping dyed wool (IARC, 1980a).

Potassium dichromate was once the most important commercial chromium compound, but it has largely been replaced in many applications by sodium dichromate. It is used in many small-volume applications such as photomechanical processing, chrome-pigment production and wool preservative formulations. The major use for potassium dichromate in Japan has been pigment production (54%); dye manufacture consumes an estimated 22%, with the remaining 24% used as an oxidizing agent in miscellaneous uses (as a catalyst and in other applications) (IARC, 1980a).

Sodium chromate is used in inks, leather tanning, wood preservation, corrosion inhibition, as a pigment in paint, water treatment, drilling muds, textile dyeing, cutting oils, catalysts, and as a raw material for the production of other chromium compounds (Sax & Lewis, 1987; American Chrome & Chemicals, undated h,i). In Japan, its principal use is as a mordant in dyeing operations (IARC, 1980a).

Sodium dichromate is the primary base material for the manufacture of chromium chemicals, which are used in leather tanning, metal treatment, drilling muds, textile dyes, catalysts, and wood and water treatment (Papp, 1983).

Demand for sodium dichromate in the USA was 146 thousand tonnes in 1978 (Anon., 1979) and 149 thousand tonnes in 1988 (Anon., 1988b). The pattern of use in 1978 was as follows: manufacture of chromium trioxide, 28%; manufacture of pigments, 24%; manufacture of leather tanning chemicals, 17%; corrosion control, 7%; metal treatment, drilling muds and textiles, 8%; and other (including chemical manufacture, catalysts, and wood preservation), 8% (Anon., 1979). The pattern of use in the USA in 1988 was as follows: manufacture of chromium trioxide, 54%; leather tanning, 9%; manufacture of chromium oxide, 9%; manufacture of pigments, 8%; wood preservation, 5%; and other (including drilling muds, catalysts, water treatment and metal finishing), 5% (Anon., 1988b).

Barium chromate is used in pyrotechnics, in high-temperature batteries, in safety matches, as a corrosion inhibitor in metal-joining compounds, as a pigment in paints, in ceramics, in fuses, in metal primers, and in ignition control devices (Hartford, 1979; Sax & Lewis, 1987). In Japan, the principal use was reported to be in explosive fuses (IARC, 1980a).

Chrome orange pigments, consisting largely of basic lead chromate, have been widely used in paints, metal protective primers and linoleum (Chalupski, 1956). In the early 1970s, use of chrome oranges in the USA was decreasing, although they were still being used in tints and rust-inhibiting paints (Schiek, 1973).

Lead chromate is used to make pigments for paints to be applied to both wood and metal. Chrome yellows (containing 52-98% lead chromate) are considered to be the most versatile of the inorganic pigments and are therefore found in many formulations designed for a wide spectrum of uses. The largest use of chrome yellows in the early 1970s was in paint for automotive finishes, farm machinery, architectural and air-dried finishes, and water-thinned coatings for exterior and interior use. Medium chrome yellow paints make up about 30% of the paint used for traffic control. Chrome yellows are also used as colourants in vinyls, rubber and paper. The second largest use of chrome yellows is in printing inks (Schiek, 1973).

The major use for lead chromate in Japan is in the production of pigments for paint and inks (85%); other uses are as a colourant for synthetic resins (14%) and miscellaneous applications (1%) (IARC, 1980a).

Molybdenum orange pigments are used in coatings, inks and plastics (National Chemical Company, undated e).

Strontium chromate was first used commercially (near the end of the nineteenth century) as a colourant in artists' paints, under the name 'citron yellow'. It was replaced for this use by organic pigments in 1936, at which time it was also being used for corrosion resistance on aluminium and magnesium alloys. Later, it was used in chemical-resistant coatings because of its low reactivity, and in epoxy polyamide vehicles and vinyl sheeting because of its heat-resistant properties. In 1973, some strontium chromate was still being used in vinyl sheeting and chemical-resistant coatings and in primer coatings for water tanks, but most of it was used, either alone or in combination with basic zinc chromate, in wash primers or in aluminium flake coatings (Lalor, 1973). Strontium chromate has also been used as an additive to control the sulfate content of solutions in electrochemical processes (Hartford & Copson, 1964). In Japan, the only known use has been as a corrosion inhibitor (IARC, 1980a).

Zinc chromates are used as pigments in paints, varnishes and oil colours. Many of them are used as a corrosion-resisting primer coatings and in metal conditioners (wash primers) applied before priming; in this case, they are used more for their chemical characteristics than their hue (Lalor, 1973; Windholz, 1983).

(*e*) *Other chromium compounds*

Chromium carbonyl has reportedly been used as an isomerization and polymerization catalyst, as a gasoline additive, and as a chemical intermediate (Sax & Lewis, 1987). It has also been used in the synthesis of 'sandwich' compounds (Hartford, 1979) from aromatic hydrocarbons, such as dibenzene(chromium) from benzene. Some of these compounds have been investigated as possible sources of vapour-deposited chromium and for the production of carbides.

2.3 Occurrence

The occurrence and distribution of chromium in the environment has been reviewed (Sayato & Nakamuro, 1980; Sequi, 1980; Balsberg-Påhlsson *et al.*, 1982; Cary, 1982; Filiberti *et al.*, 1983; Fishbein, 1984; Gauglhofer, 1984; Jin & Hou, 1984; Barceló *et al.*, 1986; Poschenrieder *et al.*, 1986; Camusso & Montesissa, 1988; Nriagu & Nieboer, 1988).

(*a*) *Natural occurrence*

Chromium is widely distributed in the earth's crust but is concentrated in the ultrabasic rocks. At an overall crust concentration of 125 mg/kg Cr (National Research Council, 1974), it is the twentieth most abundant element, ranking with vanadium, zinc, nickel, copper and tungsten (Westbrook, 1979). Only the trivalent and hexavalent compounds are detected in the environment in significant quantities (Fishbein, 1976). In reducing environments, chromium[VI] is unstable relative to chromium[III]. The average concentration of chromium in basalt, shale and granite has been reported to be 200, 100 and 20 ppm (mg/kg), respectively. The world average concentration of chromium in ultramafic, mafic, intermediate and felsic rock has been reported to be 2000, 200, 50 and 25 ppm (mg/kg), respectively. Concentrations in rock samples from Hawaiian lavas, from the Skaergaard intrusion in Greenland and from tertiary lavas of northeastern Ireland ranged from less than 1 ppm to 1750 ppm (mg/kg) chromium (Cary, 1982).

Chromium is found in nature only in the combined state and not as the free metal. It exists mainly as chromite, which has the idealized composition $FeO.Cr_2O_3$, although this composition has been found in nature only in meteorites. Chromite is a mixed metal oxide spinel containing iron, chromium, magnesium and aluminium in various proportions (Hartford, 1963) and as such is found in considerable quantities in Zimbabwe, the USSR, South Africa, New Caledonia and the Philippines (National Research Council, 1974; World Health Organization, 1988); it contains 40-50% chromium (Bidstrup & Case, 1956).

Of the chromium chemicals (other than chromite ore) included in this monograph, only two are known to occur in nature in mineral form: lead chromate as crocoite and potassium dichromate as lopezite (Hartford, 1963).

(*b*) *Occupational exposures*

Occupational exposures to a number of specific chromium compounds have been reported. With respect to hexavalent compounds, the most important exposures are to sodium, potassium, calcium and ammonium chromates and dichromates during chromate production, to chromium trioxide during chrome plating, to insoluble chromates of zinc and lead during pigment production and spray painting, to water-soluble alkaline chromates during steel smelting and welding and to other chromates during cement production and use. Trivalent compounds that are common in work place air include chromite ore during chromate production and in the ferrochromium industry, chromic oxide during pigment production and use, and chromic sulfate during leather tanning. In addition, occupational exposures to airborne dusts containing chromium metal may occur during production, welding, cutting and grinding of chromium alloys (Stern, 1982; Nieboer *et al.*, 1984; World Health Organization, 1988; see the monograph on welding, pp. 463-474). A schematic diagram of the production processes for some important commercial chromium compounds was given in Figure 1, on which those operations for which exposure data are available are indicated.

Potential occupational exposure to chromium occurs through inhalation, ingestion or skin contact (National Research Council, 1974). The US National Institute for Occupational Safety and Health (1977) estimated that about two million workers are exposed to chromium and chromium compounds. Chromium ulcers or chromate dermatitis, which are indicative of occupational exposure, have been reported in numerous occupations, involving manual handling of cement, leather, plastics, dyes, textiles, paints, printing inks, cutting oils, photographic materials, detergents, wood preservatives, anticorrosion agents and welding rods (Pedersen, 1982; Burrows, 1983; Polak, 1983; Nieboer *et al.*, 1984; Table 10; see also section 3.3(*b*), p. 182).

