ENVIRONMENTAL CONTAMINANTS ENCYCLOPEDIA

VANADIUM ENTRY

July 1, 1997

COMPILERS/EDITORS:

ROY J. IRWIN, NATIONAL PARK SERVICE

WITH ASSISTANCE FROM COLORADO STATE UNIVERSITY
STUDENT ASSISTANT CONTAMINANTS SPECIALISTS:

MARK VAN MOUWERIK
LYNETTE STEVENS
MARION DUBLER SEESE
WENDY BASHAM

NATIONAL PARK SERVICE
WATER RESOURCES DIVISIONS, WATER OPERATIONS BRANCH
1201 Oakridge Drive, Suite 250
FORT COLLINS, COLORADO 80525

WARNING/DISCLAIMERS:

Where specific products, books, or laboratories are mentioned, no official U.S. government endorsement is intended or implied.

Digital format users: No software was independently developed for this project. Technical questions related to software should be directed to the manufacturer of whatever software is being used to read the files. Adobe Acrobat PDF files are supplied to allow use of this product with a wide variety of software, hardware, and operating systems (DOS, Windows, MAC, and UNIX).

This document was put together by human beings, mostly by compiling or summarizing what other human beings have written. Therefore, it most likely contains some mistakes and/or potential misinterpretations and should be used primarily as a way to search quickly for basic information and information sources. It should not be viewed as an exhaustive, "last-word" source for critical applications (such as those requiring legally defensible information). For critical applications (such as litigation applications), it is best to use this document to find sources, and then to obtain the original documents and/or talk to the authors before depending too heavily on a particular piece of information.

Like a library or many large databases (such as EPA's national STORET water quality database), this document contains information of variable quality from very diverse sources. In compiling this document, mistakes were found in peer reviewed journal articles, as well as in databases with relatively elaborate quality control mechanisms [366,649,940]. A few of these were caught and marked with a "[sic]" notation, but undoubtedly others slipped through. The [sic] notation was inserted by the editors to indicate information or spelling that seemed wrong or misleading, but which was nevertheless cited verbatim rather than arbitrarily changing what the author said.

Most likely additional transcription errors and typos have been added in some of our efforts. Furthermore, with such complex subject matter, it is not always easy to determine what is correct and what is incorrect, especially with the "experts" often disagreeing. It is not uncommon in scientific research for two different researchers to come up with different results which lead them to different conclusions. In compiling the Encyclopedia, the editors did not try to resolve such conflicts, but rather simply reported it all.

It should be kept in mind that data comparability is a major problem in environmental toxicology since laboratory and field methods are constantly changing and since there are so many different "standard methods" published by EPA, other federal agencies, state agencies, and various private groups. What some laboratory and field investigators actually do for standard operating practice is often a unique combination of various standard protocols and impromptu "improvements." In fact, the interagency task force on water methods concluded that [1014]:

> It is the exception rather than the rule that water-quality monitoring data from different programs or time periods can be compared on a scientifically sound basis, and that...
>
> No nationally accepted standard definitions exist for water quality parameters. The different organizations may collect data using identical or standard methods, but identify them by different names, or use the same names for data collected by different methods [1014].

Differences in field and laboratory methods are also major issues related to (the lack of) data comparability from media other than water: soil, sediments, tissues, and air.

In spite of numerous problems and complexities, knowledge is often power in decisions related to chemical contamination. It is therefore often helpful to be aware of a broad universe of conflicting results or conflicting expert opinions rather than having a portion of this information arbitrarily censored by someone else. Frequently one wants to know of the existence of information, even if one later decides not to use it for a particular application. Many would like to see a high percentage of the information available and decide for themselves what to throw out, partly because they don't want to seem uniformed or be caught by surprise by potentially important information. They are in a better position if they can say: "I knew about that data, assessed it based on the following quality assurance criteria, and decided not to use it for this application." This is especially true for users near the end of long decision processes, such as hazardous site cleanups, lengthy ecological risk assessments, or complex natural resource damage assessments.

For some categories, the editors found no information and inserted the phrase "no information found." This does not necessarily mean that no information exists; it simply means that during our efforts, the editors found none. For many topics, there is probably information "out there" that is not in the Encyclopedia. The more time that passes without encyclopedia updates (none are planned at the moment), the more true this statement will become. Still, the Encyclopedia is unique in that it contains broad ecotoxicology information from more sources than many other reference documents. No updates of this document are currently planned. However, it is hoped that most of the information in the encyclopedia will be useful for some time to come even without updates, just as one can still find information in the 1972 EPA Blue Book [12] that does not seem well summarized anywhere else.

Although the editors of this document have done their best in the limited time available to insure accuracy of quotes or summaries as being "what the original author said," the proposed interagency funding of a bigger project with more elaborate peer review and quality control steps never materialized.

> The bottom line: The editors hope users find this document useful, but don't expect or depend on perfection herein. Neither the U.S. Government nor the National Park Service make any claims that this document is free of mistakes.

