VANADIUM PENTOXIDE

1. Exposure Data

1.1 Chemical and physical data

1.1.1 *Nomenclature*

The nomenclature of selected vanadium compounds is given in Table 1.
Chem. Abstr. Serv. Reg. No.: 1314-62-1
Deleted CAS Reg. No.: 12503-98-9; 56870-07-6; 87854-55-5; 87854-56-6; 166165-37-3; 172928-47-1; 184892-22-6; 200577-85-1; 203812-34-4; 251927-12-5; 410546-90-6
Chem. Abstr. Serv. Name: Vanadium oxide (V_2O_5)
IUPAC Systematic Name: Vanadium oxide
Synonyms: CI 77938; divanadium pentaoxide; pentaoxodivanadium; vanadic acid anhydride; vanadin (V) oxide (see also Table 1)

1.1.2 *Empirical formula and relative molecular mass*

V_2O_5 Relative molecular mass: 181.88

1.1.3 *Chemical and physical properties of the pure substance*

(*a*) *Description*: Yellow to rust-brown orthorhombic crystals (O'Neil, 2001; Lide, 2003); yellow-orange powder or dark-gray flakes (Bauer *et al.*, 2003; National Institute for Occupational Safety and Health, 2005)
(*b*) *Boiling-point*: 1800 °C, decomposes (Lide, 2003)
(*c*) *Melting-point*: 670 °C (Lide, 2003); 690 °C (O'Neil, 2001)
(*d*) *Density*: 3.36 (O'Neil, 2001; Lide, 2003)
(*e*) *Solubility*: Slightly soluble in water (0.1–0.8 g/100 cm^3); soluble in concentrated acids and alkalis; insoluble in ethanol (Woolery, 1997; O'Neil, 2001)
(*f*) *Stability*: Reacts with chlorine or hydrochloric acid to form vanadium oxytrichloride; absorbs moisture from the air (ESPI, 1994).

Table 1. Nomenclature of selected vanadium compounds

Molecular formula	Name used in Monograph [Registry number]	Synonyms
NH_4VO_3	Ammonium metavanadate [7803-55-6]	Ammonium monovanadate Ammonium trioxovanadate Ammonium trioxovanadate(1-) Ammonium vanadate Ammonium vanadate(V) Ammonium vanadium oxide Ammonium vanadium trioxide Vanadate (VO_3^-), ammonium Vanadic acid, ammonium salt Vanadic acid (HVO_3), ammonium salt
Na_3VO_4	Sodium orthovanadate [13721-39-6]	Sodium pervanadate Sodium tetraoxovanadate(3-) Sodium vanadate Sodium vanadate(V) (Na_3VO_4) Sodium vanadium oxide (Na_3VO_4) (9CI) Trisodium orthovanadate Trisodium tetraoxovanadate Trisodium vanadate Vanadic acid (H_3VO_4), trisodium salt (8CI) Vanadic(II) acid, trisodium salt
VO^{2+}	Vanadyl [20644-97-7]	Oxovanadium(2+) Oxovanadium(IV) ion Vanadium monoxide(2+) Vanadium oxide (VO), ion(2+) Vanadium oxide (VO^{2+}) Vanadyl(II) Vanadyl ion(2+) (8CI, 9CI)
VO_3^-	Vanadate [13981-20-9]	Metavanadate Metavanadate(1-) Trioxovanadate(1-) Vanadate (VO_3^-) Vanadate, ion –
$NaVO_4$	Sodium peroxyvanadate [15593-26-7]	Hydrogen peroxide, vanadium complex Peroxyvanadic acid ($HVO_2(O_2)$), sodium salt
Unspecified	Sodium vanadium oxide [11105-06-9]	Peroxyvanadic acid, sodium salt Sodium peroxyvanadate Sodium vanadate Vanadic acid, sodium salt

Table 1 (contd)

Molecular formula	Name used in Monograph [Registry number]	Synonyms
$VO(SO_4)$	Vanadyl sulfate [27774-13-6]	Oxo(sulfato)vanadium Oxovanadium(IV) sulfate Vanadic sulfate Vanadium oxide sulfate Vanadium(IV) oxide sulfate Vanadium oxosulfate Vanadium, oxosulfato- (8CI) Vanadium, oxo(sulfato(2-)-O)- Vanadium, oxo(sulfato(2-)-κO)- (9CI) Vanadium oxysulfate Vanadium sulfate
Unknown	Ferrovanadium [12604-58-9]	Ferrovanadium alloy Ferrovanadium dust
V_2O_3	Vanadium trioxide [1314-34-7]	Divanadium trioxide Vanadic oxide Vanadium oxide (V_2O_3) (8CI, 9CI) Vanadium(3+) oxide Vanadium sesquioxide Vanadium trioxide
V_2O_5	Vanadium pentoxide [1314-62-1]	Divanadium pentoxide Pentaoxodivanadium Vanadia Vanadic anhydride Vanadium oxide Vanadium oxide (V_2O_5) (8CI, 9CI) Vanadium(V) oxide Vanadium pentoxide
VCl_3	Vanadium trichloride [7718-98-1]	Vanadium chloride (VCl_3) (8CI, 9CI) Vanadium(3+) chloride Vanadium(III) chloride Vanadium trichloride

From STN International (2003); National Library of Medicine (2003)

1.1.4 *Technical products and impurities*

Vanadium pentoxide is commercially available in the USA in purities between 95% and 99.6%, with typical granulations between 10 mesh [~ 1600 μm] and 325 mesh [~ 35 μm] × down (Reade Advanced Materials, 1997; Strategic Minerals Corp., 2003). Vanadium pentoxide is also commercially available as a flake with the following specifications: purity, 98–99%; silicon, < 0.15–0.25%; iron, < 0.20–0.40%; and phosphorus, < 0.03–0.05%; and as a powder with the following specifications: purity, 98%; silicon dioxide, < 0.5%; iron, 0.3%; and arsenic, < 0.02% (American Elements, 2003).