Table 10. Occupations with potential exposure to chromium[a]

Abrasives manufacturers
Acetylene purifiers
Adhesives workers
Aircraft sprayers
Alizarin manufacturers
Alloy manufacturers
Aluminium anodizers
Anodizers
Battery manufacturers
Biologists
Blueprint manufacturers
Boiler scalers
Candle manufacturers
Cement workers
Ceramic workers
Chemical workers
Chromate workers
Chromium-alloy workers
Chromium-alum workers
Chromium platers
Copper etchers
Copper-plate strippers
Corrosion-inhibitor workers
Crayon manufacturers
Diesel locomotive repairmen
Drug manufacturers
Dye manufacturers
Dyers
Electroplaters
Enamel workers
Explosives manufacturers
Jewellers
Laboratory workers
Leather finishers
Linoleum workers
Lithographers
Magnesium treaters
Match manufacturers
Metal cleaners
Metal workers
Milk preservers
Oil drillers
Oil purifiers
Painters
Palm-oil bleachers
Paper waterproofers
Pencil manufacturers
Perfume manufacturers
Photoengravers
Photographers
Platinum polishers
Porcelain decorators
Pottery frosters
Pottery glazers
Printers
Railroad engineers
Refractory-brick manufacturers
Rubber manufacturers
Shingle manufacturers
Silk-screen manufacturers
Smokeless-powder manufacturers
Soap manufacturers

Table 10 (contd)

Fat purifiers
Fireworks manufacturers
Flypaper manufacturers
Furniture polishers
Fur processors
Glass-fibre manufacturers
Glass frosters
Glass manufacturers
Glue manufacturers
Histology technicians
Sponge bleachers
Steel workers
Tanners
Textile workers
Wallpaper printers
Wax workers
Welders
Wood-preservative workers
Wood stainers

[a] From National Research Council (1974)

This section summarizes data on exposure to chromium in air and the results of biological monitoring in various industries and occupations. The biological indicator levels are influenced by the solubility of chromium compounds and by the time of sampling. It should be noted that the chromium compounds, the timing of collection of biological samples (normally at the end of a shift) and the analytical methods used differ from study to study, and elevated levels of chromium in biological fluids and tissue samples are mentioned only as indications of uptake of chromium. (See also section 3.3(*b*) and the monographs on nickel and nickel compounds, and on welding.)

(i) *Ferrochromium steel and high chromium alloy production*

During the electrothermal reduction of chromite ore with coke for the production of ferrochromium, workers in the area near the furnaces are exposed to fumes containing 0.1-10% chromium (Stern, 1982).

In 1959, an industrial hygiene survey was carried out in a US plant producing ferrochromium, ferrosilicon and chromium alloys in electric furnaces. The mean concentrations of chromium trioxide [values for chromium calculated by the Working Group in square brackets] in the air were 1 [< 1] μg/m^3 in the maintenance shop, 266 [140] μg/m^3 in the charging area, 317 [160] μg/m^3 in the casting area and 2470 [1300] μg/m^3 in the finishing area. The overall mean of 127 samples was 452 μg/m^3 chromium trioxide [230 μg/m^3 chromium] (Princi *et al.*, 1962).

In 1973, workplace concentrations of hexavalent chromium were reported to be 30-60 μg/m^3 during the production of ferrochromium in the USSR (World Health Organization, 1988).

Concentrations of total dust and chromium in 1975 in a Norwegian ferrochromium plant are shown in Table 11. In various occupations, the mean level of total

Table 11. Air concentrations of total dust and chromium in a Norwegian ferrochromium plant[a]

Occupation or area	No. of samples	Mean and range of dust concentration (mg/m³)	Mean and range of chromium concentration (μg/m³)
Potmen	20	6.3 (4.0-15.7)	40 (20-70)
Cleaner-balers	5	18.2 (10.5-23.9)	90 (50-130)
Crane drivers	10	4.6 (3.1-7.6)	40 (10-50)
Packers	10	4.9 (2.3-8.3)	290 (50-1300)
Maintenance workers	9	15.6 (4.0-46.0)	90 (20-370)
Transport workers	9	12.8 (5.6-30.1)	10 (10-30)
Charge floor	5	4.8 (2.8-8.4)	50 (30-70)
Top electrode	3	15.5 (13.9-17.8)	170 (150-190)
Packing area	18	1.9 (0.3-5.5)	190 (10-1340)

[a] From Langård *et al.* (1980)

chromium was 10-290 μg/m³, about 11-13% of which was water-soluble (Langård *et al.*, 1980).

Among Swedish ferrochromium workers, exposure to hexavalent chromium was estimated at 250 μg/m³ during arc-furnace operations and 10-50 μg/m³ during transport, metal grinding, maintenance and sample preparation. The total concentration of metallic and trivalent chromium at the work sites was 500-2500 μg/m³ (Axelsson *et al.*, 1980).

In an Italian ferrochromium plant, dust samples contained 0.9-3.8% chromium, and airborne levels of total chromium were 20-158 μg/m³. The concentration of hexavalent chromium was below 1 μg/m³. Levels of urinary chromium measured at the beginning and end of a work shift were low (less than 5 μg/g creatinine), although the results indicated absorption of chromium in some groups of workers (Foa *et al.*, 1988).

In ten steel, 15 iron and 11 copper alloy foundries in Finland in 1973 and 1974, furnacemen and casters were exposed to a mean level of 1-6 μg/m³ acid-soluble chromium (Tossavainen, 1976).

During the production of chromium carbide powder in the USSR, dust concentrations were 11-20 mg/m³ during weighing of chromium[III] oxide, 260-640 mg/m³ during milling and 24-200 mg/m³ during loading, screening and packing of the product (Brakhnova, 1975). In open-hearth steel works, concentrations of chromium trioxide in work place air were 13-37 μg/m³ [7-20 μg/m³ chromium] (Belitskaya, 1981).

In Sweden, the tissue concentrations of chromium in the lungs of 20 deceased smelter workers were three to four times higher than those of eight control subjects (median level, 0.29 and 0.08 μg/g wet tissue, respectively) (Brune *et al.*, 1980).

In Finland, fumes and dusts contained 6-15% chromium during ferrochromium smelting, 1.5-5% during stainless-steel smelting, 0.2-0.3% during continuous casting and 1.6-13% during grinding of stainless steel (Koponen *et al.*, 1981). Air concentrations of total chromium were 200 μg/m^3 during ferrochrome smelting and 10 μg/m^3 during continuous casting of stainless steel. The mean concentration of hexavalent chromium during the production of stainless steel was 1.5 μg/m^3 (Koponen, 1985).

In France, air concentrations of total chromium ranged from 15 to 300 μg/m^3 in a steel production plant (Klein, 1985).

Triebig *et al.* (1987) measured the exposure of 230 workers in high-alloy steel plants to chromium in the Federal Republic of Germany. Levels of chromium trioxide [chromium] in the air were 10-2280 [5-1200] μg/m^3. Urinary levels of chromium were 0.1-79 μg/g creatinine, indicating some exposure to metal fumes and dusts in steel smelting, cutting and grinding.

(ii) *Production of chromates and of chromate pigments*

Airborne concentrations of chromates [chromium] in four US chromate plants over the period 1941-47 were 10-4600 [5-2300 μg/m^3] at kilns and mills, 40-340 [20-170] μg/m^3 at dryers, 200-21 000 [100-11 000] μg/m^3 in packing areas and 3-2170 [2-1100] μg/m^3 in other parts of the factories (Machle & Gregorius, 1948). Workplace air concentrations of chromium[III], chromium[VI] and total chromium during various operations in chromite ore processing were reported for a plant in Ohio (USA) which produced sodium dichromate (Bourne & Yee, 1950) and for a chromate production plant in the UK (Buckell & Harvey, 1951; see Table 12).

Table 12. Air concentrations of chromium[III] and chromium[VI] in US[a] and UK[b] chromate factories

Operation	Chromium[III] (mg/m^3)		Chromium[VI] (mg/m^3)	
	USA	UK	USA	UK
Chromite and lime mixing	1.52	2.14	0.03	0.005
Roasting	0.39	0.17	0.26	0.029
Filtering	0.12	0.037	0.08	0.52
Shipping	0.30	0.005	0.2	0.88

[a] From Bourne & Yee (1950)
[b] From Buckell & Harvey (1951)

In a chromate production plant in the USA, the levels of water-soluble hexavalent chromium were 100-900 μg/m³ in 1945-49 and 5-100 μg/m³ in 1950-59 (Braver *et al.*, 1985). In 1953, the US Public Health Service studied the health hazards associated with the chromate-producing industry. Six plants were directly involved in the production of alkaline chromates and dichromates from chromite ore. One of the plants also manufactured chromium pigments. In about 1600 air samples, the weighted average exposures by occupational groups were 7-890 μg/m³ insoluble chromium as chromite, 5-170 μg/m³ water-soluble chromium[VI] and 10-470 μg/m³ acid-soluble, water-insoluble chromium (Gafafer, 1953).