The following is one chemical topic entry (one file among 118). Before utilizing this entry, the reader is strongly encouraged to read the README file (in this subdirectory) for an introduction, an explanation of how to use this document in general, an explanation of how to search for power key section headings, an explanation of the organization of each entry, an information quality discussion, a discussion of copyright issues, and a listing of other entries (other topics) covered.

See the separate file entitled REFERENC for the identity of numbered references in brackets.

HOW TO CITE THIS DOCUMENT: As mentioned above, for critical applications it is better to obtain and cite the original publication after first verifying various data quality assurance concerns. For more routine applications, this document may be cited as:

> **Irwin, R.J., M. VanMouwerik, L. Stevens, M.D. Seese**, and **W. Basham.** 1997. Environmental Contaminants Encyclopedia. National Park Service, Water Resources Division, Fort Collins, Colorado. Distributed within the Federal Government as an Electronic Document (Projected public availability

on the internet or NTIS: 1998).

Vanadium (V, CAS number 7440-62-2)

Brief Introduction:

Br.Class: General Introduction and Classification Information:

Vanadium is a natural element in the earth. It is a white to gray metal which is often found as crystals. It has no particular odor. In the environment it is usually combined with other elements such as oxygen, sodium, sulfur, or chloride. The forms of vanadium most likely to be found at waste sites are not well known. One man-made form, vanadium oxide (vanadium bound to oxygen), is most often used by industry in making steel. Vanadium oxide can be a yellow-orange powder, dark-grey flakes, or yellow crystals. Much smaller amounts are used in making rubber, plastics, ceramics, and certain other chemicals [943].

Vanadium is a transition metal with complex aqueous geochemistry [190]. Vanadium is a bright white metallic chemical element of the first series of transition metals [254].

Vanadium is ubiquitous in the biosphere, resulting in detectable trace levels in most living organisms [983]. Increases in human-induced vanadium emissions, due to the combustion of fossil fuels, now equal natural emissions from continental dust, marine aerosols, and volcanic activity [983].

Vanadium is often found in ore along with uranium [190]. About 80% of the production of vanadium is used to make ferrovanadium or as a steel additive [254].

Vanadium is found in many petroleum products. Vanadium occurs naturally in fuel oils (see fuel oil entries) and coal [943]. It is also a by-product of petroleum refining [494]. The extraction of vanadium from petroleum ash is a possible future source of the element [254].

Natural vanadium consists of two isotopes, V-50 and V-51, the former being slightly radioactive with a half-life of 6x10E+15 years [254]. Seven other radioisotopes of the element have been synthesized [254].

Br.Haz: General Hazard/Toxicity Summary:

Potential hazards to fish, wildlife, invertebrates, plants, and other non-human biota:

Vanadium and its compounds are toxic, though this toxicity is variable [254,669,494]. Toxicity depends on the valence; it increases with increasing valence, with pentavalent vanadium being most toxic. In addition, vanadium is toxic as a cation & as an anion (National Research Council. Drinking Water & Health Volume 1. Washington, DC: National Academy Press, 1977. 297) [940].

In studies of subsurface agricultural irrigation drainage waters of the San Joaquin Valley of California, vanadium was determined to be a "substance of concern, additional data needed" [445].

Small amounts of vanadium in the environment tend to stimulate plants but large amounts are toxic [951]. It is considered to be one of the 14 most noxious heavy metals [83].

Vanadium toxicity is attributed to its ability to inhibit enzyme systems such as monoamine oxidase, atpase, tyrosinase, choline esterase, & cholesterol synthetase (Luckey, T.D. and B. Venugopal. Metal Toxicity in Mammals, 1. New York: Plenum Press, 1977. 180) [940].

While vanadate (vanadium in the +5 state) is recognized to be the inhibitor of several Na-K ATPases, these enzymes are largely unaffected by the reduced +4 form of vanadium. Therefore, reduction of +5 forms to +4 forms represents an effective means of reducing the impact of vanadium on a living system [983].

> Additional Detail: The following paragraphs were summarized from a 1985 study on the potential of vanadium to inhibit Na-K ATPases in plants [983]:
>
> > Results of this study, which explored the similarity between both plant uptake and transport of both the +4 and +5 ionic states of vanadium, support the hypothesis of biotransformation of vanadium during root uptake by whole plants. Although the extent of reduction is unclear, this process seems to generally involve the reduction of +5 vanadium to +4. Even at a pH of 7, the presence of chelating agents (such as ketones, aldehydes, etc.) in the cell walls would indicate the potential of ready reduction of vanadium by root

tissues. The resulting +4 complexes would be extremely stable, thus rendering the bulk of any free space vanadium physiologically unavailable. Therefore, the interaction of vanadium with common organic constituents of living matter currently appears to control vanadate's disruptive potential.

