BERYLLIUM AND BERYLLIUM COMPOUNDS

Beryllium and beryllium compounds were considered by previous Working Groups, in 1971, 1979 and 1987 (IARC, 1972, 1980, 1987a). New data have since become available, and these are included in the present monograph and have been taken into consideration in the evaluation. The agents considered herein include (a) metallic beryllium, (b) beryllium–aluminium and –copper alloys and (c) some beryllium compounds.

1. Exposure Data

1.1 Chemical and physical data and analysis

1.1.1 *Synonyms, trade names and molecular formulae*

Synonyms, trade names and molecular formulae for beryllium, beryllium–aluminium and –copper alloys and certain beryllium compounds are presented in Table 1. The list is not exhaustive, nor does it comprise necessarily the most commercially important beryllium-containing substances; rather, it indicates the range of beryllium compounds available.

1.1.2 *Chemical and physical properties of the pure substances*

Selected chemical and physical properties of beryllium, beryllium–aluminium and –copper alloys and the beryllium compounds covered in this monograph are presented in Table 2.

The French chemist Vauquelin discovered beryllium in 1798 as the oxide, while analysing emerald to prove an analogous composition (Newland, 1984). The metallic element was first isolated in independent experiments by Wöhler (1828) and Bussy (1828), who called it 'glucinium' owing to the sweet taste of its salts; that name is still used in the French chemical literature. Wöhler's name 'beryllium' was officially recognized by IUPAC in 1957 (WHO, 1990). The atomic weight and common valence of beryllium were originally the subject of much controversy but were correctly predicted by Mendeleev to be 9 and +2, respectively (Everest, 1973).

Beryllium is the lightest of all solid, chemically stable substances and has an unusually high melting-point. It has a very low density and a very high strength-to-weight ratio. Beryllium is lighter than aluminium but is more than 40% more rigid than steel. It has excellent electrical and thermal conductivities. Its only markedly adverse feature is relatively pronounced brittleness, which has restricted the use of metallic beryllium to specialized applications (WHO, 1990).

Table 1. Synonyms (Chemical Abstracts Service (CAS) names are in italics), trade names and atomic or molecular formulae of beryllium and beryllium compounds

Chemical name	CAS Reg. No.[a]	Synonyms and trade names	Formula
Beryllium metal	7440-41-7	*Beryllium*; beryllium-9; beryllium element; beryllium metallic; glucinium; glucinum	Be
Beryllium–aluminium alloy[b]	12770-50-2	*Aluminium alloy, nonbase, Al,Be*; aluminium–beryllium alloy	Al.Be
Beryllium–copper alloy[c]	11133-98-5	*Copper alloy, base, Cu,Be*; copper–beryllium alloy	Be.Cu
Beryl	1302-52-9	Beryllium aluminosilicate; beryllium aluminium silicate	$Al_2Be_3(SiO_3)_6$
Beryllium chloride	7787-47-5	Beryllium dichloride	$BeCl_2$
Beryllium fluoride	7787-49-7 (12323-05-6)	Beryllium difluoride	BeF_2
Beryllium hydroxide	13327-32-7 (1304-49-0)	Beryllium dihydroxide	$Be(OH)_2$
Beryllium sulfate	13510-49-1	*Sulfuric acid, beryllium salt (1:1)*	$BeSO_4$
Beryllium sulfate tetrahydrate	7787-56-6	*Sulfuric acid, beryllium salt (1:1), tetrahydrate*	$BeSO_4.4H_2O$
Beryllium oxide	1304-56-9	Beryllia; beryllium monoxide Thermalox™	BeO
Beryllium carbonate basic[d]	1319-43-3	*Carbonic acid, beryllium salt, mixture with beryllium hydroxide* *($Be(OH)_2$)*	$BeCO_3.Be(OH)_2$
Beryllium nitrate	13597-99-4	Beryllium dinitrate; *nitric acid*, beryllium salt	$Be(NO_3)_2$
Beryllium nitrate trihydrate	7787-55-5	*Nitric acid, beryllium salt, trihydrate*	$Be(NO_3)_2.3H_2O$
Beryllium nitrate tetrahydrate	13510-48-0	Beryllium dinitrate tetrahydrate; *nitric acid, beryllium salt, tetrahydrate*	$Be(NO_3)_2.4H_2O$
Beryllium phosphate	13598-15-7	*Phosphoric acid, beryllium salt (1:1)*	$BeHPO_4$
Beryllium silicate[e]	13598-00-0	Phenazite; *phenakite*	$Be_2(SiO_4)$
Zinc beryllium silicate	39413-47-3 (63089-82-7)	*Silicic acid, beryllium zinc salt*	Unspecified

[a] Replaced CAS Registry numbers are shown in parentheses.

[b] Related compound registered by CAS is beryllium alloy, base, Be,Al historically (Lockalloy), Al (24–44%).Be (56–76%) [12604-81-8; replaced Registry No., 12665-28-0]; 60 beryllium–aluminium alloys are registered with CAS numbers, with different percentages of the two elements.

[c] Related compound registered by CAS is beryllium alloy, base, Be,Cu [39348-30-6]; 111 beryllium–copper alloys are registered with CAS numbers, with different percentages of the two elements.

[d] CAS name and Registry number shown were selected as being closest to the formula given by Lide (1991). Related compounds registered by CAS are: bis[carbonato(2)]dihydroxytriberyllium, $(BeCO_3)_2.Be(OH)_2$ [66104-24-3]; carbonic acid, beryllium salt (1:1), tetra-hydrate, $BeCO_3.4H_2O$ [60883-64-9]; carbonic acid, beryllium salt (1:1), $BeCO_3$ [13106-47-3]; and bis[carbonato(2-)]oxodiberyllium, $(CO_3)_2Be_2O$ [66104-25-4].

[e] Related compounds registered by CAS are: bertrandite, $Be_4(OH)_2O(SiO_3)_2$ [12161-82-9]; beryllium silicate, formula unspecified [58500-38-2]; silicic acid (H_2SiO_3), beryllium salt (1:1), $Be(SiO_3)$ [14902-94-4]; silicic acid (H_4SiO_4), beryllium salt (1:2), $Be_2(SiO_4)$ [15191-85-2]

Table 2. Physical properties of pure beryllium and beryllium compounds

Chemical name	Relative atomic/ molecular mass	Melting-point (°C)	Typical physical description	Density (g/cm^3)	Solubility
Beryllium metal	9.0122	1287	Grey, close-packed, hexagonal, brittle metal	1.85 (20 °C)	Soluble in most dilute acids and alkali; decomposes in hot water; insoluble in mercury and cold water
Beryllium chloride	79.92	399.2	Colourless to slightly yellow, orthorhombic, deliquescent crystal	1.899 (25 °C)	Soluble in water, ethanol, diethyl ether and pyridine; slightly soluble in benzene, carbon disulfide and chloroform; insoluble in acetone, ammonia and toluene
Beryllium fluoride	47.01	555	Colourless or white, amorphous, hygroscopic solid	1.986	Soluble in water, sulfuric acid, mixture of ethanol and diethyl ether; slightly soluble in ethanol; insoluble in hydrofluoric acid
Beryllium hydroxide	43.03	138 (dec.[a])	White, amorphous, amphoteric powder	1.92	Soluble in hot concentrated acids and alkali; slightly soluble in dilute alkali; insoluble in water
Beryllium sulfate	105.07	550 (dec.)	Colourless crystal	2.443	Forms soluble tetrahydrate in hot water; insoluble in cold water
Beryllium sulfate tetrahydrate	177.14	NR	Colourless, tetragonal crystal	1.713	Soluble in water; slightly soluble in concentrated sulfuric acid; insoluble in ethanol
Beryllium oxide	25.01	2530	Colourless to white, hexagonal crystal or amorphous, amphoteric powder	3.01 (20 °C)	Soluble in concentrated acids and alkali; insoluble in water
Beryllium carbonate	69.02	NR	NR	NR	Soluble in acids and alkali; insoluble in cold water; decomposes in hot water
Beryllium carbonate, basic	112.05	NR	White powder		Soluble in acids and alkali; insoluble in cold water; decomposes in hot water
Beryllium nitrate, trihydrate	187.97	60	White to faintly yellowish, deliquescent mass	1.56	Very soluble in water and ethanol
Beryllium phosphate	104.99	NR	NR	NR	Slightly soluble in water

Table 2 (contd)

Chemical name	Relative atomic/ molecular mass	Melting-point (°C)	Typical physical description	Density (g/cm^3)	Solubility
Beryllium silicate	110.11	NR	Triclinic, colourless crystal	3.0	Insoluble in acids
Zinc beryllium silicate	Unspecified	NR	Crystalline solid	NR	NR

From Ballance *et al.* (1978); Walsh & Rees (1978); IARC (1980); Sax & Lewis (1987); Lewis (1988); Budavari (1989); Lide (1991); Aldrich Chemical Co. (1992). NR, not reported; dec., decomposes

[a] Decomposes to beryllium oxide (Sax & Lewis, 1987).