Concentrations of soluble and acid-insoluble chromium in lung tissues of 16 chromate manufacturing workers in the USA ranged from 3 to 161 μg/g dry tissue and 5 to 402 μg/g dry tissue, respectively; the workers had been exposed to chromite ore, sodium chromate, potassium dichromate and various intermediate chromium compounds for 1.5-42 years (Baetjer *et al.*, 1959a).

In Italy, chromic acid and alkaline chromate production workers were exposed to mean levels of 110-150 μg/m³ chromates [60-80 μg/m³ hexavalent chromium] (Vigliani & Zurlo, 1955). More recently, dust exposures and urinary excretion of chromium were studied in another Italian factory that produces potassium dichromate and chromic sulfate. A group of 22 potassium dichromate workers was exposed to levels of 10-100 μg/m³ chromium[III] and 8-212 μg/m³ water-soluble chromium[VI] (Mutti *et al.*, 1984), and their mean urinary concentration of total chromium was 31.5 μg/l (Cavalleri & Minoia, 1985). A group of 15 chromic sulphate workers were exposed to levels of 46-1689 μg/m3 chromium[III] and 2-23 μg/m³ chromium[VI] (Mutti *et al.*, 1984); their urinary chromium concentrations averaged 24.7 μg/l. Chromium levels in serum and erythrocytes were also increased among exposed workers (Cavalleri & Minoia, 1985).

In Japan, air concentrations of total chromium during sodium and potassium dichromate and chromium trioxide production in one plant ranged from 19 to 219 μg/m³; in 1960, levels of chromium trioxide [chromium] were 390-20 170 [180-10 000] μg/m³ in this factory, where enclosures and local exhausts were not properly used. Chromium content was measured in several organs of six chromate workers who had been exposed for over ten years and had died of lung cancer; the chromium concentration in the lungs averaged 51.1 μg/g wet weight, while in unexposed controls it averaged 0.31 μg/g wet weight (Kishi *et al.*, 1987). In six Japanese studies, the chromium contents of the lungs of chromate workers were 0.5-132 μg/g wet weight and 14-2368 μg/g dry weight, as compared to 0.05-3.72 μg/g wet weight and 0.47-5.14 μg/g dry weight in men without occupational exposure (Adachi, 1987). High concentrations of chromium were found in the respiratory organs of chromate workers who had died of cancer, and in the spleen, liver, kidney, brain, heart, bone marrow and skin (Hyodo *et al.*, 1980; Teraoka, 1987). In 1957, chromium trioxide [chromium] concentrations in the plant ranged from 40-8430 [20 to 4300] μg/m³, with a mean of 520 [260] μg/m³ (Hyodo *et al.*, 1980).

Chromate pigment workers are exposed primarily to zinc and lead chromates although they may also be exposed to other compounds, such as chromium trioxide, sodium chromate and dichromate and zinc oxide (Davies, 1984a).

In three Norwegian pigment plants producing zinc and lead chromates, workers mixing raw materials and filling sacks were exposed to mean concentrations of 1.2-9.8 mg/m³ total dust and 10-1350 μg/m³ chromium. The chromium levels to which foremen are exposed were taken as a measure of general exposure in the plants; in one plant it was 40 μg/m³, in another it was 190 μg/m³ (Langård & Norseth, 1975).

In India, the concentration of chromium in the urine of workers exposed to chromates in two paint manufacturing factories was about ten fold that of unexposed persons (Tandon *et al.*, 1977).

In almost all positions at a US chromate pigment plant, production workers were exposed to hexavalent chromium in the form of zinc and lead chromates. Concentrations of airborne chromium were estimated to be more than 2 mg/m³ for highly exposed workers, between 0.5 and 2 mg/m³ for moderately exposed workers and less than 0.1 mg/m³ for the low-exposure category (Sheffet *et al.*, 1982).

(iii) *Leather tanning* (see also IARC, 1981)

The most common tanning process involves the use of basic chromic sulfate liquor. Tanning is accomplished in large vats where the hides are soaked with dehairing, neutralizing, pickling, colouring and finishing chemicals. In the two-bath method, the hides are first immersed in a bath of hexavalent chromium salts (potassium or sodium dichromate), sodium chloride and sulfuric acid, and then removed and placed in a reduction bath to reduce the dichromate to trivalent chromic sulfate. An exothermic reaction takes place with a reduction agent such as sugar, starch or sulfur dioxide. The majority of tanneries do not produce their own tanning liquors, and a large number of proprietary products are available for direct use. Occupational exposure to chromium in the tanning industry may occur through contact with the trivalent chromium solutions. Wet, freshly tanned skins contain 1-2% chromium by weight, and dry leather powder contains 2-6% depending on the method and degree of tanning (Stern, 1982; Stern *et al.*, 1987).

Airborne levels of 20-50 μg/m³ trivalent chromium were measured in 1975 in an Italian tannery when tanning baths were emptied (IARC, 1980a).

Air concentrations of trivalent chromium in a Finnish tannery were 1-29 μg/m³ (personal samples). Two press operators were exposed to a mean level of 13 μg/m³, and their urinary chromium excretion varied during one working week from 5 to 62 μg/l. A diurnal variation was evident, with the highest values occurring in post-shift samples. Blood samples contained 10-22 μg/l chromium in the plasma and 4.7-11 μg/l in whole blood; plasma levels were < 1 μg/l in workers who were less exposed to tanning liquors. During press operations, splashes are common, and absorption from the gastrointestinal tract was suggested to be the main route of exposure (Aitio *et al.*, 1984).

Urine samples were collected from 34 male tannery workers in Turkey. The mean urinary concentration of chromium was 6.6 μg/l (5.6 μg/g creatinine) in tannery workers, 2.3 μg/l (1.9 μg/g creatinine) in office and kitchen workers at the same factory and 0.22 μg/l (0.26 μg/g creatinine) in unexposed controls (Saner *et al.*, 1984).

In two leather tanning facilities in the USA, the total concentration of chromium in work place air was 0.2-54 μg/m^3, with a mean of 39 μg/m^3 (Stern *et al.*, 1987).

(iv) *Chromium plating*

There are two types of chromium electroplating: decorative ('bright') and hard chromium plating. In decorative plating, a thin (0.5-1 μm) layer of chromium is deposited over nickel or nickel-type coatings to provide protective, durable, non-tarnishable surface finishes. Hard chromium plating produces a thicker (5-10 μm) coating, usually directly on the base metal, to increase its heat, wear and corrosion resistance. Plating baths contain chromium trioxide (250-350 g/l) and sulfuric acid (2.5-3.5 g/l) or a mixture of sulfuric acid and fluoride or fluorosilicate, as well as various organic additives. Electrolysis emits bubbles of oxygen and hydrogen that generate chromium trioxide mist by bursting at the liquid surface. Surfactants and floating balls may be used to control the mist emission (Guillemin & Berode, 1978; Stern, 1982; Sheehy *et al.*, 1984). Exposure to substances other than chromium occurs in a number of pretreatment and finishing operations: acid and alkali mists, nitrogen oxides, cyanide and solvents may be released during pickling, acid dipping, stripping and degreasing processes, and metal and abrasive dusts are released from grinding and polishing. In some plants, decorative-chrome platers also perform nickel plating (Sheehy *et al.*, 1984).

Air measurements made in metal plating plants since 1928 are summarized in Table 13. It is apparent that exposures to chromium have been markedly reduced with modern technology. In most studies, the levels were measured as total water-soluble chromium or hexavalent chromium and reported as a chromium trioxide concentration.

Table 13. Workplace levels of hexavalent chromium during metal plating

Reference and country	Process and sampling data	Chromium oxide (chromium VI) concentration (μg/m³)
Bloomfield & Blum (1928) USA	Chromium plating 6 plants, 19 samples	120-6900 [60-3800]
Riley & Goldman (1937) USA	Chromium plating	
	with no local exhaust	2780-3680 [1440-1910]
	with low local exhaust	11 200 [580]
	with high local exhaust	340 [180]
Gresh (1944) USA	Chromium plating 7 samples	90-1200 [45-600]
Molos (1947) USA	Chromium plating	
	with local exhaust	4500-5000 [2300-2500]
	with plastic beads on the bath	1900-3000 [950-1500]
	with plastic beads and local exhaust	20-50 [10-25]
Sheehy *et al.* (1984) USA	Chromium plating	
	with no local exhaust	[140-2960]
	with local exhaust	[0.5-270]
	with local exhaust and plastic beads on the bath	[0.5-5]
Lumio (1953) Finland	Chromium plating 16 plants	< 3 [< 1.5]
Hama *et al.* (1954) USA	Decorative chromium plating 4 plants	2-60 [1-30]
Kleinfeld & Rosso (1965) USA	Decorative chromium plating	
	with no local exhaust	180-1400 [90-730]
	with local exhaust	2-9 [2-5]
Hanslian *et al.* (1967) Czechoslovakia	Chromium plating 8 plants	23-681 [12-330]
Mitchell (1969) UK	Chromium plating (stripping)	
	with no local exhaust	240-21 300 [120-10 600]
	with local exhaust	10-30 [5-15]
Gomes (1972) Brazil	Chromium plating	
	8 hard chromium plants	< 100-1400 [< 50-700]
	63 decorative chromium plants	< 100-700 [< 50-350]