Although this reduction of +5 vanadium to +4 leading to the immobilization of vanadium within the root tissue is hypothesized to occur, it does not preclude the possibility that vanadium in the +5 state is also present in these tissues. Considering the ubiquitous nature of Na-K ATPases in the membrane system, and the ability of vanadium in the +5 state (vanadate) to inhibit Na-K ATPases, the effects of vanadate on all living systems are potentially catastrophic. Given the marked increase in human-induced atmospheric vanadium concentrations, conditions may be created which allow free access to vanadate ions in living systems.

Potential hazards to humans:

Inhalation is the main pathway of exposure in the work environment (production of vanadium & its compounds, boiler cleaning). Exposure of the general population by way of food & air is low (Friberg, L., Nordberg, G.F., Kessler, E. and Vouk, V.B. , eds,. Handbook of the Toxicology of Metals. 2nd ed. Vols I, II.: Amsterdam: Elsevier Science Publishers B.V., 1986.,p. V2 639) [940].

Vanadium fumes are highly toxic [669]. In humans, the toxic action of vanadium is largely confined to the respiratory tract (bronchitis and other maladies); a greenish blackish tongue is one sign of industrial exposure to vanadium pentoxide dust [494]. In humans, a big concern is for respirable dust [494,620].

The degree of vanadium toxicity depends largely on the dispersion & solubility of vanadium aerosols in biologic media (National Research Council. Drinking Water & Health Volume 1. Washington, DC: National Academy Press, 1977. 297) [940].

In the consolidated form, vanadium metal & its alloys pose no particular health or safety hazard.

The toxicity of vanadium alloys may depend upon other components in the alloy. (Kirk-Othmer Encyclopedia of Chemical Technology. 3rd ed., Volumes 1-26. New York, NY: John Wiley and Sons, 1978-1984.,p. 23, 83, 684) [940].

A comprehensive toxicological profile for vanadium, especially as it relates to human health, is available from ATSDR [943]. Due to lack of time, important highlights from this ATSDR document have not yet been completely incorporated into this entry.

Bionecessity:

Although vanadium is recognized as an essential element for certain species of algae, there is much debate on the role of vanadium in the metabolism in higher plants and organisms [983]. Morrell et al. (1985) state that there was only circumstantial evidence that vanadium was an essential element in animals and humans, although recent findings on the role of vanadium in Na-K ATPases inhibition may prove to challenge that belief [983].

Several reports suggest that vanadium is an essential element for chicks & rats. However, the evidence for this is tenuous because of difficulties in obtaining a consistent set of signs that are indicative of vanadium deprivation. Apparently, the difficulty is related to the sensitivity of vanadium metabolism to changes in the composition of the diet. It may be necessary to find a specific physiological role for vanadium in order to establish its essentiality. The nutritional significance of vanadium is unclear because of the incomplete knowledge concerning the conditions that produce apparent vanadium deficiency & the dietary components that affect vanadium metabolism. As a result, it is difficult to suggest a vanadium requirement for any animal species, incl humans (National Research Council. Drinking Water and Health. Volume 3. Washington, DC: National Academy Press, 1980. 352) [940].

Essential for the growth of fungi & algae; it stimulates photosynthesis in higher plants & is an oxygen carrying metal in some invertebrates (Venugopal, B. and T.D. Luckey. Metal Toxicity in Mammals, 2. New York: Plenum Press, 1978. 220) [940].

Br.Car: Brief Summary of Carcinogenicity/Cancer Information:

EPA 1996 IRIS database information [893]:

Carcinogenicity Assessment: empty

Vanadium is a questionable carcinogen with experimental tumorigenic data [620].

An acceptable assessment of carcinogenic potential in humans cannot be made [943].

In studies that looked for health effects other than cancer, rats and mice that drank water containing vanadium or breathed in air containing vanadium throughout their lives did not have more tumors than animals that were not exposed to vanadium [943].

Not considered a carcinogen for certain EPA modeling efforts (PRG, RBC) [868,903].

Various concentrations of ammonium metavanadate, vanadyl sulfate trihydrate and ortho sodium vanadate were tested in a human tumor cloning assay. Vanadium salts at low concentrations (10-10 M) can stimulate in vitro colony formation from human tumors. At higher concentrations (> 10-10 M) tumor colony formation is inhibited (Hanauske U et al; Int J Cell Cloning 5 (2): 170-8, 1987) [940].

Br.Dev: Brief Summary of Developmental, Reproductive, Endocrine, and Genotoxicity Information:

Some vanadium compounds have mutation effects [669]. Dietary vanadium has been shown to suppress egg production of laying hens [57]. However, no direct information is available on developmental effects of vanadium in humans [943].

Developmental effects in animals have been minor. Because these effects were so minor and do not have correlation to human development, the relevance of these animal findings to developmental effects in humans is not known [943].

Pregnant Sprague-Dawley rats given orally 20 mg/kg/day of vanadium (as sodium metavanadate) displayed embryotoxicicity but no teratogenicity (Paternain JL et al; Rev Esp Fisiol 43 (2): 223-8, 1987) [940].