Natural beryllium is 100% ^{9}Be isotope; four unstable isotopes with mass numbers of 6, 7, 8 and 10 have been made artificially. Because of its low atomic number, beryllium is very permeable to X-rays. Neutron emission after bombardment with α or γ rays is the most important of its nuclear physical properties, and beryllium can be used as a neutron source. Moreover, its low neutron absorptiveness and high-scattering cross-section make it a suitable moderator and reflector in structural materials in nuclear facilities; while most other metals absorb neutrons emitted during the fission of nuclear fuel, beryllium atoms only reduce the energy of such neutrons and reflect them back into the fission zone (Ballance *et al.*, 1978; Newland, 1984; WHO, 1990).

The chemical properties of beryllium differ considerably from those of the other alkaline earths, but it has a number of chemical properties in common with aluminium. Like aluminium, beryllium is amphoteric and shows very high affinity for oxygen; on exposure to air or water vapour, a thin film of beryllium oxide forms on the surface of the bare metal, rendering the metal highly resistant to corrosion, to hot and cold water and to oxidizing acids. Dichromate in water enhances this resistance by forming a protective film of chromate, similar to that formed on aluminium. In powder form, beryllium is readily oxidized in moist air and burns with a temperature of about 4500 °C when ignited in oxygen (Newland, 1984; Petzow *et al.*, 1985; WHO, 1990).

Cationic beryllium salts are hydrolysed in water; they form insoluble hydroxides or hydrated complexes at pH values between 5 and 8 and form beryllates above a pH of 8 (Reeves, 1986).

1.1.3 *Technical products and impurities*

Beryllium metal—purities: technical or nuclear grade, 98–> 99.5%; Grade A, 99.87%; Grade AA, 99.96%; distilled grade, > 99.99%; forms: single crystals, flakes, powders, plates, sheets, foils, wires, rods (Sax & Lewis, 1987; Alfa Products, 1990; CERAC, Inc., 1991; Aldrich Chemical Co., 1992; Atomergic Chemetals Corp., undated; D.F. Goldsmith Chemical & Metal Corp., undated); impurities vary with the production method (see section 1.2.1 and Tables 5 and 6).

Beryllium–aluminium alloy—composition limits for one alloy (%): Be, 4.5–6.0; Si, 0.2; Fe, 0.2; Mg, 0.5, Mn, 0.02; Cr, 0.02; Ni, 0.02; Ti, 0.02; Zn, 0.1; Cu, 0.05 (KBAlloys, 1985)

Beryllium–copper alloy—composition limits for one alloy (Alloy 20C or C82500) (%): Be, 2.0–2.25; Co, 0.35–0.65; total unnamed elements, 0.5 max; Cu, remainder (Stonehouse & Zenczak, 1991)

Beryllium chloride—purities: 97–99.5%; impurities (mg/kg): Al, 50; Fe, 100; Si, 30; Cd, 10; Ni, 120; Cu, 10; Co, 10; Zn, 10; Cr, 10; Mn, 10; Mg, 150 (Kawecki Berylco Industries, 1968; Alfa Products, 1990; CERAC, Inc., 1991; Strem Chemicals, 1992; Fluka Chemie AG, 1993)

Beryllium fluoride—purity: 99.5%; impurities (mg/kg): Al, 75; Fe, 75; Ni, 40; Cu, 10 (Kawecki Berylco Industries, 1968; CERAC, Inc., 1991; D.F. Goldsmith Chemical & Metal Corp., undated)

Beryllium hydroxide—contains different levels of several impurities depending on whether it is made from beryl ore or bertrandite ore (IARC, 1980)

Beryllium sulfate tetrahydrate—purities: 98.3–99.99%; impurities (%): chloride, Ca, Cd, Co, Cu, Fe, Ni, Pb and Zn, all < 0.005; K, Na, < 0.01 (Alfa Products, 1990; Aldrich Chemical Co., 1992; Fluka Chemie AG, 1993)

Beryllium oxide—purities: 99–99.99% (Alfa Products, 1990; CERAC, Inc., 1991; Aldrich Chemical Co., 1992; Strem Chemicals, 1992). The purity of beryllia is critical to its thermal conductivity: as the purity drops below 99.5%, thermal conductivity drops off rapidly. Impurities (mg/kg): Al, 46; Fe, 32; Cr, 8; Mn, < 2; Ni, 9; B, 2; Ca, 31; Co, < 1; Cu, 3; Si, 1861; Mg, 922; Li, 2; Zn, < 20; Ti, 5; Na, 173; Ag, < 1; Mo, < 3; Pb, 2. Silicon and magnesium silicates are added to beryllia powder as sintering aids (Brush Wellman, undated)

Beryllium carbonate—impurities (mg/kg): Al, 30; Fe, 100; Si, 150 (IARC, 1980)

Beryllium nitrate (trihydrate)—purity: 99.5% (D.F. Goldsmith Chemical & Metal Corp., undated); impurities (mg/kg): Al, 20; Fe, 30; Si, 50; Na, 20 (Kawecki Berylco Industries, 1968)

Impurities that occur in beryllium compounds that have been the subjects of previous monographs are: cadmium (IARC, 1987b), chromium (IARC, 1990a), cobalt (IARC, 1991), lead (IARC, 1987c), nickel (IARC, 1990b) and silica (IARC, 1987d).

1.1.4 *Analysis*

Beryllium metal

Selected methods for the determination of beryllium and beryllium compounds in various media are presented in Table 3. Other methods have been reviewed (IARC, 1980; Agency for Toxic Substances and Disease Registry, 1988; WHO, 1990).

Table 3. Methods for the analysis of beryllium and beryllium compounds (as Be)

Sample matrix	Sample preparation	Assay procedure	Limit of detection	Reference
Air[a]	Collect on membrane filter; dissolve in nitric acid	FLAA	0.08 μg/m^3; 0.002 μg/ml	Kleinman *et al.* (1989a)
	Collect sample on cellulose ester membrane filter; add nitric and sulfuric acids; heat; cool; evaporate to dryness; add sodium sulfate/sulfuric acid solution; heat	GFAA	0.005 μg/sample	Eller (1987) (Method 7102)
	Collect sample on cellulose ester membrane filter; ash with nitric:perchloric acid solution (4:1) v:v; heat; repeat; heat to dryness; dilute with nitric:perchloric acid solution (4:1)	ICP	1 μg/sample	Eller (1984) (Method 7300)
Water, ground- and surface	Acidify with nitric and hydrochloric acids (Method 3005)	FLAA ICP (313 nm)	0.005 mg/L 0.3 μg/L	US Environmental Protection Agency (1986a) (Method 6010)

Table 3 (contd)

Sample matrix	Sample preparation	Assay procedure	Limit of detection	Reference
Aqueous samples, extracts, wastes	Acidify with nitric acid; heat and evaporate to low volume; cool; add nitric acid; reheat and reflux with hydrochloric acid (Method 3010)	FLAA ICP (313 nm)	0.005 mg/L 0.3 μg/L	US Environmental Protection Agency (1986a,b) (Methods 6010 and 7090)
Oils, greases, waxes (organic extract)	Dissolve in xylene or methyl isobutyl ketone (Method 3040)	FLAA ICP (313 nm)	0.005 mg/L 0.3 μg/L	US Environmental Protection Agency (1986a) (Method 6010)
Sediments, sludges, soils	Digest with nitric acid and hydrogen peroxide; reflux with hydrochloric acid (Method 3050)	FLAA ICP (313 nm)	0.005 mg/L 0.3 μg/L	US Environmental Protection Agency (1986a) (Method 6010)
Aqueous samples, extracts, wastes	Acidify with nitric acid; evaporate to low volume; cool; add nitric acid; heat to complete digestion (Method 3020)	GFAA	0.2 μg/L	US Environmental Protection Agency (1986a,c) (Method 7091)
Sediments, sludges, soils	Digest with nitric acid and hydrogen peroxide; reflux with nitric acid (Method 3050)	GFAA	0.2 μg/L	US Environmental Protection Agency (1986a,c) (Method 7091)
Tissue samples	Ash in hot concentrated nitric acid	FLAA	2 μg/L	Kleinman *et al.* (1989b)
Urine	Inject untreated samples directly into a pretreated graphite tube; follow standard addition method	GFAA	0.5 μg/L	Angerer & Schaller (1985)
	Modify matrix with magnesium nitrate; follow platform technique	GFAA	0.05 μg/L	Paschal & Bailey (1986)

FLAA, flame atomic absorption spectrometry; GFAA, graphite furnace atomic absorption spectrometry; ICP, inductively coupled argon plasma emission spectrometry

[a][Digestion with a solution of nitric acid:perchloric acid:sulfuric acid and addition of several drops of hydrofluoric acid are currently recommended in sample preparation. Detection limits can be reduced to 0.001 μg/ml and sensitivity to 0.0001 μg/ml.]