Table 13 (contd)

Reference and country	Process and sampling data	Chromium oxide (chromium VI) concentration (μg/m^3)
National Institute for Occupational Safety and Health (1973-81) (reviewed by Sheehy *et al.*, 1984) USA	Hard chromium plating	
	plant 1	[1.1-48.6]
	plant 2	[0.8-9.6]
	plant 3	[3.6-66.0]
	plant 4	[3-6]
	Decorative chromium plating	
	plant 5	[< 0.5-3]
	plant 6	[0.2-5.9]
	plant 7	[0.2-9.0]
	plant 8	[< 3]
	Nickel-chromium plating	
	plant 9	[2.9]
	Zinc plating	
	plant 10	[< 1.2-3.6]
	plant 11	[0.3]
Royle (1975a) UK	Chromium plating	
	40 plants	< 30 [< 15]
	2 plants	> 30 [> 15]
Yunusova & Pavlovskaya (1975) [quoted by the World Health Organization, 1988] USSR	Chromium plating	
	8 plants	[40-400]
Michel-Briand & Simonin (1977) France	Chromium plating	5-15 [2.5-7.5]
Guillemin & Berode (1978) Switzerland	Hard chromium plating	
	6 plants, 23 samples	2-655 [1-330]
	Bright chromium plating	
	6 plants, 11 samples	2-26 [1-13]
Ekholm *et al.* (1983) Sweden	Hard chromium plating	
	4 plants	< 1-46
	Decorative chromium plating	
	9 plants	< 1-2
Mutti *et al.* (1984) Italy	Chromium plating	
	24 hard chromium platers	[4-146]
	16 bright chromium platers	[0-31]

Table 13 (contd)

Reference and country	Process and sampling data	Chromium oxide (chromium VI) concentration (μg/m³)
Sheehy *et al.* (1984) USA	Chromium, nickel, zinc, copper, cadmium and silver plating, 8 plants	
	53 personal samples	[< 1-14]
	293 tank area samples	[< 1-11 000]
	39 general area samples	[< 1-31]
Sorahan *et al.* (1987) UK	Decorative chromium plating	
	60 samples before 1973	0-8000 [0-4000]
	numerous samples after 1973	< 50 [< 25]

Typical levels of chromium in post-shift urine samples from electroplaters are given in Table 14. In one study of 21 electroplaters, chromium levels in serum were 0.2-1.3 μg/l (Verschoor *et al.*, 1988). High concentrations of chromium were found in the respiratory organs of two chromium platers as well as in the spleen, liver, kidney and heart (Teraoka, 1987).

Table 14. Urinary concentrations of chromium in electroplaters

Reference and country	Type of workers (no.)	Mean and range of chromium concentrations in urine (μg/l or μg/g creatinine)
Franzen *et al.* (1970) Federal Republic of Germany	Chromium platers (133)	< 4-32 μg/l
Schaller *et al.* (1972) Federal Republic of Germany	Chromium platers (12)	9.7 (1.4-24.6) μg/l
Guillemin & Berode (1978) Switzerland	Hard chromium platers[a] (21)	23 μg/l (18 μg/g)
	Bright chromium platers[a] (16)	5.6 μg/l (5.3 μg/g)
Sarto *et al.* (1982) Italy	Bright chromium platers (17)	6.1 μg/g
	Hard chromium platers (21)	10.0 μg/g
Lindberg & Vesterberg (1983) Sweden	Chromium platers (90)	[< 0.3-98 μg/l] Calculated by the Working Group from plots

Table 14 (contd)

Reference and country	Type of workers (no.)	Mean and range of chromium concentrations in urine (μg/l or μg/g creatinine)
Mutti *et al.* (1984) Italy	Hard chromium platers[a] (24)	15.3 μg/g
	Bright chromium platers[a] (16)	5.8 μg/g
Verschoor *et al.* (1988) Netherlands	Chromium platers (21)	9 (1-34) μg/g
Nagaya *et al.* (1989) Japan	Chromium platers (44)	0.25 (0.05-1.54 μmol/l) [13 (3-80) μg/l]

[a] Corresponding air concentrations can be found in Table 13.

(v) *Welding*

Welding produces particulate fumes that have a chemical composition reflecting the elemental content of the consumable used. For each couple of process/material of application, there is a wide range of concentrations of the elements present in the fume. Chromium and nickel are found in significant concentrations in fumes from welding by manual metal arc, metal inert gas and tungsten inert gas processes on stainless and alloy steels. Typical ranges of total fume, total chromium and hexavalent chromium found in the breathing zone of welders are presented in Table 15. Certain special process applications not listed can also produce high chromium and nickel concentrations, and welding in confined spaces produces significantly higher concentrations of total fume and elemental constituents. Exposure to welding fumes that contain nickel and chromium can lead to elevated levels of these elements in tissues, blood and urine (see monograph on welding for details).

(vi) *Other occupations*

During the production of trivalent chromium compounds (chromic oxide and chromic sulfate) in the Federal Republic of Germany, work place air contained 180-13 200 μg/m^3 chromic oxide and 850-2700 μg/m^3 chromic sulfate during filtering, drying and unloading operations (Korallus *et al.*, 1974a).

Exposures of spray painters to solvents and paint mists have been measured in a variety of industries by the US National Institute for Occupational Safety and Health. Air concentrations of total chromium in breathing zone samples were 1600 μg/m^3 during aircraft painting, 220 μg/m^3 during railroad car painting and 5-9 μg/m^3 during metal furniture painting (O'Brien & Hurley, 1981). At a US plant manu-

Table 15. Total fume and chromium concentrations found in the breathing zone of welders[a]

Process[b]	Total fume[c] (mg/m³)	Total Cr (µg/m³)	Cr(VI) (µg/m³)
MMA/SS	2-40	30-1600	25-1500[d]
MIG/SS	2-3	60	< 1
TIG/SS	1-3	10-55	< 1

[a] From van der Wal (1985)

[b] MMA, manual metal arc; SS, stainless steel; MIG, metal inert gas; TIG, tungsten inert gas

[c] 50%-90% range

[d] 50%-90% Cr(VI) from MMA/SS is soluble in water (Stern, 1982).

facturing truck bodies and refuse handling equipment, breathing zone concentrations of paint mists ranged from 4.8 to 47 mg/m³ total dust and 10 to 400 µg/m³ chromium (Vandervort & Cromer, 1975). Personal air samples had concentrations of hexavalent chromium ranging from 30 to 450 µg/m³ with a mean of 230 µg/m³ during spray painting of buses (Zey & Aw, 1984), 13 to 2900 µg/m³ with a mean of 607 µg/m³ during spray painting of aircraft wheels (Kominsky *et al.*, 1978) and 10 to 40 µg/m³ with a mean of 20 µg/m³ during spray painting of bridge girders (Rosensteel, 1974).

Breathing zone samples were also taken in a small automotive body repair workshop in the USA. One of the eight samples contained 490 µg/m³ chromium; the others were below the detection limit (Jayjock & Levin, 1984).

In a Swedish study, mean chromium levels of 1300 µg/m³ were measured during car painting and 500 µg/m³ during industrial painting, while work place levels averaged 300 µg/m³ during grinding activities (Elofsson *et al.*, 1980). Low overall levels were found for spray painters working in a fireplace manufacturing plant; the concentrations of total dust and chromium oxide [unspecified] were 1700 and 5-8 µg/m³ [chromium, 3-4 µg/m³], respectively (Hellquist *et al.*, 1983).

In Italy, 12 spray painters using lead and zinc chromate paints were exposed to levels of 450-1450 µg/m³ insoluble hexavalent chromium, and their mean urinary excretion was 13.2 µg/g creatinine at the end of a work shift (Mutti *et al.*, 1984).

At the largest wood treatment plant in Hawaii, air concentrations of 2-9 µg/m³ chromium were measured. Urinary excretion of 89 workers using chromated copper arsenate wood preservatives did not differ from that of controls (Takahashi *et al.*, 1983).

In a cement-producing factory in the USSR, concentrations of hexavalent chromium in work place air varied from 5 to 8 μg/m³, measured as chromium trioxide (Retnev, 1960). Hexavalent chromium was found in 18 of 42 US cement samples at concentrations ranging from 0.1 to 5.4 μg/g, with a total chromium content of 5-124 μg/g (Perone *et al.*, 1974). Portland cement contains 41.2 ppm (mg/kg) chromium (range, 27.5-60), due to the presence of chromium in limestone. Soluble chromium in cement averaged 4.1 mg/kg (range, 1.6-8.8), of which 2.9 mg/kg (range, 0.03-7.8) was hexavalent chromium (Fishbein, 1976). Analysis of 59 samples of Portland cement from nine European countries showed concentrations of 1-83 μg/g hexavalent chromium and 35-173 μg/g total chromium (Fregert & Gruvberger, 1972). In France and Belgium, cements manufactured in 11 plants contained 8-49 μg/g total chromium, originating from limestone, clay, gypsum, fly ash and slag used in the manufacture as well as from the refractory kiln materials (Haguenoer *et al.*, 1982). Cement in Iceland contained 5.8-9.5 mg/kg hexavalent chromium (Rafnsson & Jóhannesdóttir, 1986).