Vanadium pentoxide is commercially available in Germany as granules and powder with a minimum purity of 99.6% (GfE mbH, 2003), and in the Russian Federation as a powder with the following specifications: purity, 98.6–99.3%; iron, < 0.05–0.15%; silicon, < 0.05–0.10%; manganese, < 0.04–0.10%; chromium, < 0.02–0.07%; sulfur, < 0.005–0.010%; phosphorus, < 0.01%; chlorine, < 0.01–0.02%; alkali metals (sodium and potassium), < 0.1–0.3%; and arsenic, < 0.003–0.010% (AVISMA titanium-magnesium Works, 2001).

Vanadium pentoxide is also commercially available in South Africa as granular and R-grade powders with a minimum purity of 99.5% and grain sizes of > 45 μm and < 150 μm, respectively (Highveld Steel & Vanadium Corporation Ltd, 2003).

1.1.5 *Analysis*

Occupational exposure to vanadium pentoxide is determined by measuring total vanadium in the workplace air or by biological monitoring.

(*a*) *Monitoring workplace and ambient air*

Respirable fractions (< 0.8 μm) of airborne vanadium pentoxide are collected by drawing air in a stationary or personal sampler through a membrane filter made of polycarbonate, cellulose esters and/or teflon. The filter containing the collected air particulates can be analysed for vanadium using several methods. In destructive methods, the filter is digested in a mixture of concentrated mineral acids (hydrochloric acid, nitric acid, sulfuric acid, perchloric acid) and the vanadium concentration in the digest determined by GF–AAS (Gylseth *et al.*, 1979; Kiviluoto *et al.*, 1979) or ICP–AES (Kawai *et al.*, 1989). Non-destructive determination of the vanadium content on a filter can be performed using INAA (Kucera *et al.*, 1998).

Similar methods can be used for the measurement of vanadium in ambient air.

X-ray powder diffraction allows quantification of vanadium pentoxide, vanadium trioxide and ammonium metavanadate separately on the same sample of airborne dust (Carsey, 1985; National Institute for Occupational Safety and Health, 1994).

(*b*) *Biological monitoring*

(i) *Tissues suitable for biomonitoring of exposure*

Vanadium concentrations in urine, blood or serum have been suggested as suitable indicators of occupational exposure to vanadium pentoxide (Gylseth *et al.*, 1979; Kiviluoto *et al.*, 1979, 1981; Pyy *et al.*, 1984; Kawai *et al.*, 1989; Kucera *et al.*, 1998). The concentration of vanadium in urine appears to be the best indicator of recent exposure, since it rises within a few hours after the onset of exposure and decreases within a few hours after cessation of exposure (Kucera *et al.*, 1998). Table 2 presents data of vanadium concentrations in urine from workers exposed to vanadium.

Detailed information on the kinetics of vanadium in human blood after exposure is still lacking. Kucera *et al.* (1998) regarded vanadium concentrations in blood as the most suitable indicator of the long-term body burden (see Section 4.1.1). However, in a study of vanadium pentoxide exposure in rats, blood concentrations showed only marginal increases. This seems to indicate that there was limited absorption of vanadium (National Toxicology Program, 2002).

(ii) *Precautions during sampling and sample handling*

Biological samples are prone to contamination from metallic parts of collection devices, storage containers, some chemicals and reagents; as a result, contamination-free sampling, sample handling and storage of blood and urine samples prior to analysis are of crucial importance (Minoia *et al.*, 1992; Sabbioni *et al.*, 1996). There is also a great risk of contamination during preconcentration, especially when nitric acid is used (Blotcky *et al.*, 1989).

(iii) *Analytical methods*

Several reviews are available on analytical methods used for the determination of vanadium concentrations in biological materials (Seiler, 1995) and on the evaluation of normal vanadium concentrations in human blood, serum, plasma and urine (Versieck & Cornelis, 1980; Sabbioni *et al.*, 1996; Kucera & Sabbioni, 1998). Determination of vanadium concentrations in blood and/or its components and in urine is a challenging analytical task because the concentrations in these body fluids are usually very low (below the μg/L level). A detection limit of < 10 ng/L is therefore required and only a few analytical techniques are capable of this task, namely GF–AAS, isotope dilution mass spectrometry (IDMS), ICP–MS and NAA. Furthermore, sufficient experience in applying well-elaborated analytical procedures is of crucial importance for accurate determination of vanadium concentrations in blood, serum and urine.

Direct determination of vanadium concentrations in urine or diluted serum by GF–AAS is not feasible because the method is not sufficiently sensitive and because the possibility of matrix interferences; however, GF–AAS with a preconcentration procedure has been applied successfully (Ishida *et al.*, 1989; Tsukamoto *et al.*, 1990).