Methods used up to the 1960s included spectroscopic, fluorometric, gamma activation, spectrophotometric and automatic titrimetric techniques (Ballance *et al.*, 1978). The main deficiency of spectrophotometric methods lies in the nonspecificity of the complexing agents used to form coloured complexes with beryllium. The limit of detection of these methods was about 100 ng/sample. The fluorimetric method, which is based on fluorescent dyes (preferably morin), has a very low limit of detection, 0.02 ng/sample; its sensitivity is exceeded only by that of the gas chromatographic method. The fluorimetric method may, however, be subject to error unless several time-consuming, cumbersome processing steps are undertaken prior to analysis (WHO, 1990).

Atomic absorption spectrometry is a rapid, very convenient method for analysing biological and environmental samples. The limit of detection for the flame technique is 2–10 µg/L and lower when the sample is concentrated before analysis (WHO, 1990). The graphite furnace method is much more sensitive, with a detection limit of approximately 0.1 µg/L. Blood, urine and tissue samples can be analysed by this technique with or without digestion of the biological matrix (see Table 3).

Inductively coupled plasma atomic emission spectrometry has been introduced to determine beryllium directly in a variety of biological and environmental matrices, because of its high sensitivity and low level of interference. Owing to its high sensitivity and specificity, gas chromatography is also used for determining beryllium in environmental and biological media, particularly at ultratrace levels. Beryllium can be converted into a volatile form by chelation with trifluoroacetylacetone before injection into the chromatographic column (WHO, 1990).

1.2 Production and use

1.2.1 *Production*

More than 40 beryllium-bearing minerals are known, but only two are of economic significance. The first beryllium mineral to be exploited commercially was beryl ($3BeO.Al_2O_3.6SiO_2$), an aluminosilicate (WHO, 1990). The largest deposits of beryl are found in Brazil and the former USSR (Petkof, 1982; Stonehouse & Zenczak, 1991). Beryl ore contains about 11% beryllium oxide (up to 4% beryllium) and is often obtained as a by-product of feldspar quarrying (for typical ore composition, see Table 17). In addition to the other major components, aluminium oxide and silicon dioxide, the principal impurities in the ores include alkali metals, alkaline-earth metals, iron, manganese and phosphorus. In its purest gem quality, it occurs as emerald (chromium-containing beryl), aquamarine (iron-containing beryl) and some other semiprecious stones (Petzow *et al.*, 1985; WHO, 1990).

The other mineral of economic significance, bertrandite ($4BeO.2SiO_2.H_2O$), is a beryllium silicate hydrate. Although bertrandite ore contains less than 1% beryllium, it became economically important in the late 1960s because it can be processed to beryllium hydroxide highly efficiently. Bertrandite mined in the USA accounts for about 85% of US consumption of beryllium ore. The total world reserves of beryllium that can be recovered by mining bertrandite are estimated at 200 000 tonnes (Petzow *et al.*, 1985; WHO, 1990).

Known deposits of other beryllium-containing minerals are being studied for possible commercialization. Most notable among these are phenakite ($2BeO.SiO_2$) at Yellowknife, Northwest Territory, Canada, the chrysoberyl ($BeO.Al_2O_3$) deposits of the Seward Peninsula, Alaska, and the Sierra Blanca deposits near El Paso, Texas, USA (Stonehouse & Zenczak, 1991).

Beryllium production started in some industrialized countries around 1916. Beryllium gained commercial importance in the early 1930s, following the realization that beryllium–copper alloys are extraordinarily hard, resistant to corrosion, non-magnetic, do not spark and withstand high temperatures. In addition, the nuclear and thermal properties and high specific modulus of beryllium metal made it attractive for nuclear and aerospace applications, including weapons. The latter use is the main reason why reliable data on the production and consumption of beryllium have been scarce and incomplete. Considerable fluctuations in the supply and demand of beryllium result from variations in government programmes in armaments, nuclear energy and aerospace. For example, the demand for beryllium in the USA that was created by the programme for development of the atomic bomb was about equivalent to total world demand up to 1940 (WHO, 1990).

Production in the rest of the world paralleled those fluctuations in the beryllium market, with 222 tonnes produced in 1965, 320 tonnes in 1969 and 144 tonnes in 1974. Data on US production are now available, and world production of beryllium as beryl is shown in Table 4. If production from bertrandite is included, the USA appears to be the world's largest producer of beryllium raw materials (WHO, 1990).

(*a*) *Processing of beryl and bertrandite*

The first step in the processing of beryl ore is normally hand-sorting to select beryl crystals containing at least 10% beryllium oxide (Ballance *et al.*, 1978) on the basis of shape and colour (Powers, 1991).

Two commercial methods have been used to process beryl to beryllium hydroxide: the fluoride process and the sulfate process. In the *fluoride process*, which was discontinued in the 1970s, beryl was sintered together with sodium hexafluorosilicate, or the less expensive sodium fluoroferrate, at 700–800 °C to convert beryllium oxide to a water-soluble salt, sodium beryllium tetrafluoride (Na_2BeF_4). The reaction product was then leached with water at room temperature and precipitated from the purified solution with caustic soda as beryllium hydroxide (Petzow *et al.*, 1985; WHO, 1990).

The *sulfate process*, the only process currently used, involves either alkali or heat treatment of beryl. With alkali treatment, which was discontinued in the 1960s, finely ground beryl was heated until fusion or sintered below the melting-point with suitable alkalis, such as hydroxides and carbonates of sodium, potassium and calcium. With heat treatment, which has been used since the 1970s, beryl is melted without additives and quenched with water; the water insoluble portion, a solid solution with silicon dioxide, is reheated to 900 °C to render a total of 90–95% of the beryl soluble. Heat-treated or alkali-treated beryl is then extracted with sulfuric acid and carried through several additional purification steps to produce a fine-grained, readily filtered beryllium hydroxide (Petzow *et al.*, 1985; WHO, 1990).

The beryllium-poor bertrandite ores ($\leq$ 0.5–0.8% BeO) mined in the USA since 1960 cannot be smelted economically by conventional methods, and a less complicated procedure has been developed in which a very pure beryllium hydroxide is produced by liquid–liquid extraction. This so-called 'SX-carbonate process' involves direct leaching of bertrandite ore with sulfuric acid, extraction of the sulfuric acid leachate with di(2-ethylhexyl)phosphoric acid in kerosene, stripping of beryllium from the organic phase with aqueous ammonium carbonate, and, through a series of heat, hydrolysis and precipitation steps, production of beryllium hydroxide (Petzow *et al.*, 1985; WHO, 1990). Beryllium hydroxide is the starting material for the production of beryllium, beryllia and beryllium alloys. For further processing, it is ignited to form the oxide (BeO) or converted to the fluoride (BeF_2) (WHO, 1990).