In open-cast chromium mining in the USSR, concentrations of total airborne dust ranged from 1.3 to 16.9 mg/m³; in the crushing and sorting plant, dust levels were 6.1-188 mg/m³. The chromium content of settled dust varied from 3.6 to 48% (calculated as chromic oxide). No hexavalent chromium was found in the dust (Pokrovskaya *et al.*, 1976; World Health Organization, 1988).

During the manufacture of chromium[III] lignosulfonate in Finland, five packing workers were exposed to dust containing about 2% trivalent chromium. The product contained 6% trivalent chromium attached to wood lignin. In personal samples, the concentration of chromium in the air was 2-230 μg/m³, and three-day averages ranged from 11 to 80 μg/m³. Urinary levels in samples from workers were 0.01-0.59 μmol/l (0.5-30 μg/l), and mean excretion was 0.02-0.23 μmol/l (1-12 μg/l). It was concluded that chromium occurred exclusively in a trivalent state in both dust and urine (Kiilunen *et al.*, 1983).

(*c*) *Air*

Chromium is generally associated with particulates in ambient air at concentrations of 0.001-0.1 μg/m³ (Fishbein, 1976; O'Neill *et al.*, 1986). In the USA in 1966, only seven of 58 cities in the National Air Sampling Network had annual average chromium levels of 0.01 μg/m³ or more, and only 16 had maximal single values above that level. In approximately 200 urban stations in the USA during 1960-69, annual mean concentrations were 0.01-0.03 μg/m³ (minimal level detectable, 0.01 μg/m³). In nonurban areas, the level of chromium was less than 0.01 μg/m³. Levels of 0.9-21.5 μg/m³ were reported in 23 localities in northern England and Wales in 1956-58 (Fishbein, 1976). In 1957-74, the amount of chromium in the atmospheric aerosol at a rural site in the UK declined at an average yearly rate of 11.3% (Salmon *et al.*, 1977).

During the period May 1972-April 1975, the range of average levels of chromium determined at 15 stations in Belgium was 0.01-0.04 μg/m³ (maximal value, 0.54 μg/m³). The values were stated to reflect background pollution and levels representative of those in air inhaled by the majority of the population. Sampling station locations were selected to avoid, as much as possible, a direct influence of local sources (Kretzschmar *et al.*, 1977).

Coal from many sources can contain as much chromium as soils and rocks, i.e., up to 54 ppm (mg/kg); consequently, the burning of coal can contribute to chromium levels in air, particularly in cities (Fishbein, 1976; Merian, 1984). Particulates emitted from coal-fired power plants contained 2.3-31 ppm (mg/kg) chromium, depending on the type of boiler firing; the emitted gases contained 0.22-2.2 mg/m³. These concentrations were reduced by fly ash collection to 0.19-6.6 ppm (mg/kg) and 0.018-0.5 mg/m³, respectively (Fishbein, 1976). Fly ash has been shown to contain 1.4-6.1 ppm (mg/kg) chromium[VI] (Stern *et al.*, 1984).

Mean concentrations in the air of US cities with metallurgical chromium or chromium chemical producers or with refractories were 0.012-0.016 μg/m³, all of which were higher than the US national average. Cement-producing plants are probably an additional source of chromium in the air. When chromate chemicals are used as rust inhibitors in cooling towers, they are dissolved in recirculating water systems, which continually discharge about 1% of their flow to waste. Additionally, chromate and water are lost to the atmosphere (Fishbein, 1976).

The concentration of chromium in the air at the South Pole was reported to be 0.005 ng/m³. Concentrations in samples taken over the Atlantic Ocean ranged from 0.007 to 1.1 ng/m³. Airborne chromium concentrations were reported to be 0.7 ng/m³ in the Shetland Islands and Norway, 0.6 in northwestern Canada, 1-140 in Europe, 1-300 in North America, 20-70 in Japan and 45-67 in Hawaii, USA (Cary, 1982).

(*d*) *Water*

Naturally occurring chromium concentrations in water arise from mineral weathering processes, soluble organic chromium, sediment load and precipitation (Cary, 1982).

Concentrations of chromium in rivers have been found to be 1-10 μg/l. Chromium (both hexavalent and trivalent) is generally found at lower concentrations in seawater (well below 1 μg/l) than in rivers and wells. It has been estimated that 6.7 million kg of chromium are added to the oceans every year. As a result, much of the chromium lost from the land by erosion and mining is eventually deposited on the ocean floor (Fishbein, 1976).

The mean chromium concentration in ocean water in 1979 was 0.3 μg/l, with a range of 0.2-50 μg/l. Samples taken from the first 100 m of water from several areas of the Pacific Ocean contained about 0.12 μg/l chromium, about 83% being hexavalent chromium; below 100 m, total chromium increased to about 0.16 μg/l, with hexavalent chromium accounting for 90%. In saline waters of Australia, 62-87% of the labile chromium present (< 1 μg/l) was hexavalent (Cary, 1982).

Of 1500 samples of US surface waters taken between 1960 and about 1968, 24.5% contained chromium detectable spectrographically; the maximal and mean levels observed were 112 and 9.7 μg/l, respectively (Kroner, 1973). A survey of chromium content of 15 North American rivers showed levels of 0.7-84 μg/l, with most in the range of 1-10 μg/l (Hartford, 1979). Levels in 3834 samples of tap water taken from 35 regions of the USA in 1974-75 ranged from 0.4 to 8 μg/l chromium, with the median 1.8 μg/l (US Environmental Protection Agency, 1984).

Of 170 samples taken from lakes in the higher Sierra Mountains of California, USA, in 1968, only two contained as much as 5 μg/l chromium. Chromium concentrations in 1977 in the Amazon (Brazil) and Yukon (USA) Rivers were 2.0 and 2.3 ppb (μg/l), respectively; the two rivers were considered to represent unpolluted systems draining watersheds of a wide variety of mineral types from extremely different climates. The concentration of chromium in 96% of the 4342 samples of stream- and river-water in Canada was less than 10 μg/l; about 2% of the samples contained 15-500 μg/l chromium (Cary, 1982).

The mean concentration of dissolved chromium compounds in the Rhine River during 1975 was 6.5 μg/l with a range of 3.7-11.4 μg/l; the concentration in drinking-water was 0.29 μg/l (Nissing, 1975). The concentration of chromium compounds in Austrian medicinal and table waters was determined as 1.2-4.2 μg/l (Sontag *et al.*, 1977). The average levels of chromium in three tributaries of the Han River in the Republic of Korea were found to be 96, 106 and 65 μg/l (Min, 1976).

Municipal sewage sludge can contain chromium at levels up to 30 000 mg per kg dry sludge (Pacyna & Nriagu, 1988).

Surface waters and groundwaters contaminated with wastewaters from electroplating operations, leather tanning and textile manufacturing, or through deposition of airborne chromium, may also be sources of chromium exposure. Other sources are solid wastes resulting from the roasting and leaching steps of chromate manufacture and improper disposal of municipal incineration wastes in landfill sites (Beszedits, 1988; Calder, 1988; Handa, 1988).

(*e*) *Soil and plants*

Chromium is present in the soil at levels which vary from traces to 250 mg/kg (as chromic[III] oxide) (Davis, 1956) and is particularly prevalent in soil derived from basalt or serpentine (US Environmental Protection Agency, 1984).

Virtually all plants contain detectable levels of chromium, taken up by the roots or through the leaves. Vegetables from 25 botanical families were found to contain chromium in amounts varying from 10-1000 μg/kg of dry matter, with most samples in the range of 100-500 μg/kg (Davis, 1956). Strong seasonal variations in chromium levels were found in three kinds of grass (World Health Organization, 1988).

The chromium content of mosses and liverworts collected in 1951 in a remote rural area in Denmark was compared with that in the same plants collected in 1975: an increase of about 62% was observed, which coincided with increases in industrial activity and fossil fuel combustion (Rasmussen, 1977).

The chromium content of cigarette tobacco from different sources has been reported as follows: Iraq, 8.6-14.6 mg/kg (two varieties); Iran, 4.3-6.2 mg/kg (two brands); and the USA, 0.24-6.3 mg/kg (Al Badri *et al.*, 1977).