IDMS has good potential for the determination of low concentrations of vanadium. This technique has been applied for the determination of vanadium concentrations in human

Table 2. Vanadium concentrations in workplace air and urine from workers occupationally exposed to vanadium

Industrial process	No. of subjects	Vanadium in air mean ± SD or range of means in mg/m^3	Vanadium in urine mean ± SD (range) in µg/L[b]	Reference
Ferrovanadium production	16	NK[c]	152 (44–360) nmol/mmol creatinine	Gylseth *et al.* (1979)
Smelting, packing and filtering of vanadium pentoxide	8	0.19 ± 0.24	73 ± 50 nmol/mmol creatinine	Kiviluoto *et al.* (1981)
Vanadium pentoxide processing	2	NK	13.9	Pyy *et al.* (1984)
Boiler cleaning	4	2.3–18.6 (0.1–6.4)[a]	(2–10.5)	White *et al.* (1987)
Vanadium pentoxide staining	2	[< 0.04–0.13]	(< 7–124)	Kawai *et al.* (1989)
Boiler cleaning	21	NK	0.7 (0.1–2.1)	Arbouine & Smith (1991)
Vanadium alloy production	5	NK	3.6 (0.5–8.8)	Arbouine & Smith (1991)
Removal of ashes in oil-fired power station	11	NK	2.2–27.4	Pistelli *et al.* (1991)
Boiler cleaning	10 (– RPE)[d] 10 (+ RPE)	NK	92 (20–270) 38 ± 26	Todaro *et al.* (1991)
Boiler cleaning	30	0.04–88.7	(0.1–322)	Smith *et al.* (1992)
Maintenance in oil-fired boiler	NK	0.28	57.1 ± 15.4 µg/g creatinine	Barisione *et al.* (1993)
Vanadium pentoxide production	58	Up to 5	28.3 (3–762)	Kucera *et al.* (1994)
Waste incineration workers	43	NK	0.66 ± 0.53 (< 0.01–2)	Wrbitzky *et al.* (1995)

Table 2 (contd)

Industrial process	No. of subjects	Vanadium in air mean ± SD or range of means in mg/m^3	Vanadium in urine mean ± SD (range) in μg/L[b]	Reference
Boilermakers	20	0.02 (0.002–0.032)	1.53 ± 0.53 mg/g creatinine	Hauser *et al.* (1998)

Updated from WHO (2001)

[a] Time-weighted average (TWA)

[b] Unless stated otherwise

[c] NK, not known

[d] RPE, respiratory protective equipment

serum in only one study (Fassett & Kingston, 1985); however, the high mean value obtained (2.6 ± 0.3 mg/L) suggested the possibility of contamination (Sabbioni *et al.*, 1996; Kucera & Sabbioni, 1998).

ICP–MS cannot be used for the determination of low concentrations of vanadium because of spectral and non-spectral interferences, unless high-resolution ICP–MS is used (Moens *et al.*, 1994; Moens & Dams, 1995).

The problems of various interferences encountered with the above methods are mostly avoided by using NAA (Byrne, 1993). However, interfering radionuclides such as ^{24}Na or ^{38}Cl must be removed, preferably by post-irradiation radiochemical separation, so-called radiochemical NAA (RNAA). Also, because of the short half-life of the analytical radionuclide ^{52}V ($T_{1/2}$, 3.75 min), sample decomposition by irradiation and vanadium separation must be completed within 6–12 min (Byrne & Kosta, 1978a; Sabbioni *et al.*, 1996). This technique has been mastered by only a few research groups (Byrne & Kosta, 1978b; Cornelis *et al.*, 1980, 1981; Byrne & Versieck, 1990; Heydorn, 1990; Byrne & Kucera, 1991a,b; Kucera *et al.*, 1992, 1994). If dry ashing is carried out prior to irradiation, the separation time can be shortened by a few minutes and a lower detection limit can be achieved (Byrne & Kucera, 1991a,b). Various procedures of pre-irradiation separation have been employed to circumvent the necessity for speedy operations with radioactive samples; however, high values were obtained, indicating that contamination and problems with blank samples could not be excluded (Heydorn, 1990). The only exception to date is an analysis performed by NAA in a clean Class 100 laboratory (Greenberg *et al.*, 1990), which yielded a vanadium concentration in serum similar to that determined by RNAA.

(iv) *Reference values in occupationally non-exposed populations*

The values for blood and serum vanadium concentrations obtained by RNAA (Byrne & Kosta, 1978a; Cornelis *et al.*, 1980, 1981; Byrne & Versieck, 1990; Heydorn, 1990; Byrne & Kucera, 1991a,b; Kucera *et al.*, 1992, 1994), by NAA with pre-irradiation separation (Greenberg *et al.*, 1990), by GF–AAS with preconcentration (Ishida *et al.*, 1989; Tsukamoto *et al.*, 1990) and by high-resolution ICP–MS (Moens *et al.*, 1994) suggest that the true normal vanadium concentration in blood and serum of occupationally non-exposed populations is in the range of 0.02–0.1 μg/L. The accuracy of the results obtained by RNAA was confirmed by concomitant analysis of a variety of biological reference materials and comparison of the values obtained with certified or literature values. For the Second Generation Biological Reference Material (freeze-dried human serum), vanadium concentrations of 0.67 ± 0.05 μg/kg (dry mass) and 0.66 ± 0.10 μg/kg (dry mass) obtained by RNAA in two separate studies (Byrne & Versieck, 1990; Byrne & Kucera, 1991a) were consistent with the mean of 0.83 ± 0.09 μg/kg (dry mass) obtained by high-resolution ICP–MS (Moens *et al.*, 1994). These values correspond to serum concentrations of 0.060–0.075 μg/L, which are in the range of the normal vanadium concentrations in blood and/or serum suggested above. [The concentration in μg/kg dry mass can be converted into a concentration in μg/L by dividing by a factor of 11 (Versieck *et al.*, 1988).]