Table 4. World production of beryl (tonnes)

Country	1980	1981	1982	1983	1984	1986	1987	1988	1989	1990	1991[a]
Argentina	31	7	6	24[b]	15[a]	50	46	39	89[c]	85[a]	80
Brazil[d]	550	854[c]	1062	1252[a,c]	1252	907[c]	1000	913	800	850[a]	850
Madagascar	10	10	10	10	10	50 kg	35 kg	3 kg	154 kg	150 kg[c]	3
Mozambique	20	18	15	15[a]	15	1	ND	ND	ND	ND	ND
Portugal	19	18	19	18	18	ND	4	4	4	4	4
Rwanda	108	59	69	33	36	ND	ND	ND	ND	ND	ND
Republic of South Africa	ND	122	58	22	ND	3	135 kg	72 kg	ND	1[c]	1
Russia[a]	1800	1800	1800	1900	1900	1900	2000	2000	2000	1600	1300
USA[e]	6756[c]	6653[c]	4945	6046	5470[c]	5927	5499	5313	4592	4548	4339[c]
Zimbabwe	9	42	52	50[a]	50	103	83	33	46	28[c]	30
World[f]	9319	9597	8051	9375	8772	8891	8632	8302	7532	7119	6607

From Kramer (1985a, 1991a, 1992a) [some figures are estimates]; beryl has also been produced in China, perhaps in Bolivia and Namibia and in small amounts in Nepal, but the available information is inadequate to formulate reliable estimates of production. ND, no data

[a] Estimated

[b] Preliminary

[c] Revised

[d] Export data for 1980–84

[e] Includes bertrandite ore calculated as equivalent to beryl containing 11% BeO

[f] Totals are not the sum of the columns, because world values are revised figures.

(*b*) *Beryllium metal*

The chief difficulties involved in the production of beryllium metal are the reactivity and high melting-point of the metal and the extreme stability of the oxide. Of the many possible methods of producing beryllium, two have been used in industry: fusion electrolysis and reduction of halides by metals. The only industrial process currently in use, developed in the 1930s, is reduction of beryllium fluoride with magnesium. The reaction is started by heating a mixture of relatively coarse-grained beryllium fluoride and magnesium in a graphite crucible. At a temperature of about 1300 °C, the reaction produces a mixture of beryllium pebbles and magnesium fluoride (Petzow *et al.*, 1985).

All practical electrolytic methods of production are based on decomposition of beryllium fluoride, beryllium oxide or beryllium chloride mixed with halides of the alkali metals or alkaline-earth metals. Several methods for the electrolysis of beryllium fluoride were developed in the 1920s. Electrolysis was carried out at above the melting-point of beryllium, at 1290–1400 °C; these methods are now obsolete. Electrolysis of beryllium chloride can be carried out at temperatures so low that the metal neither melts nor oxidizes. The beryllium is obtained as solid flakes, which are separated by washing out the electrolyte. This method was used in France, Japan, the United Kingdom and the former USSR (Petzow *et al.*, 1985).

Beryllium pebbles or flakes still contain many impurities and must be refined before they can be used to fabricate structural pieces. The main impurities in electrolytically produced beryllium are sodium and chloride; the main impurities in beryllium produced by the magnesium reduction process are magnesium and magnesium fluoride. Other impurities include beryllium oxide, carbon and metals, the most important being aluminium, iron and silicon (Petzow *et al.*, 1985). Beryllium is available mainly as block and rolled sheet and, to a lesser extent, as extruded bar, wire and near net shapes (Smugeresky, 1986).

Several commercial grades of beryllium are produced for specific uses: structural, nuclear, instrument, optical and electronic (Smugeresky, 1986). Commercial grades of beryllium are refined exclusively by vacuum melting in beryllium oxide or magnesium oxide crucibles and casting in graphite ingot moulds. The melting of magnesium-reduced beryllium in a high vacuum produces a metal of a purity comparable to that of electrolytic beryllium. Melting the electrolytic flakes in a vacuum further reduces the content of halides and low-boiling metals. A very pure grade of beryllium, particularly with respect to the content of oxide, aluminium, iron, silicon, carbon and halides, can be produced by electrolytic refining (SR flakes) (Ballance *et al.*, 1978; Petzow *et al.*, 1985).

(*c*) *Beryllium–aluminium alloy*

Beryllium–aluminium alloys (originally termed ‘lockalloy’ by the inventors, who were working for the Lockheed Co.) exhibit high bend ductility and high strength and are weldable and easy to machine. A major factor in their successful development was the preparation of a relatively fine, two-phase microstructure by a gas atomization process with quenching into water. The resultant powders are dried, then hot degassed, hot compacted and extruded to bars, from which thin sheet and thin-section extrusion are produced. Lockalloys were produced commercially from the late 1960s until 1975 (Lewis, 1988). The one remaining US manufacturer currently produces beryllium–aluminium alloys under the trade name AlBeMet^{TM} (Brush Wellman, 1992).

(*d*) *Beryllium–copper alloy*

Alloys with copper are the most important beryllium alloys. Copper–beryllium master alloy is manufactured commercially by an arc-furnace method in which beryllium oxide is reduced by carbon in the presence of molten copper at 1800–2000 °C; the resulting alloy typically contains 4.0–4.25 wt % beryllium. The master alloy is then melted together with virgin copper or copper scrap to produce the desired alloy, which is usually cast into billets (Ballance *et al.*, 1978; Stonehouse & Zenczak, 1991).

(*e*) *Beryllium chloride*

Beryllium chloride can be prepared either directly from beryl by the chloride process or by chlorination of beryllium oxide under reducing conditions. Beryllium chloride is purified by distillation in a stream of hydrogen, followed by fractional condensation (Petzow *et al.*, 1985).

(*f*) *Beryllium fluoride*

In the production of beryllium fluoride, beryllium hydroxide is dissolved in an ammonium hydrogen fluoride solution to produce ammonium tetrafluoroberyllate. Impurities can be precipitated as hydroxides. Upon concentration, ammonium tetrafluoroberyllate crystallizes from solution and is separated; after heating, it dissociates into ammonium fluoride and beryllium fluoride (Petzow *et al.*, 1985).

(*g*) *Beryllium hydroxide*

Beryllium hydroxide exists in three forms. By adding alkali to a beryllium salt solution to make a slightly basic pH, a gelatinous beryllium hydroxide is produced. Aging of this amorphous product results in a metastable tetragonal crystalline form, which, after months of standing, is transformed into a stable, orthorhombic crystalline form. The orthorhombic modification is also precipitated by hydrolysis from a hot sodium beryllate solution containing more than 5 g/L beryllium. Granular beryllium hydroxide is the readily filtered product from sulfate extraction processing of beryl (Walsh & Rees, 1978).

(*h*) *Beryllium sulfate*

Beryllium sulfate can be obtained by heating beryllium sulfate dihydrate in air to 400 °C and from the reaction of beryl ore or beryllium oxide with sulfuric acid (Walsh & Rees, 1978; Petzow *et al.*, 1985).

(*i*) *Beryllium sulfate tetrahydrate*

Beryllium sulfate tetrahydrate is produced commercially in a highly purified state by fractional crystallization from a beryllium sulfate solution obtained by reacting beryllium hydroxide with sulfuric acid. The tetrahydrate crystallizes from the aqueous solution in well-developed crystals (Walsh & Rees, 1978; Petzow *et al.*, 1985).

(*j*) *Beryllium oxide*

Beryllium oxide is produced by the following processes: beryllium hydroxide is first converted to high-purity beryllium sulfate tetrahydrate, as described above. This salt is calcined at carefully controlled temperatures, between 1150 and 1450 °C, selected to give the properties of the beryllium oxide powders required by individual beryllia ceramic fabricators. Alternatively, beryllium hydroxide may be purified first and then calcined directly to beryllium oxide powder (Walsh & Rees, 1978). In another process, beryl ore is fused with sodium silicic fluoride at 700–800 °C, with conversion to sodium fluoroberyllate and precipitation by means of caustic soda from the purified leached solution as beryllium hydroxide, from which the anhydrous chloride can be obtained by reaction with carbon and chlorine at 800 °C (US National Library of Medicine, 1992).

Today, practically all of the beryllium oxide produced commercially is calcined at temperatures of 1000 °C or higher and is referred to as 'high-fired'. Beryllium oxide that is calcined at temperatures lower than 1000 °C is referred to as 'low-fired'; it consists of poorly crystallized, small particles which are more reactive and more soluble in dilute acid than those of high-fired beryllium oxide (Finch *et al.*, 1988).

(*k*) *Beryllium carbonate*

Basic beryllium carbonate is formed in the reaction of beryllium salt solutions with alkali metal or ammonium carbonate solutions. If excess ammonium carbonate is used, a readily filtered precipitate of variable composition is formed on boiling. This salt is a suitable starting material for the preparation of beryllium salts of all types. Gentle calcining causes ammonia to escape, leaving beryllium basic carbonate. Further heating drives off the carbon dioxide to produce beryllium hydroxide (Petzow *et al.*, 1985).