Autopsy data have not provided detectable levels of vanadium in human reproductive organs [943]. Only one animal study was located that specifically tests the effects of vanadium on reproduction. In this well-conducted rat study, no adverse effects on fertility, reproduction, or parturition were noted when male and female rats were exposed to sodium metavanadate and then mated [943].

The only information on genotoxicity of vanadium is from in vitro studies. The majority of these studies show positive effects in test systems using bacteria, yeast, and mouse cells in culture for end points such as recombination repair, gene mutation, or DNA synthesis [943].

Br.Fate: Brief Summary of Key Bioconcentration, Fate, Transport, Persistence, Pathway, and Chemical/Physical Information:

Preliminary data suggests the potential for bioaccumulation or bioconcentration of vanadium is low or limited for the following biota: mammals, birds, and fish. It appears to be high to very high for mollusks, crustacea, and lower animals and moderate for higher plants, mosses, lichens, and algae [83]. Vanadium has natural affinity for fats & oils [366,494].

Vanadium is found in soil and is deposited in water as a result of fallout from air pollution [83]

If vanadium is in the air, humans can breathe it and it is thus transported to lungs. Most of it leaves the human body in the air breathed out, but some stays in the lungs. The part that isn't breathed out can go through human lungs and get into the bloodstream. Humans may eat or drink small amounts of vanadium in food and water. Most of this does not enter the bloodstream, but leaves the body in feces. However, small amounts that are swallowed can enter the bloodstream. Most of the vanadium that enters the bloodstream leaves the human body quickly in the urine. If human get vanadium on their skin, it is unlikely that it will enter their bodies by passing through skin [943].

The most likely way for the chemical to get into the air is when fuel oil is burned. When rocks and soil containing vanadium are broken down into dusts by wind and rain, vanadium can get into the air, groundwater, surface water, or soil. It does not dissolve well in water, but it can be carried by the water, much as particles of sand might be carried [943].

Plants take up vanadium from soil, groundwater, surface water, and air pollution [83]. Animals take up vanadium from contaminated air, contaminated water, and contaminated food [83].

Natural vanadium consists of two isotopes, V-50 and V-51, the former being slightly radioactive with a half-life of 6E+15 years [254].

The outer electronic configuration of vanadium exhibits oxidation states of -1, 0, +1, +2, +3, +4, and +5 in a wide variety of complex ions and coordination complexes [254]. Three oxidation states (+3 to +5) can be stable in water [190]. These three states are the only forms with any biological significance [983]. The +4 and +5 states are the most significant oxidation states in living organisms, while the +3 state occurs solely in one group of marine chordates [983].

In aqueous solution, vanadium in the +5 state exists as various oxoions referred to as "vanadates." The exact nature of the vanadate species in solution is pH and concentration dependant. Also, the exact species present cannot be determined unless the solution is allowed to stand for many days since equilibrium among species is slowly attained [983].

The chemistry of vanadium in the +4 state centers around the VO(2+) ion. This species undergoes a number of hydrolysis reactions with increasing solution pH. At lower pH (< 5.0), VO(2+) and VOOH(+) dominate, whereas at more alkaline pH (> 5.0), a variety of forms prevail. In an alkaline environment, these ionic forms are also subject to air oxidation in the absence of suitable chelating agents [983].

Both the +4 and +5 oxidation states have a notable tendency to form stable chelates with a variety of organic and inorganic ligands (such as ketones, aldehydes, catechols, amino compounds and phenols). Chelate formation can alter the oxidation state from +5 to +4 [983].

Synonyms/Substance Identification:

Molecular Formula [940]:
V

Associated Chemicals or Topics (Includes Transformation Products):

Relationships between this metal versus indicator plants, other metals, and various rock types was summarized by Brooks in 1972 [951].

Certain uranium deposits contain appreciable quantities of vanadium [951].

Concentrations of vanadium in selenium rich soils tends to be high [951]. Certain contaminants, such as selenium, thorium

230, and vanadium, tend to occur together in and leach out of uranium mining tailing piles in the U.S.; thorium is quite dangerous and is often leached out of acid process uranium piles (Ward Whicker, Colorado State University, personal communication, 1996).

Vanadium pentoxide and many other vanadium compounds are associated compounds.

Even at maximum tolerated concentration, vanadium did not increase metallothionein (Bracken WM, Klaassen CD; J Toxicol Environ Health 22 (2): 163-74, 1987) [940].

Water Data Interpretation, Concentrations and Toxicity (All Water Data Subsections Start with "W."):

W.Low (Water Concentrations Considered Low):

No information found.

W.High (Water Concentrations Considered High):

No information found.

W.Typical (Water Concentrations Considered Typical):

Typical Freshwater Concentrations: EPA 1981: 0.001 mg/l [83].