Vanadium concentrations in urine of occupationally non-exposed populations determined by RNAA (Kucera *et al.*, 1994) and by GF–AAS with preconcentration (Buchet *et al.*, 1982; Buratti *et al.*, 1985; Ishida *et al.*, 1989; Minoia *et al.*, 1990) have been shown consistently to have mean values ranging from 0.2 to 0.8 μg/L.

1.2 Production and use

1.2.1 *Production*

Although vanadium is widely dispersed and relatively abundant in the earth's crust, deposits of ore-grade minable vanadium are rare (see Section 1.3.1). The bulk of vanadium production is derived as a by-product or coproduct in processing iron, titanium, phosphorus and uranium ores. Vanadium is most commonly recovered from these ores in the form of pentoxide, but sometimes as sodium and ammonium vanadates.

Only about a dozen vanadium compounds are commercially significant; of these, vanadium pentoxide is dominant (Woolery, 1997; Nriagu, 1998; O'Neil, 2001; Atomix, 2003).

Vanadium was discovered twice. In 1801, Andres Manuel del Rio named it erythronium, but then decided he had merely found an impure form of chromium. Independently, Nils Gabriel Sefstrom found vanadium in 1830, and named it after the Scandinavian goddess of beauty and youth — the metal's compounds provide beautiful colours in solution. Henry Enfield Roscoe first isolated the metal in 1867, from vanadium dichloride. It was not until 1925 that relatively pure vanadium was obtained — by reducing vanadium pentoxide with calcium metal (Atomix, 2003).

According to the US Geological Survey (2002), nearly all the world's supply of vanadium comes from primary sources. Seven countries (China, Hungary, Japan, Kazakhstan, the Russian Federation, South Africa and the USA) recover vanadium from ores, concentrates, slag or petroleum residues. In five of the seven countries, the mining and processing of magnetite-bearing ores was reported to be an important source of vanadium production. Japan and the USA are believed to be the only countries to recover significant quantities of vanadium from petroleum residues. World demand for vanadium fluctuates in response to changes in steel production. It is anticipated to increase due to the demands for stronger and lighter steels and new applications, such as the vanadium battery (Magyar, 2002).

Raw materials processed into vanadium compounds include the titanomagnetite ores and their concentrates, which are sometimes processed directly, vanadium slags derived from ores, oil combustion residues, residues from the hydrometallization process and spent catalysts (secondary raw materials) (Hilliard, 1994; Bauer *et al.*, 2003). Primary industrial compounds produced directly from these raw materials are principally 98% (by weight) fused pentoxide, air-dried (technical-grade) pentoxide and technical-grade ammonium metavanadate (Woolery, 1997).

The titanomagnetite ore in lump form, containing approximately 1.5–1.7% vanadium pentoxide, is first reduced by coal at approximately 1000 °C in directly-heated rotary kilns. A further reduction is then performed in an electric furnace to obtain a pig iron which contains approximately 1.4% vanadium pentoxide. The molten pig iron is oxidized in a shaking ladle, causing the vanadium to be transferred to the slag in the form of a water-soluble trivalent iron spinel. A typical vanadium slag has the following approximate composition: 14% vanadium (equivalent to 25% vanadium pentoxide), 9% metallic iron, 32% total iron, 7% silica, 3.5% manganese, 3.5% titanium, 2.5% magnesium, 2.0% aluminium and 1.5% calcium. This is the world's principal raw material for vanadium production (Hilliard, 1994; Bauer *et al.*, 2003).

The main process used today to produce vanadium pentoxide from vanadium slags is alkaline roasting. The same process, with minor differences, can also be used for processing titanomagnetite ores and vanadium-containing residues. The slag is first ground to < 100 µm, and the iron granules are removed. Alkali metal salts are added, and the material is roasted with oxidation at 700–850 °C in multiple-hearth furnaces or rotary kilns to form water-soluble pentavalent sodium orthovanadate. The roasted product is leached with water, and ammonium polyvanadate or sparingly-soluble ammonium metavanadate are precipitated in crystalline form from the alkaline sodium orthovanadate solution by adding sulfuric or hydrochloric acid and ammonium salts at elevated temperature. These compounds are converted to high-purity, alkali-free vanadium pentoxide by roasting. The usual commercial 'flake' form of vanadium pentoxide is obtained from the solidified melt (Hilliard, 1994; Bauer *et al.*, 2003).

Hydrometallurgical methods or a combination of pyrometallurgical and hydrometallurgical processes are used to produce vanadium oxides and salts from other raw materials. In the combined processes, thermal treatment is followed by alkaline or, more rarely, acid processing (Hilliard, 1994; Bauer *et al.*, 2003).

Uranium production from carnotite and other vanadium-bearing ores also yields significant amounts of vanadium pentoxide (Atomix, 2003).

Total world production of vanadium pentoxide in 1996 was approximately 131 million pounds [59 500 tonnes] (Woolery, 1997). Based on vanadium pentoxide production capacity in 1994 from all sources, it has been estimated that the world's production of vanadium was split as follows: South Africa, 43%; USA, 17%; the Russian Federation, 15%; China, 13%; Venezuela, 4%; Chile, 4%; and others, 4% (Perron, 1994). In 2001, vanadium production capacity was estimated as follows: South Africa, 44%; the Russian Federation, 21%; Australia, 10%; USA, 8%; China, 8%; New Zealand, 4%; Kazakhstan, 2%; Japan, 1%; and others, 4% (Perron, 2001).