(*l*) *Beryllium nitrate*

Beryllium nitrate trihydrate is prepared by crystallizing a solution of beryllium hydroxide or carbonate that has been treated with a slight excess of concentrated nitric acid; the dihydrates and monohydrates are also formed, depending on the concentration of the acid used. The anhydrous form may be obtained by treating an ethyl acetate solution of beryllium chloride with dinitrogen tetroxide but not by dehydration of one of the hydrated species; the latter operation results in thermal decomposition of the nitrate, with evolution of nitrous fumes (Drury *et al.*, 1978).

(*m*) *Beryllium phosphate*

Beryllium phosphate can be produced by the reaction of disodium hydrophosphate with a beryllium salt solution or by reaction of beryllium hydroxide solution with phosphoric acid (Mellor, 1946).

(*n*) *Beryllium silicate*

No information was available to the Working Group.

(*o*) *Zinc beryllium silicate*

No information was available to the Working Group.

1.2.2 *Use*

Typical use patterns for beryllium, beryllium alloys and beryllium compounds in the USA are presented in Table 5.

Table 5. Use patterns for beryllium in the USA (%)

Use category	1985	1987	1990	1991	1992
Metal and alloy in nuclear reactors and in military and aerospace applications	40	40	23	29	29
Alloy and oxide in electrical equipment	36	35	17	19	20
Alloy and oxide in electronic components	17	17	35	47	45
Alloy, metal and oxide in other applications	7	8	25	5	6

From Kramer (1985b, 1987, 1990, 1991b, 1992b)

(*a*) *Beryllium metal*

Some of the typical uses of beryllium metal are: structural material in space technology; moderator and reflector of neutrons in nuclear reactors; source of neutrons when bombarded with α particles; special windows for X-ray tubes; in gyroscopes, computer parts, inertial guidance systems; additives in solid propellant rocket fuels; beryllium–copper alloys; heat-sink material in low-weight, high-performance aircraft brakes; scanning mirrors and large mirror components of satellite optical systems; hardening of copper; and in developmental brass alloys (Sax & Lewis, 1987; WHO, 1990).

(*b*) *Beryllium–aluminium alloy*

The use of beryllium in alloys is based on a combination of properties that beryllium confers on other metals. Low density combined with strength, high melting-point, resistance to oxidation and a high modulus of elasticity make beryllium alloys light-weight materials that can withstand high acceleration and centrifugal forces. Most metals, however, form very brittle compounds with beryllium, and this and the low solubility of most elements in solid beryllium are the reasons why beryllium-rich alloys have not found extensive use (WHO, 1990). Historically, the only alloy with a high beryllium content was lockalloy, which contained 62% beryllium and 38% aluminium (Petzow *et al.*, 1985). Recently, Brush Wellman (1992) introduced a family of beryllium–aluminium alloys containing 20–60% beryllium and sold as AlBeMet^{TM}.

Aluminium–beryllium alloys are used mainly to save weight, reduce life-cycle cost and increase reliability in aerospace structures of advanced design. Small additions of beryllium to aluminium impart high strength, thermal stability and unusual resistance to oxidation (Lewis, 1988; WHO, 1990). These alloys are also used in computer information storage devices.

(*c*) *Beryllium–copper alloy*

The principal uses of beryllium stem from the discovery in the 1920s that the addition of only 2% beryllium to copper results in an alloy six times stronger than copper. Beryllium–copper alloys withstand high temperatures, are extraordinarily hard, are resistant to corrosion, do not spark and are non-magnetic. These alloys are used in many critical moving parts of aircraft engines and in key components of precision instruments, electrical relays and switches. An alloy containing 25% beryllium has limited application in camera shutters. Beryllium–copper hammers, wrenches and other tools are used in petroleum refineries where sparks from steel against steel might cause explosions (Newland, 1984). A representative use for beryllium–copper alloys in the electronics industry is in integrated circuit sockets and electronic connectors (Stonehouse & Zenczak, 1991). These alloys are also used in sports equipment (e.g., golf clubs).

(*d*) *Beryllium chloride*

Beryllium chloride has been used as a raw material in the electrolytic production of beryllium and as the starting material for synthesis of organoberyllium compounds (Petzow *et al.*, 1985).

(*e*) *Beryllium fluoride*

Beryllium floride is used as an intermediate in the preparation of beryllium and beryllium alloys. It was used as an additive to welding and soldering fluxes because it dissolves metal oxides readily; it was also used in nuclear reactors and glass manufacture (Petzow *et al.*, 1985; Sax & Lewis, 1987). It is being investigated for use in fibre optic cables because of its low absorbance of ultraviolet radiation.

(*f*) *Beryllium hydroxide*

Beryllium hydroxide is used as an intermediate in the manufacture of beryllium and beryllium oxide (Budavari, 1989).

(*g*) *Beryllium sulfate tetrahydrate*

Beryllium sulfate tetrahydrate is used as an intermediate in the production of beryllium oxide powder for ceramics (Walsh & Rees, 1978).

(*h*) *Beryllium oxide*

Beryllium oxide has an extremely high melting-point, very high thermal conductivity, low thermal expansion and high electrical resistance. It can either be moulded or applied as a coating to a metal or other base; through the process of sintering (1480 °C), a hard, compact mass with a smooth glassy surface is formed. The ceramic properties of sintered beryllium oxide make it suitable for the production or protection of materials to be used at high temperatures in corrosive environments. Beryllium oxide ceramics have the highest thermal conductivity of the oxide ceramics (Newland, 1984; WHO, 1990). They are also used as dental materials (ceramic crowns).

Specific applications include: transistor mountings, semiconductor packages and microelectronic substrates. Transparency to microwaves has led to its use as windows, radomes and antennae in microwave devices; it is also used in high-power laser tubes. Its low density and other properties make it attractive for aerospace and military applications, such as gyroscopes and armour; general refractory uses include thermocouple sheaths and crucibles. It is also used as an additive to glass, ceramics and plastics; in the preparation of beryllium compounds; as a catalyst for organic reactions; and in nuclear reactor fuels and moderators (Livey, 1986; Sax & Lewis, 1987; US Environmental Protection Agency, 1987; Budavari, 1989).

(*i*) *Beryllium nitrate*

Beryllium nitrate was used until the late 1960s for stiffening incandescent gas mantles (Petzow *et al.*, 1985).

(*j*) *Beryllium phosphate*

Beryllium phosphate is not known to be produced commercially.

(*k*) *Beryllium silicate*

Beryllium silicate is not known to be produced commercially.

(*l*) *Zinc beryllium silicate*

Zinc beryllium silicate is not known to be produced or used commercially at present. It was used until about 1950 as a fluorescent lamp phosphor (WHO, 1990).

1.3 Occurrence

The environmental occurrence of beryllium has been reviewed extensively (Agency for Toxic Substances and Disease Registry, 1988; WHO, 1990).

1.3.1 *Natural occurrence*

Beryllium is the forty-fourth most abundant element in the Earth's crust (Drury *et al.*, 1978; Reeves, 1986), with an average content of about 6 mg/kg. It occurs in rocks and minerals (mica schist, granite, pegmatite and argillite) at concentrations of 0.038–11.4 mg/kg (Drury *et al.*, 1978). The most highly enriched beryllium deposits are found in granitic pegmatites, in which independent beryllium minerals crystallize (WHO, 1990).

Some 40 beryllium-containing minerals have been identified. Only ores containing beryl ($3BeO.Al_2O_3.6SiO_2$) and bertrandite ($4BeO.2SiO_2.H_2O$) have achieved commercial significance (Drury *et al.*, 1978). The most important environmental source of beryllium is the burning of coal. Coals contain 1.8–2.2 mg beryllium/kg dry weight (US Environmental Protection Agency, 1987), and beryllium occurs in the ash of many coals at concentrations of about 100 mg/kg (WHO, 1990). These waste products could represent an extensive beryllium reserve. The beryllium content of fuel oils has been estimated to be less than 0.1 ppm (Drury *et al.*, 1978).