(*f*) *Food*

The chromium content of most foods is extremely low; small amounts were found in vegetables (20-50 μg/kg), fruits (20 μg/kg) and grains and cereals (excluding fats, 40 μg/kg). The mean daily intakes of chromium from food, water and air have been estimated to be 280, 4 and 0.28 μg, respectively (Fishbein, 1976). Hartford (1979) indicated that nearly all foodstuffs contain chromium in the range of 20-590 μg/kg, resulting in a daily intake for humans of 10-400 μg, with an average of about 80 μg. In a more recent study, the mean daily intake of chromium for 22 healthy subjects was about 24.5 μg (Bunker *et al.*, 1984).

(*g*) *Animal tissues*

Table 16 summarizes data on chromium levels in tissues from various food and feral animals.

The report of the US National Status and Trends Program for Marine Environmental Quality, conducted by the National Oceanic and Atmospheric Administration (1987), gave concentrations of chromium at 0.1-11.0 μg/g (dry weight) in mussels and oysters collected in 1986 at East, West, and Gulf Coast sites, and 0.02-1.4 μg/g (dry weight) in livers of ten species of fish collected in 1984 throughout the USA.

Table 16. Chromium levels found in food and feral animals

Animal	Tissue	Range (mean) (μg/kg)	Comments	Reference
Largemouth bass	Muscle	1-2	Collected near Savannah River, SC, USA, nuclear plant	Koli & Whitmore (1983)
Bluegill		1		
Catfish		1		
Redbreast sunfish		1		
Crappie, American eel		2		
Spotted sunfish		1-2		
American shad	Gonad	ND-180	Collected in 1979, USA	Eisenberg & Topping (1986)
	Flesh	ND		
Finfish	Flesh	ND-1900	Collected in 1978-79	
Striped bass	Gonad	ND	Collected in 1978-79	
	Liver	ND	Collected in 1978-79	
	Flesh	ND	Collected in 1978-79	
Striped bass	Liver	2600-9800 (6000)	Collected from Chesapeake Bay, MD, USA	Heit (1979)
	Muscle	2700-9500 (5000)		
Cattle	Blood	(25/10)	Grazed on pasture treated/untreated with sludge (from Chicago, IL, USA)	Fitzgerald *et al.* (1985)
	Bone	(614/934)		
	Brain	(209/306)		
	Diaphragm	(206/215)		
	Heart	(172/434)		
	Kidney	(231/390)		
	Liver	(186/365)		
	Milk	(248/160)		
Cattle	Liver	200-3000		Stowe *et al.* (1985)
Cattle	Kidney	< 10-30	Collected from slaughter-houses in Queensland, Australia	Kramer *et al.* (1983)
	Liver	< 10-910 (10)		
	Muscle	< 10-100		
Cattle			Oklahoma, USA	Kerr & Edwards (1981)
	Blood	6-66 (22)	Unexposed animals	
		1080	Animal found dead near an oil-well drilling site	
	Kidney	500-6200 (2970)	Unexposed animals	
		15 800	Animal found dead near a recently completed oil well	

Table 16 (contd)

Animal	Tissue	Range (mean) (µg/kg)	Comments	Reference
Clam	Body	(2100-3800)	Collected from Lake Pontchartrain, LA, USA	Byrne & DeLeon (1986)
American oyster		(1300)		
Pike-perch	Body	10-20 (10)	The Netherlands Hollands Diep	Vos *et al.* (1986)
Cod		10-20 (10)	Collected near the coast	
Baltic herring		10-70 (20)		
Sole		10-20 (20)		
Eel		20-340 (80)	Collected from Lake Ijssel	
Pike-perch		10-70 (20)		
Blue mussel		210-810 (430)	Collected from Eastern Scheldt	
Shrimp		100-710 (260)	Collected from Western Wadden Sea	
Killifish	Body	(3600-7600)	Collected near electroplating industry, RI, USA	Custer *et al.* (1986)
Common tern	Liver	ND-18 310		
Cape oyster	Body	< 100-4600	Collected along the coast of South Africa	Watling & Watling (1982)
Sponge	Body	1 000 000-2 000 000 (1 520 000)	Collected near the Tarapur coast, India	Patel *et al.* (1985)
Snapping turtle	Kidney	(930-1260)	Collected from uncontaminated areas of MD, USA	Albers *et al.* (1986)
	Liver	(100-1970)		
	Kidney	(1130-2970)	Collected from contaminated areas of NJ, USA	
	Liver	(360-600)		
Crab	Body	40-200 (120)	Collected in sewage outfall area of the Arabian Gulf, Saudi Arabia	Sadiq *et al.* (1982)
Shrimp		29-133 (59)		
Pacific oyster	Body	(93 000, 113 000)	Collected from two culture beds in Deep Bay, Hong Kong	Wong *et al.* (1981)
	Gills	(40 000, 170 000)		
	Intestine	(42 000, 106 000)		
	Mantle	(47 000, 188 000)		
	Muscle	(35 000, 111 000)		

ND, none detected

(*h*) *Human tissues and secretions*

As with most metals that occur in trace quantities, the normal concentrations of chromium in human tissues are usually reported wrongly because of extraneous additions during sampling and analysis. However, recent developments in the analytical chemistry of chromium permit the reliable routine determination of nanogram quantities in biological samples (Nieboer & Jusys, 1988). Selected current reference values for chromium concentrations in a few biological materials are presented in Table 17.

Table 17. Chromium concentrations in specimens from non-occupationally exposed persons[a]

Sample	Median	Range
Serum	0.19 μg/l	0.12-2.1 μg/l
Blood	< 0.5 μg/l	-
Urine	0.4 μg/l	0.24-1.8 μg/l
Liver	[c]	8-72 ng/g wet weight
Lung[b]	204 ng/g wet weight	29-898 ng/g wet weight

[a] From Iyengar & Woittiez (1988), except when noted
[b] From Raithel *et al.* (1987)
[c] Too few measurements to determine median values

(*i*) *Regulatory status and guidelines*

The 1970 WHO European and 1978 Japanese standard for chromium[VI] in drinking-water (World Health Organization, 1970; Ministry of Health & Welfare, 1978) and the European standard for total chromium in surface water intended for the abstraction of drinking-water (Commission of the European Communities, 1975) are 0.05 mg/l. The US Environmental Protection Agency (1988) has established the same maximal contaminant level for chromium in drinking-water, as the maximal permissible level in water delivered to any user of a public water system.

The US Environmental Protection Agency (1979) also established pretreatment standards that limit the concentration of chromium that may be introduced into a publicly owned wastewater treatment facility by leather tanning and finishing plants. The maximal total chromium permitted in existing sources on any one day is 6 mg/l, and the average daily values for 30 consecutive days must not exceed 3 mg/l.

Table 18 gives occupational exposure limits for airborne chromium in various forms.

Table 18. Occupational exposure limits for airborne chromium in various forms[a]

Country or region	Year	Form of chromium	Concentration (mg/m³)	Interpretation[b]
Austria	1987	Cr, soluble compounds (as Cr)	0.1	TWA
Belgium	1987	Cr, compounds (as Cr)	0.05	TWA
		Cr, soluble compounds (as Cr)	0.1	TWA
Brazil	1987	Cr, compounds (as Cr)	0.04	TWA
Bulgaria	1987	Cr, compounds (as Cr)	0.1	TWA
Chile	1987	Cr, compounds (as Cr)	0.04	TWA
China	1987	Cr, compounds (as CrO_3), chromium trioxide, chromates, dichromates (as CrO_3)	0.5	TWA
Czechoslovakia	1987	Cr, compounds (as Cr)	0.05	Average
		Cr, compounds (as Cr)	0.1	Maximum
Denmark	1988	Cr and inorganic Cr compounds, except those mentioned below	0.5	TWA
		Chromates, chromium trioxide (as Cr)	0.02	TWA
Egypt	1987	Cr, compounds (as Cr)	0.1	TWA
Finland	1987	Cr, Cr[II] and Cr[III] compounds (as Cr)	0.5	TWA
		Cr[VI] compounds (as Cr)	0.05	TWA
France	1986	Cr[VI] and derivatives	0.05	TWA
German Democratic Republic	1987	Cr, compounds, except those mentioned below	0.5 1.0	TWA STEL
		Chromium trioxide, chromates, dichromates (as CrO_3)	0.1 0.1	TWA STEL
Hungary	1987	Cr, compounds (as Cr)	0.05 0.1	TWA STEL
India	1987	Cr, compounds (as Cr)	0.05	TWA
		Cr, soluble compounds (as Cr)	0.5	TWA
Indonesia	1987	Cr, compounds (as Cr)	0.1	TWA
Italy	1987	Cr, compounds (as Cr)	0.05	TWA
		Cr, soluble compounds (as Cr)	0.5	TWA
Japan	1987	Cr, compounds (as Cr)	0.1	TWA
Korea, Republic of	1987	Cr, compounds (as Cr)	0.05	TWA
Mexico	1987	Chromite ore (as Cr)	0.05	TWA
		Cr, compounds (as Cr); insoluble, soluble Cr[II], Cr[III], Cr[VI] compounds (as Cr)	0.5	TWA

Table 18 (contd)