Median Concentration Large North American Rivers: USGS 1985: 0.9 ug/L [190].

Median Concentration in Public Water Supplies: USGS 1985: <4.3 ug/L [190].

Municipal water supplies may contain on the average about 1-6 ppb (Doull, J., C.D. Klaassen, and M. D. Amdur (eds.). Casarett and Doull's Toxicology. 2nd ed. New York: Macmillan Publishing Co., 1980. 460) [366].

Typical Ocean Concentrations: EPA 1981: 0.002 mg/l [83].

Information from ATSDR [943] (see ATSDR for identification of embedded references):

> Levels of vanadium in fresh water illustrate geographic variations produced by differences in effluents and leachates, from both anthropogenic and natural sources, entering the water table. Measurements of vanadium in such natural fresh waters as the Animas, Colorado, Green, Sacramento, San Joaquin, and San Juan Rivers, as well as some fresh water supplies in Wyoming, range from 0.3 to

200 ug vanadium/L (Byerrum et al. 1974; Van Zinderen Bakker and Jaworski 1980). The presence of naturally occurring uranium ores resulted in rivers in the Colorado Plateau containing vanadium levels of up to 70 ug/l, and in Wyoming levels were found to range from 30 to 220 ug/l (Byerrum et al. 1974). Some municipal waters have been found to contain levels of between 1 and 6 ug vanadium/L (Van Zinderen Bakker and Jaworski 1980), although levels of 19 ug vanadium/L have been reported in nine New Mexico municipalities (Byerrum et al. 1974). Levels in sea water are considerably lower than those in freshwater because much of the vanadium is precipitated (Byerrum et al. 1974; Van Zinderen Bakker and Jaworski 1980). The concentrations measured usually average 1-3 ug vanadium/L (Van Zinderen Bakker and Jaworski 1980) although levels as high as 29 ug/l have been reported (Byerrum et al. 1974). The total content of vanadium in sea water has been estimated to be 7.5x10 to 12th kg (7.5x10 to 9th metric tons) [943].

W.Concern Levels, Water Quality Criteria, LC50 Values, Water Quality Standards, Screening Levels, Dose/Response Data, and Other Water Benchmarks:

W.General (General Water Quality Standards, Criteria, and Benchmarks Related to Protection of Aquatic Biota in General; Includes Water Concentrations Versus Mixed or General Aquatic Biota):

EPA 1996 IRIS database information [893]:

No information given.

Oak Ridge National Lab, 1994: Ecological Risk Assessment Freshwater Screening Benchmarks for concentrations of contaminants in water [649]. To be considered unlikely to represent an ecological risk, field concentrations should be below all of the following benchmarks [649]:

For Vanadium, CAS 7440-62-2 (ug/L):

NATIONAL AMBIENT WATER QUALITY CRITERION - ACUTE: No information found.

NATIONAL AMBIENT WATER QUALITY CRITERION - CHRONIC: No information found.

SECONDARY ACUTE VALUE: 284

SECONDARY CHRONIC VALUE: 19.1

LOWEST CHRONIC VALUE - FISH: 80

LOWEST CHRONIC VALUE - DAPHNIDS: > 940

LOWEST CHRONIC VALUE - NON-DAPHNID INVERTEBRATES: No information found.

LOWEST CHRONIC VALUE - AQUATIC PLANTS: No information found.

LOWEST TEST EC20 - FISH: 41

LOWEST TEST EC20 - DAPHNIDS: 430

SENSITIVE SPECIES TEST EC20: No information found.

POPULATION EC20: 32

W.Plants (Water Concentrations vs. Plants):

Shallow Groundwater Ecological Risk Assessment Screening Benchmark for Terrestrial Plants Listed by Oak Ridge National Lab, 1994 [651]:

To be considered unlikely to represent an ecological risk, field concentrations in shallow groundwater or porewater should be below the following benchmark for any aqueous solution in contact with terrestrial plants. Toxicity of groundwater to plants may be affected by many variables (pH, Eh, cation exchange capacity, moisture content, organic content of soil, clay content of soil, differing sensitivities of various plants, and various other factors). Thus, the following solution benchmark is a rough screening benchmark only, and site specific tests would be necessary to develop a more rigorous benchmark for various combinations of specific soils and plant species [651]:

For CAS 7440-62-2, VANADIUM, the Benchmark is 0.5 mg/L (porewater or groundwater).

Ten to 20 ppm vanadium in solution are harmful to plants but larger amounts can be tolerated by legumes that use vanadium in the nitrogen fixation process [951].

As little as 0.5 mg V/kg reduced the growth of flax, peas, soybeans (V given as VOCl2) and cabbage affected by aqueous vanadium levels as low as 10-20 mg/l. Usually the vanadium induces iron deficiency chlorosis by interfering with iron absorption. Levels of other essential elements such as manganese, copper, calcium, and phosphorus are also reduced by vanadium. Excess vanadium can thus affect the trace element nutritional value of plants (Nat'l Research Council Canada; Effects of Vanadium in the Canadian Environment p.38, 1980, NRCC No. 18132 [940].