Available information indicates that vanadium pentoxide is produced by 12 companies in China, seven companies in the USA, six companies in India, five companies in Japan, four companies in the Russian Federation, two companies each in Germany and Taiwan, China, and one company each in Austria, Brazil, France, Kazakhstan, South Africa and Spain (Chemical Information Services, 2003).

1.2.2 *Use*

The major use of vanadium pentoxide is in the production of metal alloys. Iron–vanadium and aluminium–vanadium master alloys (e.g. for automotive steels, jet engines and airframes) are produced preferably from vanadium pentoxide fused flakes because of the low loss on ignition, low sulfur and dust contents, and high density of the molten oxide compared with powder.

Vanadium pentoxide is also used as an oxidation catalyst in heterogeneous and homogeneous catalytic processes for the production of sulfuric acid from sulfur dioxide, phthalic anhydride from naphthalene or *ortho*-xylene, maleic anhydride from benzene or *n*-butane/butene, adipic acid from cyclohexanol/cyclohexanone, acrylic acid from propane and acetaldehyde from alcohol. Minor amounts are used in the production of oxalic acid from cellulose and of anthraquinone from anthracene. Vanadium pentoxide has not found any significant uses in microelectronics but does have some applications in cathodes in primary and secondary (rechargeable) lithium batteries and in red phosphors for high-pressure mercury lamps and television screens. Vanadium pentoxide is used in the industries of enamelling, electrics and electronics, metallurgy, glass, catalysts, petrochemistry, and paint and ceramics. It is also used as a corrosion inhibitor in industrial processes for the production of hydrogen from hydrocarbons, as a coating for welding electrodes, as ultraviolet absorbent in glass, as depolariser, for glazes, for yellow and blue pigments, as a photographic developer, and in colloidal solution for anti-static layers on photographic material. It is also used as starting material for the production of carbides, nitrides, carbonitrides, silicides, halides, vanadates and vanadium salts (Woolery, 1997; O'Neil, 2001; ACGIH Worldwide®, 2003; Bauer *et al.*, 2003).

1.3 Occurrence and exposure

1.3.1 *Natural occurrence*

Vanadium is widely but sparsely distributed in the earth's crust at an average concentration of 150 mg/kg and is found in about 80 different mineral ores, mainly in phosphate rock and iron ores. The concentration of vanadium measured in soil appears to be closely related to that of the parent rock from which it is formed and a range of 3–300 mg/kg has been recorded, with shales and clays exhibiting the highest concentrations (200 mg/kg and 300 mg/kg, respectively) (Byerrum *et al*., 1974; Waters, 1977; WHO, 1988; Nriagu, 1998).

Vanadium is also found in fossil fuels (oil, coal, shale). It is present in almost all coals, in concentrations ranging from extremely low to 10 g/kg. It is found in crude oil and residual fuel oil, but not in distillate fuel oils. Venezuelan crude oils are thought to have the highest vanadium content, reaching 1400 mg/kg. Flue-gas deposits from oil-fired furnaces have been found to contain up to 50% vanadium pentoxide. In crude oil, residual fuel oil and asphaltenes, the most common form of vanadium is the +4 oxidation state (Byerrum *et al*., 1974; Lagerkvist *et al.*, 1986; WHO, 1988; Nriagu, 1998).

1.3.2 *Occupational exposure*

Exposure to vanadium pentoxide in the workplace occurs primarily during the processing and refining of vanadium-rich ores and slags, during production of vanadium and vanadium-containing products, during combustion of fossil fuels (especially oil), during the handling of catalysts in the chemical industry, and during the cleaning of oil-fuelled boilers and furnaces (Plunkett, 1987). Data on vanadium concentrations in workplace air and the urine of workers exposed to vanadium in various industries are summarized in Table 2.

The processing of metals containing vanadium includes chemical treatment and high-temperature operations. However, only moderate concentrations of vanadium have been recorded in air in the breathing zone of workers engaged in these operations: 0.006–0.08 mg/m^3 during the addition of vanadium to furnaces, 0.004–0.02 mg/m^3 during tapping, 0.008–0.015 mg/m^3 during oxyacetylene cutting and 0.002–0.006 mg/m^3 during arc-welding (WHO, 1988).

In the main work areas of vanadium pentoxide production facilities where vanadium slag is processed, Roshchin (1968) recorded vanadium concentrations in dust of 20–55 mg/m^3 (reported to be mainly vanadium trioxide) and < 0.17 mg/m^3 vanadium pentoxide (cited by WHO, 1988). In another study in a vanadium pentoxide production plant, Kucera *et al.* (1998) recorded the highest concentration of total air particulates of 271 mg/m^3 at a pelletizer, with a corresponding vanadium concentration of 0.5 mg/m^3; the highest concentrations of vanadium were detected in air at a vibratory conveyer and reached 4.9 mg/m^3. Similarly high concentrations of vanadium (4.7 mg/m^3) were reported in air in the breathing zone of workers in the steel industry (Kiviluoto *et al*., 1979).