Country or region	Year	Form of chromium	Concentration (mg/m^3)	Interpretation[b]
Netherlands	1986	Cr, soluble compounds (as Cr)	0.5	TWA
		Chromyl chloride	0.15	TWA
		Cr, insoluble compounds; chromium trioxide (as Cr)	0.05	TWA
Norway	1981	Cr, Cr[II] and Cr[III] compounds (as Cr)	0.5	TWA
		Chromates, chromium trioxide (as Cr)	0.02	TWA
Sweden	1987	Cr and inorganic Cr compounds, except those mentioned below	0.5	TWA
		Chromates, chromium trioxide (as Cr)	0.02	TWA
Switzerland	1987	Cr, compounds (as Cr); Cr, soluble compounds (as Cr)	0.5	TWA
		Cr[II] and Cr[III] soluble compounds; chromium oxychloride dust (as Cr)	0.05	TWA
Taiwan	1987	Cr and compounds (as Cr)	0.1	TWA
UK	1987	Cr, Cr[II] and Cr[III] compounds (as Cr)	0.5	TWA
		Cr[VI] compounds (as Cr)	0.05	TWA
USA[c]				
ACGIH	1988	Zinc chromates (as Cr)	0.01	TWA
		Chromite ore (chromate) (as Cr); water-soluble and certain (confirmed human carcinogens) water-insoluble Cr[VI] compounds (as Cr); lead chromate (as Cr)	0.05	TWA
		Chromium metal, Cr[II] and Cr[III] compounds (as Cr)	0.5	TWA
NIOSH	1988	Carcinogenic Cr[VI]	0.001	TWA
		Other Cr[VI]; chromic acid	0.025	TWA
		(as noncarcinogenic Cr[VI])	0.05	Ceiling (15 min)
OSHA	1987	Soluble chromium, chromic and chromous salts	0.5	TWA
		Chromium metal and insoluble salts	1.0	TWA
USSR	1987	Cr and compounds (as Cr)	0.01	MAC
		Chromium phosphate uni-substituted (as Cr[III])	0.02	MAC

Table 18 (contd)

Country or region	Year	Form of chromium	Concentration (mg/m^3)	Interpretation[b]
Yugoslavia	1987	Cr and compounds (as Cr)	0.1	TWA

[a] From Arbeidsinspectie (1986); Institut National de Recherche et de Sécurité (1986); Arbetarskyddsstyrelsens (1987); Cook (1987); Health and Safety Executive (1987); US Occupational Safety and Health Administration (1987); Työsuojeluhallitus (1987); American Conference of Governmental Industrial Hygienists (1988); Arbejdstilsynet (1988); National Institute for Occupational Safety and Health (1988)

[b] TWA, time-weighted average; STEL, short-term exposure limit; MAC, maximum allowable concentration

[c] ACGIH, American Conference of Governmental Industrial Hygienists; NIOSH, National Institute for Occupational Safety and Health; OSHA, Occupational Safety and Health Administration

2.4 Analysis

Numerous analytical methods have been developed for the qualitative and quantitative determination of chromium in a wide variety of matrices. Methods for analysing urban, industrial and work-place air, fresh water, sea-water, sewage effluents, sediments, soil, foodstuffs, crops, plants and biological materials such as human milk, blood, serum, urine and faeces and human and animal tissues, have been reviewed (National Research Council, 1974; Whitney & Risby, 1975; US Environmental Protection Agency, 1977, 1978; Slavin, 1981; Torgrimsen, 1982; Love, 1983; Nieboer *et al.*, 1984; US Environmental Protection Agency, 1984; O'Neill *et al.*, 1986; Harzdorf, 1987; Cornelis, 1988; World Health Organization, 1988).

Typical methods for the analysis of chromium are summarized in Table 19.

Most instrumental procedures are not specific for the oxidation states of chromium and are suitable for total chromium determinations only, unless accompanied by prior separations or supportive qualitative analyses. The reagent *sym*-diphenylcarbazide forms a violet complex with chromium[VI] but not with other chromium compounds, and the stability of the colour contributes to the high sensitivity of the analysis of soluble chromate in aerosols, water, cement and other materials. Interfering, reducing or oxidizing substances, if present in the sample, must be taken into account, since they tend to cause erroneous results during sampling, sample storage and preparation and spectrometric measurement (National Institute for Occupational Safety and Health, 1975). The chromium content of single particles can be determined by electron microscopy combined with X-ray microanalysis. Electron spectroscopy can be used to measure the valency state of chromium in thin surface layers of solid samples (Lautner *et al.*, 1978).

Table 19. Analytical methods for chromium and chromium compounds

Sample matrix	Sample preparation	Assay procedure[a]	Limit of detection[b]	Reference
Formulations				
Tanning liquors (trivalent chromium)	Oxidize to Cr[VI] (dichrmate) with ammonium persulfate (oxidant) and cupric sulfate-cobaltous nitrate mixture (catalyst)	IT	NR	Makarov-Zemlyanskii *et al.* (1978)
Pigments	Dissolve in hydrofluoric acid	EAAS	0.1 mg/kg	Kolihova *et al.* (1978)
Air				
Total chromium	Collect particulate sample on polystyrene filter; irradiate for 5 min at a flux of 2×10^{12} neutrons/ $cm^2 \times sec$; count with a Ge(Li) detector	NAA	0.02 μg	Dams *et al.* (1970)
Total chromium	Extract collection filter with mixture of hot hydrochloric and nitric acids; concentrate extraction liquid; hold overnight; dilute	AAS	NR	Smith *et al.* (1976)
Total chromium	Collect particulate sample on acetate fibre superfilter; use filter as thin target sample and bombard in a proton beam for 10 min	X-REA	0.01 μg	Li *et al.* (1979)
Total chromium	Collect particulate sample on 0.8 μm cellulose ester membrane; extract with hydrochloric and nitric acids; dilute	AAS	0.06 μg	National Institute for Occupational Safety and Health (1984a); Eller (1984) [Method 7024]
Total chromium	Extract collection filter with mixture of concentrated nitric and perchloric acids; evaporate to dryness; redissolve in dilute nitric/perchloric acid mixture	ICP/AES	1 μg	Eller (1984) [Method 7300]; O'Neill *et al.* (1986)

Table 19 (contd)

Sample matrix	Sample preparation	Assay procedure[a]	Limit of detection[b]	Reference
Total chromium	Collect particulate sample on cellulose nitrate membrane; extract with nitric acid; dilute	EAAS	0.09 μg	Kettrup *et al.* (1985)
Hexavalent chromium	Extract collection filter with 0.5 N sulfuric acid; filter to remove suspended dust; add *sym*-diphenylcarbazide	VIS	0.05 μg	Eller (1984) [Method 7600]; O'Neill *et al.* (1986)
Hexavalent chromium	Extract collection filter with hot 2% sodium hydroxide/3% sodium carbonate solution; add 6 N sulfuric acid and *sym*-diphenylcarbazide	VIS	0.05 μg	Eller (1984) [Method 7600]; O'Neill *et al.* (1986)
Hexavalent chromium	Collect particulate sample on 5.0-μm polyvinylchloride membrane; extract with sulfuric acid or with sodium hydroxide-sodium carbonate solution; add *sym*-diphenylcarbazide; measure absorption at 540 nm	VIS	0.05 μg	Abell & Carlberg (1974); Carelli *et al.* (1981); Bhargava *et al.* (1983); National Institute for Occupational Safety and Health (1984b)
Soluble chromium compounds	Collect aerosol sample compounds in sodium hydroxide solution with a midget impinger; oxidize Cr[III] compounds with bromine; add *sym*-diphenylcarbazide; measure absorption at 540 nm	VIS	2.3 μg/m^3	Kettrup *et al.* (1985)
Chromic acid	Collect aerosol sample on a cellulose ester membrane; chelate Cr[VI] with ammonium pyrrolidine dithiocarbamate; extract with methyl isobutyl ketone	EAAS	0.2 μg	National Institute for Occupational Safety and Health (1973)

Table 19 (contd)

Sample matrix	Sample preparation	Assay procedure[a]	Limit of detection[b]	Reference
Water				
Wastewaters	–	PP		Heigl (1978)
Total chromium			0.04 mg/l	
Hexavalent chromium			0.01 mg/l	
River water	Separate suspended particles by centrifugation; add diethyldithiocarbamate; filter through acetate superfilter; use filter as thin target sample and bombard in a proton beam for 10 min	X-REA	NR	Li *et al.* (1979)
Seawater Hexavalent and total chromium	Extract with ammonium pyrrolidine dithiocarbamate into chloroform at pH 2	IDMS	0.001 μg/l	Osaki *et al.* (1976)
Hexavalent and trivalent chromium, selective	Extract hexavalent chromium with Aliquat-336 (a mixture of methyl tri-*n*-alkyl ammonium chlorides) at pH 2; extract trivalent chromium by adding thiocyanate to at least 1M; adjust pH to 6-8	EAAS	0.01 μg/l [VI] 0.03 μg/l [III]	de Jong & Brinkman (1978)
Drinking-water, surface water, groundwater, domestic and industrial wastewaters Total chromium	Various acidification/evaporation/dilution steps, depending on specific matrix and method	AAS	0.05 mg/l	US Environmental Protection Agency (1983, 1986) [Methods 218.1, 218.3, 3005, 3010, 7190]
		ICP/AES	7 μg/l	[Methods 200.7, 6010]
		EAAS	1 μg/l	[Methods 218.2, 3020, 7191]
Hexavalent chromium	Acidify to pH 3.5 with acetic acid; add lead nitrate, glacial acetic acid and ammonium sulfate; centrifuge and discard supernatant; dissolve precipitate in concentrated nitric acid	EAAS	2 μg/l	US Environmental Protection Agency (1983, 1986) [Methods 218.5, 7195]