W.Invertebrates (Water Concentrations vs. Invertebrates):

No information found.

W.Fish (Water Concentrations vs. Fish):

No information found.

W.Wildlife (Water Concentrations vs. Wildlife or Domestic Animals):

Oak Ridge National Lab, 1994: Risk Assessment Screening Benchmarks for Wildlife derived from No-Observed-Adverse-Effect (NOAEL) levels (see Tis.Wildlife, B) for these). To be considered unlikely to represent an ecological risk, water concentrations should be below the following benchmarks for each species present at the site [650]:

CAS 7440-62-2 (VANADIUM, AS SODIUM VETAVANADATE):

SPECIES	WATER CONCENTRATION (ppm)
Rat (test species)	0.00000
Short-tailed Shrew	2.44700
Little Brown Bat	4.22900
White-footed Mouse	1.58100
Meadow Vole	2.76800
Cottontail Rabbit	1.31100
Mink	1.36000
Red Fox	0.97100
Whitetail Deer	0.54300

Wistar rats of both sexes received vanadium in drinking water in the amount of 23-29 mg/kg body weight in the form of ammonium metavanadate for a period of 2, 4 and 8 weeks. Animals treated in this way ate less food and drank less ammonium metavanadate solution as compared with the amount of water consumed by the controls; they suffered from diarrhea, and owing to this, the increment in body weight was reduced. Vanadium decreased erythropoiesis and maturation of red blood cells, which was expressed by a reduced erythrocyte count and hemoglobin level and increased reticulocyte and polychromatophilic erythrocyte count in the peripheral blood. The composition percentage of the bone marrow cells and the peripheral blood leukocyte count did not undergo noticeable changes under the influence of vanadium (Zaporowska H, Wasilewski W; Comp Biochem Physiol (C) 93 (1): 175-80, 1989) [940].

The effect of oral administration of vanadate, in normalizing blood glucose levels of streptozotocin-treated rats is determined. The effects of orally administered doses of sodium metavanadate /were examined/. High concentrations of orally administered vanadate (0.8 mg/ml in drinking water) reduced blood glucose levels within 2-4 days ... and led to the appearance of hypoglycemia in test animals. Lower concentrations of vanadate (0.2 mg/ml in drinking water) also lowered blood glucose levels within 4 days, but did not lead to hypoglycemia for at least 3 weeks. These effects of vanadate were found to be reversible; hyperglycemia recurred within 2 days after removal of vanadate from the drinking water. In streptozotocin-treated rats receiving low vanadate treatment, circulating levels of vanadate were about 0.8 microgram/ml after 3 weeks of treatment. These rats became anabolic, while rats receiving high vanadate treatment remained catabolic. Subsequent to vanadate treatment, adipocytes derived from streptozotocin-treated rats responded to lower insulin concentrations. In addition, vanadate treatment lowered the increased insulin binding capacity of liver plasma membranes derived from streptozotocin-treated rats. Insulin binding capacity under these conditions approached that of control non-streptozotocin-treated rats. Basal rates of hexose uptake in muscle and liver tissues were doubled in vanadate-treated streptozotocin-treated rats. The oral administration of vanadate leads to normoglycemia by stimulating glucose uptake. Treatment with "low vanadate" leads to the formation of a stable anabolic and normoglycemic state in streptozotocin-treated rats and appears to restore insulin responsiveness of target tissues, without apparent signs of toxicity. Vanadate treatment did not impair either kidney or liver function, as assayed by the measurement of serum urea, creatinine, and glutamic-oxaloacetic transaminase (Meyerovitch J et al; J Biol Chem 262 ,14: 6658-62, 1987) [940].

W.Human (Drinking Water and Other Human Concern Levels):

EPA 1996 IRIS database information [893]:

Drinking Water Health Advisories: empty

No other information given for vanadium in general. For vanadium pentoxide, the following note pertains to MCLG, MCL, SMCL, and RMUC.

Note: Listed in the January 1991 Drinking Water Priority List and may be subject to future regulation (56 FR 1470, 01/14/91)

No other MCL information given on vanadium in general [893].

EPA 1996 Water Health Based Limits: 3E-01 mg/L based on RfD [952].

EPA 1995 Region 9 Tap Water Preliminary Remediation Goal: 260 ug/L [868].

Virginia DEQ alternate concentration levels for groundwater: 110 ug/L (Mike Brennan, National Park Service, personal communication, 1996).

Vanadium is considered a beneficial nutrient at ug/l levels, having been suggested as protective against atherosclerosis (National Research Council. Drinking Water & Health Volume 1. Washington, DC: National Academy Press, 1977. 315) [940].

State Drinking Water Guidelines [940]:

(AZ) ARIZONA 7 ug/l [USEPA/Office of Water; Federal-State Toxicology and Risk Analysis Committee (FSTRAC). Summary of State and Federal Drinking Water Standards and Guidelines (11/93)].