Breaking, loading and unloading, crushing and grinding, and magnetic separation of vanadium slag (about 120 g/kg vanadium pentoxide) causes formation of thick dust, with vanadium concentrations of 30–120 mg/m^3. About 70–72 % of the particles were reported to have a diameter of < 2 μm and 86–96% a diameter of < 5 μm. When the slag is roasted, free vanadium pentoxide is discharged and concentrations of vanadium in the vicinity of the furnace have been found to range from 0.04 to 1.56 mg/m^3. During leaching and precipitation, vanadium concentrations in the air can exceed 0.5 mg/m^3. Smelting and granulation of technical-grade vanadium pentoxide are accompanied by the formation of a vanadium-containing aerosol. During the loading of smelting furnaces, vanadium pentoxide concentrations in the surrounding air have been found to range from 0.15 to 0.80 mg/m^3; during smelting and granulation, from 0.7 to 11.7 mg/m^3; during the crushing, unloading and packaging of pure vanadium pentoxide, dusts are formed in the facilities and concentrations of 2.2–49 mg/m^3 vanadium pentoxide in air have been recorded (Roshchin, 1968; cited by WHO, 1988).

In the production of ferrovanadium alloys, a continuous discharge of vanadium pentoxide occurs during the smelting process. Vanadium pentoxide concentrations in air were reported to be 0.1–2.6 mg/m^3 in the work area of smelters and helpers, 2–124.6 mg/m^3 during charging of vanadium pentoxide in furnace, 0.07–9.43 mg/m^3 in the crane driver's cabin during smelting, 0.97–12.6 mg/m^3 during cutting up of ferrovanadium and 7.5–30 mg/m^3 during furnace maintenance (Roshchin, 1968; cited by WHO, 1988).

When ductile vanadium is produced by the aluminothermic process (based on the reduction of pure vanadium pentoxide with aluminium), a condensation aerosol of vanadium pentoxide is released, with 98% of the particles having a diameter of < 5 μm and 82% a diameter of < 2 μm. Vanadium pentoxide concentrations recorded in the surrounding air were 19–25.1 mg/m^3 during the preparation of the charge mixture, 64–240 mg/m^3 during placing of the burden inside the smelting chambers and 0.2–0.6 mg/m^3 in smelting operator's workplace (Roshchin, 1968; cited by WHO, 1988).

Usutani *et al.* (1979) measured vanadium pentoxide concentrations in air in a vanadium refinery. The highest concentrations (> 1 mg/m^3) were detected in samples collected during removal of vanadium pentoxide flakes from the slag (cited by WHO, 1988).

In facilities producing aluminium from bauxite, concentrations of vanadium pentoxide up to 2.3 mg/m^3 have been recorded in workplace air during tapping, packing and loading (Roshchin, 1968; cited by WHO, 1988).

Workers may be exposed to vanadium pentoxide in air during the handling of catalysts in chemical manufacturing plants. Exposure depends on the type of operations being carried out. During the removal and replacement of the catalyst, exposure to 0.01–0.67 mg/m^3 have been reported. Sieving of the catalyst can lead to higher exposures, and concentrations between 0.01 and 1.9 mg/m^3 (total inhalable vanadium) have been observed. Air-fed respiratory protective equipment is normally worn during catalyst removal and replacement and sieving (WHO, 2001).

Concentrations of vanadium pentoxide in the air during vanadium catalyst production have been reported as 1–7 mg/m^3 during grinding and unloading of vanadium pentoxide, 3.2–7.5 mg/m^3 during loading into the bin and 0.1–1 mg/m^3 during sifting and packing granules of contact substance (Roshchin, 1968; cited by WHO, 1988).

Hery *et al.* (1992) assessed exposures to chemical pollutants during the handling (loading and unloading of reactors, sieving of catalysts) of inorganic catalysts, including vanadium pentoxide. Concentrations of vanadium pentoxide in air were reported to be 0.08–0.9 mg/m^3 during unloading, 1.1–230 mg/m^3 during screening and 600–1200 mg/m^3 during loading.

Hery *et al.* (1994) assessed exposures during the manufacture and reprocessing of inorganic catalysts, including vanadium pentoxide. In one of four 1-h air samples taken in a reprocessing plant during the oven-cleaning operation, a vanadium pentoxide concentration of 2.2 mg/m^3 was measured.

Fuel oil combustion results in the formation of vanadium-containing dust, and large amounts of dust result from operations connected with removal of ash encrustations when cleaning boilers and the blades of gas turbines. Dust concentrations in the air inside the boilers have been reported to range from 20 to 400 mg/m^3, the most common range being 50–100 mg/m^3, with the dust containing 5–17% vanadium pentoxide (Roshchin, 1968; cited by WHO, 1988).

Occupational exposure to vanadium occurs during the cleaning of oil-fired boilers and furnaces in oil-fired heating and power plants and ships, although workers probably spend less than 20% of their time cleaning oil-fired boilers. Vanadium concentrations in air (total inhalable fraction) as high as 20 mg/m^3 were recorded when these tasks were performed, but typically were lower than 0.1 mg/m^3. The lowest results were obtained where wet cleaning methods were used. Respiratory protective equipment was usually worn during boiler cleaning operations (WHO, 2001).

Williams (1952) published air sampling data on boiler-cleaning operations in the British power industry. A vanadium concentration of 40.2 mg/m^3 was recorded in air in the superheater chamber, while the concentration was 58.6 mg/m^3 in the combustion chamber; 93.6% of the dust particles had a diameter of 0.15–1 μm (cited by WHO, 1988).

Kuzelova *et al.* (1977) reported dust concentrations during boiler-cleaning operations of about 136–36 000 mg/m^3 in the workplace air, in which vanadium concentrations ranged from 1.7 to 18.4 mg/m^3 (cited by WHO, 1988).