1.3.2 *Occupational exposure*

The range of industrial processes in which occupational exposure to beryllium occurs has expanded over the past two decades: The number of uses has increased, and the occupational settings have diversified. It is used in many manufacturing industries (see above) and in a growing industry for recycling and processing. Nonsiliceous mineral slag used for sand blasting is also frequently contaminated with beryllium. Potential exposure settings are summarized in Table 6.

Table 6. Industries and trades in which there is potential exposure to beryllium

Ceramics
Electrical connectors
Nonferrous foundries
Nonferrous smelters
Sandblasting
Aerospace
Nuclear control equipment
Electronics
Refractories
Beryllium smelting or fabrication
Hazardous waste processing
Dental equipment and supplies
Engineering and scientific equipment
Mechanical measuring devices
Tool and die making
Soldering
Welding or flame cutting
Metal plating
Automotive parts
Telecommunication equipment
Golf club manufacture

From Cullen *et al.* (1986); WHO (1990)

The US Occupational Safety and Health Administration summarized data on occupational exposure to beryllium for the period 1 June 1979 to 31 January 1984 (Table 7), based on inspections of work places. Exposure levels in excess of the threshold limit value of 2 $\mu g/m^3$ were found mainly in the traditional beryllium industry but also in high technology industries.

(*a*) *Processing and manufacturing*

Substances to which potential exposure occurs during ore processing include ore dust, silicon dioxide fumes and acid mists and fumes of beryllium sulfate; those during beryllium oxide production include fumes of lead sulfide, copper sulfide and sulfur trioxide and dusts of beryllium oxide; those during production of beryllium metal include acid fluoride mists, fumes and dusts of beryllium ammonium fluoride, beryllium fluoride, hydrogen fluoride, ammonium fluoride, beryllium metal and beryllium oxide; and those during production of beryllium–copper alloy include beryllium oxide, copper and beryllium–copper alloy dusts and fumes. Machining potentially involves exposure to respirable particles of beryllium alloys in the absence of adequate controls (Laskin *et al.*, 1950; Preuss, 1988). Exposure concentrations in various industries have been reviewed (WHO, 1990).

Table 7. Occupational exposure to beryllium compounds (1 June 1979 to 31 January 1984)

Type of industry	No. of samples in which beryllium is detected	No. of samples ≥ 0.5 μg/m^3[a]	No. of samples ≥ 2 μg/m^3[b]
Traditional[c]	25	16	9
High-technology[d]	3	3	2
Secondary process[e]	5	1	0
Dental laboratory	1	0	0
Total	34	20	11

From Cullen *et al.* (1986)

[a] Criterion of the US National Institute for Occupational Safety and Health

[b] Standard of the US Occupational Safety and Health Administration

[c] Including particulate blasting, shipbuilding and repair, nonferrous foundries, nonclay refractories, beryllium machining and fabrication and metalworking

[d] Including the semiconductor industry, precision electronics industry and spacecraft and missile manufacture

[e] Including secondary nonferrous smelters, nonferrous foundries and hazardous waste reclamation

Although there are few quantitative data on exposure to beryllium before 1947, there seems to be little doubt that extremely high concentrations were encountered in the work place (US National Institute for Occupational Safety and Health, 1972). In the USA, concentrations greater than 1000 μg/m^3 were not uncommon in beryllium extraction facilities (Eisenbud & Lisson, 1983). Exposures measured in December 1946 (by the filter-paper dust sampler method) ranged from 110 to 4710 μg/m^3 in the furnace area of a beryllium extraction plant (Laskin *et al.*, 1950). Concentrations of 590–43 300 μg/m^3 were found in a beryllium–copper alloy plant in Lorain, Ohio, USA, monitored by the Atomic Energy Commission in 1947 and 1948 (Zielinski, 1961). After institution of control measures in 1949 in a new beryllium-copper alloy production plant in Elmore, Ohio, the limit of 2 μg/m^3 was considerably exceeded between 1953 and 1960, with time-weighted average values of 3.8–9.5 μg/m^3 in 1953, 6.8–19.1 μg/m^3 in 1956 and 23.1–54.6 μg/m^3 in 1960 (Zielinski, 1961; US National Institute for Occupational Safety and Health, 1972). In the same beryllium–copper alloy plant, a new furnace was installed between 1960 and 1966. Concentrations ranged from < 0.1 μg/m^3 in the mixing areas to 1050 μg/m^3 in the oxide areas in 1960 and from 0.2 μg/m^3 in the saw area to 249 μg/m^3 in the arc furnace area in 1966. Five-day average beryllium concentrations in this plant were 60.3 μg/m^3 in 1960 and 18.1 μg/m^3 in 1966 (see Table 8) (Cholak *et al.*, 1967).

In a summary of beryllium concentrations in 2627 air samples taken during 1950–57 in two US beryllium production plants, Breslin and Harris (1959) reported that 10–15% of workers were exposed to concentrations greater than 2 μg/m^3 and that the average concentration in each plant in many operations was 10 μg/m^3. Exposures may have been higher in plants that were not monitored by the Atomic Energy Commission (US National Institute for Occupational Safety and Health, 1972).

Table 8. Concentrations of beryllium in air at a number of locations in a beryllium–copper alloy plant in Ohio (USA) during two cycles of air monitoring six years apart

Location	Year	Beryllium concentration (μg/m³) of air per 2-h period		
		Average	Median	Range
Oxide area	1960	149.4	72.5	0.4–1050.0
	1966	10.7	8.1	0.8–29.3
Arc furnace area	1960	87.6	50.0	22.1–502.0
	1966	25.9	36.9	7.7–249.0
Mixing area	1960	21.6	14.4	< 0.1–452.0
	1966	20.0	14.7	5.9–88.5
Casting area	1960	39.8	14.6	0.2–535.0
	1966	25.4	20.5	8.5–210.5
Fisher furnace area	1960	40.8	28.8	0.2–340.0
	1966	7.3	5.5	1.5–37.8
Saw area	1960	25.6	21.1	< 2.5–92.5
in rolling mill	1966	5.7	4.0	0.2–18.4
Cropping area	1960	52.8	33.6	14.0–399.0
Ajax furnace area[a]	1966	14.4	11.1	4.6–87.5
All areas	1960	60.3	28.4	< 0.1–1050.0
	1966	18.1	11.4	0.2–249.0

From Cholak *et al.* (1967)

[a] Approximately same area as cropping area in 1960

The US Atomic Energy Commission presented exposure data from five major beryllium-processing plants for various periods during 1950–61. Up to 40–75% of the daily weighted average exposures exceeded 2 μg/m³ (US National Institute for Occupational Safety and Health, 1972).

[The Working Group noted the uncertainty of the representativeness for exposure of workers of air monitoring data obtained in the 1940s, 1950s and 1960s.]

In the early 1970s in a beryllium extraction and processing plant in northeastern USA, peak concentrations up to 1310 μg/m³ were observed (Kanarek *et al.*, 1973). Follow-up analyses in 1974 showed a significant decrease (Sprince *et al.*, 1978).

The US National Institute for Occupational Safety and Health conducted several surveys of air in different beryllium plants in the USA. In a beryllium production plant, concentrations of 0.3–160 μg/m³ were found in 1971, the high values occurring in powdering operations (H.M. Donaldson, 1971; cited in WHO, 1990). In another beryllium production plant, the concentrations of airborne beryllium in 1972 rarely exceeded the threshold limit value of 2 μg/m³ (H.M. Donaldson & P.J. Shuler, 1972; cited in WHO, 1990). Beryllium concentrations in 50 personal samples collected at a secondary copper smelter in 1982–83 ranged between < 0.2 and 0.5 μg/m³ (Cherniak & Kominsky, 1984). In 1983, the concentrations of beryllium in 121 personal air samples obtained in the refinery and manufacturing melt areas of a precious metals refinery ranged from 0.22 to 42 μg/m^3 (mean, 1.4 μg/m^3) (K.P. McManus *et al.*, 1986; cited in WHO, 1990). Concentrations in the beryllium shop of another plant in 1985 ranged from < 0.2 to 7.2 μg/m^3 and exceeded 0.5 μg/m^3 in 6/33 breathing-zone samples (Gunter & Thoburn, 1986).