W.Misc. (Other Non-concentration Water Information):

No information found.

Sediment Data Interpretation, Concentrations and Toxicity (All Sediment Data Subsections Start with "Sed."):

Sed.Low (Sediment Concentrations Considered Low):

No information found.

Sed.High (Sediment Concentrations Considered High):

No information found.

Sed.Typical (Sediment Concentrations Considered Typical):

Averages and ranges of concentrations of elements in soils and other surficial materials in the Unites States (1971): The mean concentration of vanadium was 76 ppm. The range was <7-500 ppm [347].

Sed.Concern Levels, Sediment Quality Criteria, LC50 Values, Sediment Quality Standards, Screening Levels, Dose/Response Data and Other Sediment Benchmarks:

Sed.General (General Sediment Quality Standards, Criteria, and Benchmarks Related to Protection of Aquatic Biota in General; Includes Sediment Concentrations Versus Mixed or General Aquatic Biota):

No information found.

Sed.Plants (Sediment Concentrations vs. Plants):

No information found.

Sed.Invertebrates (Sediment Concentrations vs. Invertebrates):

No information found.

Sed.Fish (Sediment Concentrations vs. Fish):

No information found.

Sed.Wildlife (Sediment Concentrations vs. Wildlife or Domestic Animals):

No information found.

Sed.Human (Sediment Concentrations vs. Human):

No information found.

Sed.Misc. (Other Non-concentration Sediment Information):

No information found.

Soil Data Interpretation, Concentrations and Toxicity (All Soil

Data Subsections Start with "Soil."):

Soil.Low (Soil Concentrations Considered Low):

No information found.

Soil.High (Soil Concentrations Considered High):

No information found.

Soil.Typical (Soil Concentrations Considered Typical):

Typical Igneous Rocks (Earth's Crust) Concentrations: EPA 1981: 135.0 mg/kg dry weight [83]. Vanadium has a mean crustal abundance of 150 mg/kg [983].

Igneous Rocks Concentrations: 90 ppm [951].

Typical Soil Concentrations: EPA 1981: 100 mg/kg dry weight [83].

Typical U.S. Soil Concentrations: 200 mg/kg [943].

The mean elemental concentration of this metal in plants was 1 ppm in the same areas where rocks were 150 ppm [951]. Concentration in soils is 100 ppm [951].

Averages and ranges of concentrations of elements in soils and other surficial materials in the Unites States (1971): The mean concentration of vanadium was 76 ppm. The range was <7-500 ppm [347].

Although soil concentrations depend on the parent material, vanadium concentrations generally range between 10-150 ug/g (10-150 mg/kg) dry weight [983].

Soil.Concern Levels, Soil Quality Criteria, LC50 Values, Soil Quality Standards, Screening Levels, Dose/Response Data and Other Soil Benchmarks:

Soil.General (General Soil Quality Standards, Criteria, and Benchmarks Related to Protection of Soil-dwelling Biota in General; Includes Soil Concentrations Versus Mixed or General Soil-dwelling Biota):

Maximum allowable concentration of vanadium in the soil in the Soviet Union (1984): 150 ppm [347].

Soil.Plants (Soil Concentrations vs. Plants):

Oak Ridge National Lab, 1994: Risk Assessment Screening Benchmarks for Terrestrial Plants. To be considered unlikely to represent an ecological risk to terrestrial plants, field concentrations in soil should be below the following dry weight benchmark for soil [651]:

> For CAS 7440-62-2 (VANADIUM), the benchmark is 2 mg/kg in soil (EPA, 1975).

Levels of vanadium (ppm dry weight) considered phytotoxic: 150 (Warsaw), 50 (Warsaw) and 60 (Ontario) [719].

Acceptable level of vanadium for production of healthy food: 150 ppm dry weight (Moscow) [719]

Levels as low as 1-2 ug/g vanadium in fertilizer nutrient solution can produce reductions in shoot biomass. Although vanadium can relieve symptoms of excess manganese in soybeans, this treatment may lead to vanadium toxicity (such as apical chlorosis and abnormal root growth). An increased supply of iron can counteract these toxic responses [983].

As little as 0.5 mg V/kg reduced the growth of flax, peas, soybeans (V given as $VOCl_2$) and cabbage affected by aqueous vanadium levels as low as 10-20 mg/l. Usually the vanadium induces iron deficiency chlorosis by interfering with iron absorption. Levels of other essential elements such as manganese, copper, calcium, and phosphorus are also reduced by vanadium. Excess vanadium can thus affect the trace element nutritional value of plants (Nat'l Research Council Canada; Effects of Vanadium in the Canadian Environment p.38, 1980, NRCC No. 18132 [940].

Toxicity to plants: moderate [951].

Soil.Invertebrates (Soil Concentrations vs. Invertebrates):

No information found.