Barisione *et al.* (1993) assessed the acute exposure to vanadium pentoxide in maintenance personnel working inside an oil-fired boiler at an electric power station in Italy. The vanadium pentoxide concentration in the air in the work room was 0.28 mg/m^3, which exceeded exposure standards. The concentration of vanadium in the urine of the arc welders did not correlate with vanadium pentoxide concentration in the air (see Table 2).

In 26 boilermakers overhauling an oil-powered boiler in the USA, Hauser *et al.* (1995a) investigated exposure to air particulates with an aerodynamic diameter of $\leq$ 10 μm (PM_{10}) and respirable vanadium-containing dust for up to 15 work days. The peak PM_{10} concentration (1- to 10-h TWA) ranged from 1.48 to 7.30 mg/m^3; the peak vanadium concentration ranged from 2.2 to 32.2 μg/m^3, with a mean (SD) of 20.2 (11.4) μg/m^3. In a later study, the authors determined vanadium concentrations in the urine of a subgroup of workers (Hauser *et al.*, 1998; see Table 2).

In another study of boilermakers overhauling an oil-fired boiler in the USA, lower exposures to PM_{10} particulates and to respirable vanadium-containing dust were reported (median, 0.6 mg/m^3 and 12.7 μg/m^3, respectively) (Woodin *et al.*, 1999).

The National Institute of Occupational Safety and Health in the USA conducted surveys on exposure to vanadium pentoxide in the industry. The National Occupational Hazard Survey, conducted in 1972–74, estimated that 2562 workers in 333 plants were potentially exposed to vanadium pentoxide in 1970. The largest number of workers exposed worked in the stone, clay and glass products industries, and the second largest group was involved with electric, gas and sanitary services (National Institute for Occupational Safety and Health, 1976). The National Occupational Exposure Survey, conducted in 1980–83, reported that approximately 5319 workers in 151 plants were potentially exposed to vanadium in 1980. Among them, 84% were exposed specifically to vanadium pentoxide. The largest number of workers were exposed in the chemical and allied products industry (National Institute for Occupational Safety and Health, 1984).

Workers in the manufacture of vanadium-containing pigments for the ceramics industry may be exposed to vanadium compounds. Exposure is controlled by the use of local exhaust ventilation, and data indicate that vanadium concentrations in air are normally below 0.2 mg/m^3 (total inhalable fraction) (WHO, 2001).

Other reports of occupational exposures to vanadium have been reviewed (Zenz, 1994).

1.3.3 *Environmental exposure*

(*a*) *Air*

(i) *Natural sources*

Natural sources of atmospheric vanadium include continental dust, marine aerosols (sea salt sprays) and volcanic emissions. The quantities entering the atmosphere from each of these sources are uncertain; however, continental dust is believed to account for the largest portion of naturally-emitted atmospheric vanadium; contributions from volcanic emissions are believed to be small (Zoller *et al.*, 1973; Byerrum *et al.*, 1974). Atmospheric emissions of vanadium from natural sources had been estimated at 70 000 to 80 000 tonnes per year. However, more recent estimates report much lower values (1.6–54.2 tonnes per year) and suggest that fluxes from natural sources were overestimated by earlier workers (Mamane & Pirrone, 1998; Nriagu & Pirrone, 1998).

Concentrations of vanadium in the atmosphere in unpopulated areas such as Antarctica have been found to range from 0.0006 to 0.0024 ng/m^3 (Zoller *et al.*, 1974). Measurements taken over the eastern Pacific Ocean averaged 0.17 ng/m^3 (range of means, ≤ 0.02–0.8 ng/m^3) (Hoffman *et al.*, 1969). Measurements over rural north-western Canada and Puerto Rico were one order of magnitude higher (0.2–1.9 ng/m^3) (Martens *et al.*, 1973; Zoller *et al.*, 1973).

(ii) *Anthropogenic sources*

Estimates of global anthropogenic emissions of vanadium into the atmosphere over the last decade range from 70 000 tonnes to 210 000 tonnes per year (Hope, 1994; Mamane & Pirrone, 1998; Nriagu & Pirrone, 1998).

The major point sources are metallurgical works (30 kg vanadium/tonne vanadium produced), and coal and residual oil burning (0.2–2 kg vanadium/1000 tonnes and 30–300 kg/10^6 L burnt, respectively) (Zoller *et al*., 1973; Lagerkvist *et al*., 1986). Crude oils have an average vanadium content of 50 mg/kg (see above). [*Residual fuel oils* (heavy fuel oils) are petroleum refining residues remaining after distillation or cracking, and blends of these residues with distillates. They are used primarily in industrial burners and boilers as sources of heat and power (IARC, 1989). During refining and distillation, the vanadium remains in the residual oil because of its low volatility, and as a result becomes more concentrated than in the original crude.] During combustion, most of the vanadium in residual oils is released into the atmosphere in the form of vanadium pentoxide as part of fly ash particulates. Vanadium concentrations in coal fly ash range from 0.1 to 1 mg/g, and in residual oil from 10 to 50 mg/g (Mamane & Pirrone, 1998).

Vanadium was found in 87% of all air samples taken in the vicinity of large metallurgical plants at concentrations in the range of 0.98–1.49 μg/m^3, and in 11% of the samples exceeded 2 μg/m^3 (Pazhynich, 1967). At a steel plant in the USA in 1967, concentrations of vanadium in ambient air ranged from 40 to 107 ng/m^3 and averaged 72 ng/m^3 (WHO, 1988). Concentrations as high as 1000 ng/m^3 vanadium pentoxide were found in air by Pazhynich (1967) in the former Soviet Union at a site 1500 m from areas of extensive metallurgical activity unconnected with vanadium production. In the same country, near a plant producing technical vanadium pentoxide, 24-h mean concentrations of vanadium pentoxide of 4–12, 1–6, and 1–4 μg/m^3 in air were recorded at distances of 500, 1000 and 2000 m from the source, respectively (WHO, 1988).