Kriebel *et al.* (1988a) described the beryllium concentrations in a plant in which most of the beryllium refined in the USA since 1934 has been produced, the principal product always having been beryllium–copper alloys (containing ≤ 2–4% beryllium). Table 9 summarizes the daily weighted average concentrations in 16 departments in four periods. The concentrations were high for many years, with some estimated to have been in excess of 100 μg/m^3; as late as 1975, average exposures to beryllium in some jobs were greater than 10 μg/m^3. After about 1977, the levels were in compliance with the permissible exposure limit of 2 μg/m^3. The median cumulative exposure of 297 white male workers surveyed in 1977 was 65 μg/m^3-years; their median exposure was 0.4 μg/m^3, and the mean number of years worked was 17. [The Working Group noted that there was some overlap in the plants surveyed.]

Table 9. Daily weighted average concentrations of beryllium (μg/m^3) in 16 departments[a] in a US beryllium production plant in four periods

Department	Approximate no. of workers in 1943	No. of jobs in department	Period			
			1935–54	1955–64	1965–76	1977–83
Oxide	46	14	46	16	8.8	0.5
Arc furnace room	26	6	80	51	11	0.7
Detroit furnaces	24	4	51	51	33	NA
Foundry	27	5	19	19	13	NA
Melt and cast	105	6	18	18	7.6	1.1
Hot rolling	19	8	9.3	9.3	2.5	0.2
Cold rolling	29	8	9.2	5.7	2.5	0.2
Rod and wire	39	8	5.9	5.9	2.0	0.2
Annealing	10	5	13	13	5.7	0.1
Pickling	11	3	0.2	0.2	0.2	0.1
Machining, grinding	60	5	1.7	1.7	0.9	0.1
Maintenance	73	13	6.2	5.7	3.5	0.1
Inspection	12	7	1.6	1.6	0.9	0.1
Laundry	–	1	2.5	2.5	1.0	0.1
Laboratories, research and development	28	6	1.4	1.4	1.2	0.2
Stores, shipping	20	3	3.6	3.6	2.0	0.1
Total	529	102				

From Kriebel *et al.* (1988a); NA, not applicable; these departments were not operational during 1977–83.

[a] Smaller departments were grouped for presentation.

(*b*) *Machining and use*

Personal air samples taken at US factories in which machining of beryllium metal and alloys involved drilling, boring, cutting and sanding did not contain any detectable amount of beryllium (Gilles, 1976; Boiana, 1980; Lewis, 1980). In a US boat factory in which workers were engaged in grid blasting, beryllium concentrations of 6–134 μg/m^3 were measured (Love & Donohue, 1983). Breathing-zone air samples taken from workers during grinding, polishing, cutting and welding of beryllium-containing alloys in a German metal processing plant contained < 0.1–11.7 μg/m^3 beryllium in total dust; 0.1–10.0 μg/m^3 during hand cutting; 1.4–11.7 μg/m^3 during automatic cutting; 2.1–3.63 μg/m^3 during welding without exhaust extraction; and 1.12–1.34 μg/m^3 during welding with exhaust extraction (Minkwitz *et al.*, 1983; WHO, 1990).

Dental laboratory technicians were exposed to < 2 μg/m^3 beryllium in the breathing zone during the processing of beryllium-containing dental alloys in the USA when exhaust ventilation was used (Dvivedi & Shen, 1983). Air measurements in three dental laboratories in Italy where melting and finishing of dental prostheses were carried out revealed beryllium concentrations in the breathing area in the range of 0.04–1.7 μg/m^3. The mean concentration of beryllium in the urine of 46 dental technicians (0.34 μg/L; range, 0.05–1.7) was higher than that of non-occupationally exposed subjects (mean, 0.26 μg/L; range, < 0.03–0.8) (Apostoli *et al.*, 1989a). [The Working Group noted that the smoking habits of the technicians were not defined.]

1.3.3 *Air*

The major source of atmospheric beryllium is combustion of coal, and its most prevalent chemical form is probably beryllium oxide, mainly bound to particles smaller than 1 μm (WHO, 1990). In earlier reports, average atmospheric background concentrations of beryllium were reported to be less than 0.1 (Bowen, 1966) and 0.2 ng/m^3 (Sussmann *et al.*, 1959). The air of over 100 cities in the USA, sampled in 1964–65, did not contain detectable amounts of beryllium (detection limit, 0.1 ng/m^3) (Drury *et al.*, 1978). Annual average background concentrations during 1977–81 throughout the USA were around the detection limit of 0.03 ng/m^3. Annual averages at urban monitoring stations where concentrations exceeded 0.1 ng/m^3 ranged between 0.11 and 6.7 ng/m^3 during 1981–86 (US Environmental Protection Agency, 1987; WHO, 1990). These data are similar to those found in other countries: Ikebe *et al.* (1986) found an average of 0.042 ng/m^3 in 76 air samples collected in 17 Japanese cities between 1977 and 1980; the highest values were found in Tokyo (0.22 ng/m^3) and in an industrial area in Kitakyushu (0.21 ng/m^3). R. Freise and G.W. Israel (1987, cited in WHO, 1990) found annual mean values in Berlin (Germany) of 0.2–0.33 ng/m^3. A concentration of 0.06 ng/m^3 was measured in a residential area, an office area and the inner city area of Frankfurt, whereas 0.02 ng/m^3 was measured in a rural area near Frankfurt (Müller, 1979).

Atmospheric concentrations of beryllium in the vicinity of beryllium processing plants are often higher than those elsewhere. A mean concentration of 15.5 ng/m^3 and a maximum concentration of 82.7 ng/m^3 were reported near a Pennsylvania (USA) factory, whereas background levels in several locations in the area averaged only 0.2 ng/m^3 (Sussman *et al.*, 1959).

The average concentration of beryllium in air 400 m from a beryllium extracting and processing plant in the former USSR, which was not equipped with emission control devices, was 1 μg/m^3; at 1000 m, it was 10–100 ng/m^3. Between 500 and 1500 m from a mechanical beryllium-finishing plant with operational filter facilities, no beryllium was detected in air [detection limit not given] (Izmerov, 1985). Bencko *et al.* (1980) reported beryllium concentrations of 3.9–16.8 ng/m^3 (average, 8.4 ng/m^3) in the vicinity of a power (coal) plant in former Czechoslovakia.

1.3.4 *Tobacco smoke*

In a German study of three brands of cigarettes [origin of tobaccos and number of samples not given], 0.47–0.75 μg beryllium was found per cigarette. Less than 10% of the beryllium content (0.011–0.074 μg/cigarette) was released into mainstream smoke during smoking (Zorn & Diem, 1974).

1.3.5 *Water*

Beryllium concentrations in surface waters are usually in the range 0.01–0.1 μg/L (WHO, 1990). The concentrations in 15 major US river basins ranged from 0.01 to 1.22 μg/L, with a mean of 0.19 μg/L (Safe Drinking Water Committee, 1977). Water samples taken from various areas near the Seward Peninsula in Alaska contained beryllium concentrations of 0.034–2.4 μg/L (Gosink, 1976). Surface water in eastern USA and Siberia contained beryllium at concentrations ranging from 0.1 to 0.9 μg/L (Safe Drinking Water Committee, 1977). Groundwater samples from Germany contained < 5–9 ng/L, with a mean of 8 ng/L; beryllium concentrations in seawater were 10 times lower than those in surface water (Reichert, 1974). Concentrations of 0.2–0.9 ng/L (mean, 0.5) (Merrill *et al.*, 1960) and 2 ng/L (Meehan & Smythe, 1967) were reported in the Pacific Ocean. Measures and Edmond (1982) found still lower concentrations, 0.04–0.06 ng/L, in the mixed layer—up to about 500 m.

In a survey of 380 US drinking-water sources in 1962–67, beryllium was found in only 1.1% of samples, at concentrations ranging from 20 to 170 ng/L (mean, 100) (Safe Drinking Water Committee, 1977). Sauer and Lieser (1986) found beryllium at 27 ± 8 ng/L in drinking-water samples from Germany.

1.3.6 *Soils*

Beryllium occurs in most soils. Drury *et al.* (1978) reported an average of 6 mg/kg (range, 0.1–4.0) worldwide and 0.04–1.45 mg/kg in Kenya. Of 847 samples of agricultural soils collected at a depth of 20 cm throughout the USA, 66% contained < 1 mg/kg, 22% between 1 and 2 mg/kg and 12% between 2 and 7 mg/kg (Shacklette *et al.*, 1971). The mean beryllium concentration in 27 soil profiles (with 129 horizons) of uncontaminated soil from various locations in Japan was 1.31 mg/kg (Asami & Fukazawa, 1985).