Table 19 (contd)

Sample matrix	Sample preparation	Assay procedure[a]	Limit of detection[b]	Reference
Hexavalent chromium	Chelate with ammonium pyrrolidine dithiocarbamate or pyrrolidine dithiocarbamic acid in chloroform; extract with methyl isobutyl ketone	AAS	NR	US Environmental Protection Agency (1983, 1986) [Methods 218.4, 7197]
Hexavalent chromium	Use ammonium hydroxide/ammonium chloride as supporting electrolyte	DPP	10 μg/l	US Environmental Protection Agency (1986) [Method 7198]
Hexavalent chromium	Remove interfering metals by adding aluminium sulfate; filter; add sodium hypochlorite solution; add phosphoric acid solution and sodium chloride; add *sym*-diphenylcarbazide	VIS	NR	Deutsches Institut für Normung (1987) [DIN 38405]; (see also US Environmental Protection Agency (1986) [Method 7196]
Oily waste samples: oils, greases, waxes, crude oil (soluble chromium)	Dissolve in xylene or methyl isobutyl ketone	AAS	0.05 mg/l	US Environmental Protection Agency (1986) [Methods 3040, 7190]
		ICP	7 μg/l	[Method 6010]
Sediments, sludges, soils and solid wastes (total chromium)	Digest with nitric acid and hydrogen peroxide; dilute with dilute hydrochloric or nitric acid	AAS	0.05 mg/l	US Environmental Protection Agency (1986) [Methods 3050, 7190]
		ICP	7 μg/l	[Method 6010]
		EAAS	1 μg/l	[Methods 3050, 7191]
Sediments	Activate with neutrons for 6 h	NAA	1.5 mg/kg	Ackermann (1977)
Food				
Tinned foods	Oxidize to hexavalent chromium with hydrogen peroxide; treat with *sym*-diphenylcarbazide	VIS	0.05 mg/kg	Il'inykh (1977)

Table 19 (contd)

Sample matrix	Sample preparation	Assay procedure[a]	Limit of detection[b]	Reference
Biological samples				
SRM 1569 brewers' yeast; SRM 1577 bovine liver; SRM 1570 spinach; human hair and nails	Chemical procedures developed for digestion of biological matrices and separation of chromium without large analytical blanks or significant losses by volatilization	IDMS	1 μg	Dunstan & Garner (1977)
Blood, plasma, urine	Dilute with Triton X100 solution; standard addition method	EAAS	NR	Morris *et al.* (1989)
Tissue	Digest sample with nitric and sulfuric acids with a defined time-temperature programme; dilute with water; standard addition method	EAAS	0.3 μg/g wet wt	Raithel *et al.* (1987)
Serum	–	NAA	NR	Versieck *et al.* (1978)
Serum, human milk, urine	Dilute with water	EAAS	0.05 ng/ml (urine, serum) 0.1 ng/ml (milk)	Kumpulainen *et al.* (1983)
Blood or tissue	Digest with mixture of nitric, perchloric and sulfuric acids; heat for 4-5 h; cool; dilute with deionized water or add yttrium internal standard	ICP/AES	0.01 μg/g blood 0.2 μg/g tissue	Eller (1985) [Method 8005]
Blood erythrocytes	Wash with isotonic saline; dilute with Triton X100 solution	EAAS	1 μg/l	Lewalter *et al.* (1985)
Human urine Total chromium	Adjust pH to 2.0 with sodium hydroxide; add polydithiocarbamate resin; filter, saving filtrate and resin; adjust filtrate to pH 8.0 and add more resin; ash filters and resins; add nitric/perchloric acid mixture and warm	ICP/AES	0.1 μg	Eller (1984) [Method 8310]

Table 19 (contd)

Sample matrix	Sample preparation	Assay procedure[a]	Limit of detection[b]	Reference
Total chromium	Dilute and acidify with nitric acid	EAAS	0.1-0.5 μg/l	Nise & Vesterberg (1979); Kiilunen *et al.* (1987); Angerer & Schaller (1988)
Plant materials	Dry in an oven at 120°C for 2-4 h; ash in a muffle furnace at 550°C for 6 h	ES	2 mg/kg	Dixit *et al.* (1976)
Airborne chromium				
Welding fumes Hexavalent chromium	Extract with sodium carbonate; remove precipitate by filtration; add *sym*-diphenylcarbazide; measure absorption at 540 nm	EAAS	0.8 μg	Thomsen & Stern (1979)
Total and hexavalent chromium	Extract with sodium hydroxide and carbonate or fuse with sodium carbonate; remove precipitate by filtration; acidify with sulfuric acid; add *sym*-diphenylcarbazide; measure absorption at 540 nm	VIS	1 μg/m³	Moreton *et al.* (1983)
Hexavalent and trivalent chromium	Collect on polycarbonate membranes	ESCA, NAA	0.001 μg	Lautner *et al.* (1978)
Total, hexavalent and trivalent chromium	Collect on cellulose ester membranes	PIXE, ESCA, TEM, EDXA	0.0001-0.01 μg	Bohgard *et al.* (1979)
Welding fumes; complex matrices with redox systems				
Insoluble and total hexavalent chromium	Add sodium carbonate; warm; remove precipitate by filtration	AAS	1 μg/m³	Thomsen & Stern (1979)
Total chromium	Add phosphoric acid:sulfuric acid (3:1)	AAS	1 μg/m³	Pedersen *et al.* (1987)
Welding and brazing fumes	Sample on cellulose ester membrane filter; load sample and irradiate	XRF	2 μg	Eller (1984) [Method 7200]

Table 19 (contd)

Sample matrix	Sample preparation	Assay procedure[a]	Limit of detection[b]	Reference
Cement (hexavalent chromium)	Extract with water; add ammonium acetate and ethylene diamine	DPP	0.3 μg/g	Vandenbalck & Patriarche (1987)
Grinding dusts	Collect particulate sample on polycarbonate membrane	SEM, EDXA	NR	Koponen (1985)
Paint aerosols (hexavalent chromium)	Extract with a sodium hydroxide—sodium carbonate solution; dilute with buffer solution	IC	0.003 μg	Molina & Abell (1987)

[a] Abbreviations: IT, iodometric titration; EAAS, electrothermal atomic absorption spectrometry; NAA, neutron activation analysis; AAS, atomic adsorption spectrometry; X-REA, X-ray emission analysis; ICP/AES, inductively coupled argon/plasma/atomic emission spectroscopy; VIS, visible absorption spectrometry; PP, pulse polarography; IDMS, isotope dilution mass spectrometry; DPP, differential pulse polarography; ES, emission spectrography; ESCA, electron spectroscopy for chemical analysis; PIXE, proton induced X-ray emission; TEM, transmission electron microscopy; EDXA, energy dispersive X-ray analysis; XRF, X-ray fluorescence; SEM, scanning electron microscopy; IC, ion chromatography

[b] NR, not reported

The American Society for Testing and Materials (ASTM) has established standard methods for determining the chromium (or chromium compound) content of various commercial products. These include methods for the chemical analysis of chromium-containing refractory materials and chromium ore (ASTM C572-81), for chromium in water (ASTM D1687-86), for strontium chromate pigment (ASTM D1845-86) and for chromic oxide in leather that has been partly or completely tanned with chromium compounds (ASTM D2807-78); a colorimetric method for the determination of soluble chromium (trivalent and hexavalent chromium) in workplace atmospheres (ASTM D3586-85); methods for the determination of chromium (including chromium oxide) in the solids of liquid coatings (paint) or in dried films obtained from previously coated substrates (ASTM D3718-85a), for chromium in residues obtained by air sampling of dusts of lead chromate and lead silicochromate-type pigments (ASTM D4358-84), for chromium and ferrochromium (ASTM E363-83), for chromium oxide in chromium ores (ASTM E342-71), for yellow, orange and green pigments containing lead chromate and chromium oxide green (ASTM D126-87) and for zinc yellow pigment (zinc chromate yellow) (ASTM D444-88) (American Society for Testing and Materials, 1971, 1978, 1981, 1983, 1984b, 1985a,b, 1986a,b, 1987c, 1988b).