According to the US Toxic Release Inventory (TRI, 1987–2001), the amount of vanadium released into the atmosphere from manufacturing and processing facilities in the USA fluctuated between 5–9 tonnes between 1987 and 1997 and had dramatically increased to over 100 tonnes by 2001. However, this estimate is believed to be limited because the largest anthropogenic releases of vanadium to the atmosphere are attributed to the combustion of residual fuel oils and coal, which are probably not included.

Vanadium-containing particulates emitted from anthropogenic sources into the atmosphere are simple or complex oxides (Byerrum *et al*., 1974) or may be associated with sulfates (Mamane & Pirrone, 1998). Generally, lower oxides formed during combustion of coal and residual fuel oils, such as vanadium trioxide, undergo further oxidation to the pentoxide form before leaving the stacks (Environmental Protection Agency, 1985).

Concentrations of vanadium measured in ambient air vary widely between rural and urban locations; in general, these are higher in urban than in rural areas. Earlier reports suggested concentrations of 1–40 ng/m^3 (van Zinderen Bakker & Jaworski, 1980) or 0.2–75 ng/m^3 (Environmental Protection Agency, 1977) in air in rural sites, although the annual average was below 1 ng/m^3. This was attributed to the local burning of fuel oils with a high vanadium content. Recent data from rural areas show concentrations ranging from 0.3 to about 5 ng/m^3, with annual averages frequently below 1 ng/m^3, which can be regarded as the natural background concentration in rural areas (Mamane & Pirrone, 1998).

Annual average concentrations of vanadium in air in large cities may often be in the range of 50–200 ng/m^3, although concentrations exceeding 200–300 ng/m^3 have been recorded, and the maximum 24-h average may exceed 2000 ng/m^3 (WHO, 1988). In the USA, cities can be divided into two groups based on the concentrations of vanadium present in their ambient air. The first group consists of cities widely distributed throughout the USA and characterized by vanadium concentrations in ambient air that range from 3 to 22 ng/m^3, with an average of 11 ng/m^3. Cities in the second group, primarily located in the north-eastern USA, have mean concentrations of vanadium that range from 150 to 1400 ng/m^3, with an average of about 600 ng/m^3. The difference is attributed to the use of large quantities of residual fuel oil in cities in the second group for the generation of heat and electricity, particularly during winter months (Zoller *et al.*, 1973; WHO, 2000). Vanadium concentrations in ambient urban air vary extensively with the season. However, there are indications that vanadium concentrations in urban locations in 1998 were lower than those reported in the 1960s and 1970s (Mamane & Pirrone, 1998).

Hence, the general population may be exposed to airborne vanadium through inhalation, particularly in areas where use of residual fuel oils for energy production is high (Zoller *et al.*, 1973). For instance, assuming vanadium concentrations in air of approximately 50 ng/m^3, Byrne and Kosta (1978b) estimated a daily intake of 1 μg vanadium by inhalation.

(*b*) *Water*

Vanadium dissolved in water is present almost exclusively in the pentavalent form. Its concentration ranges from approximately 0.1 to 220 μg/L in fresh water and from 0.3 to 29 μg/L in seawater. The highest concentrations in fresh waters were recorded in the vicinity of metallurgical plants or downstream of large cities (WHO, 1988; Bauer *et al.*, 2003). Anthropogenic sources account for only a small percentage of the dissolved vanadium reaching the oceans (Hope, 1994).

(*c*) *Food*

Vanadium intake from food has been reasonably well established, based on the analysis of dietary items (Myron *et al.*, 1977; Byrne & Kosta, 1978b; Minoia *et al.*, 1994) and total diets (Myron *et al.*, 1978; Byrne & Kucera, 1991a). Considering consumption of about 500 g (dry mass) total diet, daily dietary vanadium intake in the general population has been estimated at 10–30 μg per person per day, although it can reach 70 μg per day in some countries (Byrne & Kucera, 1991a).

An increased daily intake of vanadium may result from the consumption of some wild-growing mushrooms (Byrne & Kosta, 1978b) and some beverages (Minoia *et al.*, 1994), especially beer. Contamination of the marine environment with oil in the Gulf War resulted in increased concentrations of vanadium in certain seafood (WHO, 2001).

Considering the poor absorption of vanadium from the gastrointestinal tract, dietary habits can be expected to have only a minor influence on vanadium concentrations in body fluids (WHO, 1988; Sabbioni *et al.*, 1996) (see Section 4.1).

1.4 Regulations and guidelines

Occupational exposure limits and guidelines for vanadium pentoxide in workplace air are presented in Table 3.

ACGIH Worldwide® (2003) recommends a semi-quantitative BEI for vanadium in urine of 50 μg/g creatinine. ACGIH recommends monitoring vanadium in urine collected at the end of the last shift of the work week as an indicator of recent exposure to vanadium pentoxide. Germany recommends a biological tolerance value for occupational exposure for vanadium in urine of 70 μg/g creatinine. Germany also recommends monitoring vanadium in urine collected at the end of the exposure, for example at the end of the shift or, for long-term exposures, after several shifts (Deutsche Forschungsgemeinschaft, 2002).