In some small, unpolluted areas in which rocks contain large amounts of beryllium, the overlying soils show relatively high beryllium concentrations; e.g., soils in the Lost River Valley, Alaska, USA, contained up to 300 mg/kg, with an average of 60 mg/kg (WHO, 1990).

1.3.7 *Food*

Only limited, variable data are available on beryllium contents of food (WHO, 1990). The concentrations in various foods collected in New South Wales, Australia, ranged from 10 to 470 μg/kg ash weight (0.07–1175 μg/kg fresh weight); the highest concentrations were found in peanut shells (Meehan & Smythe, 1967).

Owing to the limited data, the daily human intake of beryllium from food has not been determined. In a study in the United Kingdom (Hamilton & Minsky, 1973), the average total dietary intake was estimated to be < 15 μg/day. The US Environmental Protection Agency (1987) estimated a total daily consumption of about 420 ng, most of which came from food (120 ng/day) and drinking-water (300 ng/day); air and dust reportedly contributed very little to the total intake of beryllium.

1.3.8 *Human tissues and secretions*

The measured concentrations of beryllium in body fluids and tissues have diminished substantially over the past 10 years, probably as a consequence of improved analytical techniques, including better procedures for minimizing beryllium contamination during collection and assay. The validity of the data reported in the older literature is therefore somewhat doubtful.

Sprince *et al.* (1976) analysed specimens taken at autopsy from patients without granulomatous disease and found less than 20 μg/kg dry weight of beryllium in lung tissue (mean, 5 μg/kg; range, 3–10; six cases) and mediastinal lymph nodes (mean, 11 μg/kg; range, 6–19; seven cases). These concentrations are within the range of 90% of the values of 2–30 μg/kg dry lung tissue found in 125 lung specimens obtained during thoracic surgery (Baumgardt *et al.*, 1986).

Caroli *et al.* (1988) analysed different parts of lung tissue from 12 subjects in an urban area of Rome (Italy), who were nonsmokers, 50 or more years old and had not been occupationally exposed to beryllium during their lifetime. The overall mean of 5 μg/kg fresh weight indicates a smaller concentration range than those above, which were expressed in dry weight.

In a survey of 66 patients with beryllium disease in the US Beryllium Case Registry, the concentrations of beryllium ranged from 4 to 45 700 μg/kg dried tissue; 82% of the patients had concentrations of more than 20 μg/kg dry weight. Peripheral lymph-node specimens from five patients contained 2–490 μg/kg beryllium and mediastinal specimens, 56–8500 μg/kg (Sprince *et al.*, 1976).

Beryllium concentrations in urine specimens from non-occupationally exposed subjects are summarized in Table 10. The mean beryllium concentration in blood from 20 non-occupationally exposed German subjects was 0.9 μg/L (SD, 0.5) (Stiefel *et al.*, 1980).

Smoking appears to influence the concentration beryllium in urine: the beryllium concentration in the urine of heavy smokers (0.31 ± 0.17 μg/L) was significantly greater than that of nonsmokers (0.20 ± 0.14 μg/L) (Apostoli *et al.*, 1989b).

An exposure concentration of 2 μg/m^3 beryllium in air was found to correspond to about 7 μg/L in urine and about 4 μg/L in blood (Zorn *et al.*, 1988).

Table 10. Urinary concentrations of beryllium, identified by graphite furnace atomic absorption, in specimens from non-occupationally exposed subjects

Country	No. of subjects	Concentration (µg/L; mean ± SD)	Reference
USA	120	0.9 ± 0.4	Grewal & Kearns (1977)
Italy	56	0.6 ± 0.2	C. Minoia *et al.* (1985; cited by Apostoli *et al.*, 1989b)
USA	NR	0.13	Paschal & Bailey (1986)
Italy	163	0.24 ± 0.16 (range, < 0.03–0.8)	Apostoli *et al.* (1989b)
Italy	579	0.4 (range, < 0.02–0.82)	Minoia *et al.* (1990)

Modified from Apostoli *et al.* (1989b); NR, not reported

1.4 Regulatory status and guidelines

Occupational exposure limits and guidelines for beryllium and beryllium compounds established in different parts of the world are given in Table 11.

Table 11. Occupational exposure limits and guidelines for beryllium and beryllium compounds

Country or region	Year	Concentration (µg/m^3)	Interpretation[a]
Argentina	1991	2	TWA, potential carcinogen
Australia	1990	2	TWA, probable human carcinogen
Belgium	1990	2	TWA, probable human carcinogen
Bulgaria	1984	1	TWA
China	1979	1	TWA
Denmark	1992	1	TWA[b]
Finland	1990	0	Suspected of having carcinogenic potential
France	1990	2	TWA, carcinogen
Germany	1992	0	A2[c]
Hungary	1990	1	STEL, probable human carcinogen, irritant, sensitizer
Indonesia	1978	2	TWA
Italy	1978	2	TWA
Japan	1991	2	TWA, probable human carcinogen
Korea, Republic of	1983	2	TWA
Mexico	1984	2	TWA
Netherlands	1986	2	TWA
Poland	1985	1	TWA

Table 11 (contd)

Country or region	Year	Concentration ($\mu g/m^3$)	Interpretation[a]
Romania	1975	1	STEL
Sweden	1991	2	TWA, causes cancer, sensitizer
Switzerland	1990	2	TWA, inhalable dust, absorbed through skin
Taiwan	1981	2	TWA
United Kingdom	1994	2 (proposal)	STEL
USA[e]			
OSHA	1989	2	TWA (PEL)
		5	Ceiling
		25	Max
NIOSH	1990	0.5	TWA, carcinogen (REL)
ACGIH	1992	2	TWA, A2[d] (TLV)
Venezuela	1978	2	TWA
		25	Ceiling

From Arbeidsinspectie (1986); Cook (1987); US Occupational Safety and Health Administration (OSHA) (1989); Arbetarskyddsstyrelsens (1991); Institut National de Recherche et de Sécurité (1990); US National Institute for Occupational Safety and Health (1990); International Labour Office (1991); American Conference of Governmental Industrial Hygienists (ACGIH) (1992); Anon. (1992); Arbejdstilsynet (1992); Deutsche Forschungsgemeinschaft (1992); UNEP (1993).

[a] The concentrations given may or may not have regulatory or legal status in the various countries; for interpretation of the values, the original references or other authoritative sources should be consulted. TWA, time-weighted average; STEL, short-term exposure limit; Max, acceptable maximal peak (of 30-min maximal duration) above the acceptable ceiling concentration for an 8-h shift; PEL, proposed exposure limit; REL, recommended exposure limit; TLV, threshold limit value

[b] Beryllium and beryllium compounds are on a list of dangerous compounds but not classified for carcinogenic effect.

[c] Compounds which in the Commission's opinion have proven so far to be unmistakably carcinogenic in animal experimentation only; namely under conditions which are comparable to those for possible exposure of a human being at the workplace, or from which such comparability can be deduced

[d] Suspected human carcinogen; chemical substance, or substances associated with industrial processes, which are suspected of inducing cancer, on the basis of either limited epidemiological evidence or demonstration of carcinogenesis in one or more animal species by appropriate methods

Stationary sources (extraction plants, ceramic plants, foundries, incinerators and propellant plants for the processing of beryllium ore, beryllium, beryllium oxide, beryllium alloys and beryllium-containing waste; machine shops for the processing of beryllium, beryllium oxide and any alloy containing more than 5% beryllium by weight) are subject to the US national emission standard for beryllium, which is 0.01 $\mu g/m^3$ (30-day average) in ambient air for those production facilities which qualify for regulation through ambient air monitoring. Other facilities must meet a total site emission limit of 10 g per 24 h (US Environmental Protection Agency, 1992).

In the European Economic Community, beryllium and beryllium compounds are not permitted in cosmetic products (Commission of the European Communities, 1991a, 1992). Waste (except domestic waste) containing or contaminated by beryllium and beryllium compounds is classified as hazardous waste (effective date, 12 December 1993) (Commission of the European Communities, 1991b). Member States must take the necessary steps to limit the introduction of beryllium and its compounds into groundwater (effective date, 26 January 1982) (Commission of the European Communities, 1980). Beryllium and beryllium compounds (except aluminium beryllium silicates) are classified as very toxic and irritant (effective date, 1 July 1992) (Commission of the European Communities, 1991c).