Soil.Wildlife (Soil Concentrations vs. Wildlife or Domestic Animals):

No information found.

Soil.Human (Soil Concentrations vs. Human):

EPA 1996 National Generic Soil Screening Level (SSL) designed to be conservative and protective at the majority of sites in the U.S. but not necessarily protective of all known human exposure pathways, land uses, or ecological threats [952]:

SSL = 550 mg/kg for ingestion pathway [952].

SSL = None given for inhalation pathway [952].

SSL = 300 to 6000 mg/kg for protection from migration to groundwater at 1 to 20 Dilution-Attenuation Factor (DAF) [952].

EPA 1995 Region 9 Preliminary remediation goals (PRGs), 1995 [868]:

Residential Soil: 540 mg/kg wet wt.
Industrial Soil: 12000 mg/kg wet wt.

NOTE:
1) PRGs focus on the human exposure pathways of ingestion, inhalation of particulates and volatiles, and dermal absorption. Values do not consider impact to groundwater or ecological receptors.
2) Values are based on a non-carcinogenic hazard quotient of one.
3) PRGs for residential and industrial landuses are slightly lower concentrations than EPA Region III RBCs, which consider fewer aspects [903].

EPA 1995 Region 3 Risk based concentration (RBC) to protect from transfers to groundwater:

None given [903].

Acceptable level of vanadium for production of healthy food: 150 ppm dry weight (Moscow) [719]

Soil.Misc. (Other Non-concentration Soil Information):

Contact with vanadium-rich ash has been reported to cause direct plant damage [983].

Tissue and Food Concentrations (All Tissue Data Interpretation Subsections Start with "Tis."):

Tis.Plants:

A) As Food: Concentrations or Doses of Concern to Living Things Which Eat Plants:

No information found.

B) Body Burden Residues in Plants: Typical, Elevated, or of Concern Related to the Well-being of the Organism Itself:

The mean elemental concentration of this metal in plants was 1 ppm in the same areas where rocks were 150 ppm [951].

In unpolluted environments, plants generally contain from 0.5 to 2.0 ug/g dry weight vanadium concentrations. Plants in the genus Astragalus growing in the highly mineralized soils of the Colorado plateau, Utah, have contained concentrations up to 144 ug/g [983].

Plant Concentrations [940]:

The aerial portions of most plants are not correlated to soil vanadium levels. Mean concn in higher plants were found to be 0.16 mg vanadium/kg (fresh wt). In freshwater plants concn of 0.4 to 80 mg vanadium/kg were reported with the maximum value accumulated by the pickerel weed (Pontedaris cordata). [Seiler, H.G., H. Sigel and A. Sigel (eds.). Handbook on the Toxicity of Inorganic Compounds. New York, NY: Marcel Dekker, Inc. 1988. 750].

Tis.Invertebrates:

A) As Food: Concentrations or Doses of Concern to Living Things Which Eat Invertebrates:

No information found.

B) Concentrations or Doses of Concern in Food Items Eaten by Invertebrates:

No information found.

C) Body Burden Residues in Invertebrates: Typical, Elevated, or of Concern Related to the Well-being of the Organism Itself:

No information found.

Tis.Fish:

A) As Food: Concentrations or Doses of Concern to Living Things Which Eat Fish (Includes FDA Action Levels for Fish and Similar Benchmark Levels From Other Countries):

EPA Region III Risk Based Concentration (RBC) for fish tissue: 9.5 mg/kg [903].

B) Concentrations or Doses of Concern in Food Items Eaten by Fish:

A growth-feeding trial was conducted in which ... juvenile, rainbow trout (initial weight 2.9 g/fish) were fed ... diets supplemented with from 0 to 10 g vanadium (as sodium orthovanadate)/kg diet for 12 wk at 15 deg C. All levels of supplemented vanadium ... significantly reduced growth and feeding response in the trout. At high levels of dietary vanadium (> 493 mg/kg), feed avoidance and increased mortalities were apparent in the trout. The vanadium retention factor (carcass vanadium/total amount of vanadium consumed) and carcass concentration factor (carcass vanadium concentration/dietary vanadium content) increased in relation to the dietary vanadium level indicating a bioaccumulation of vanadium in this fish. This is in direct contrast to the apparently low bioaccumulation of waterborne vanadium in trout. The minimum dietary vanadium toxicity level could not be determined; however, it is probably less than 10 mg vanadium/kg diet. The major biochemical and/or physiological effect of vanadium in the trout would appear to be increased in vivo lipid oxidation (Hilton JW, Bettger WJ; Aquat Toxicol 12 (1): 63-72, 1988) [940].

C) Body Burden Residues in Fish: Typical, Elevated, or of Concern Related to the Well-being of the Organism Itself:

No information found.

Tis.Wildlife: Terrestrial and Aquatic Wildlife, Domestic Animals and all Birds Whether Aquatic or not:

A) As Food: Concentrations or Doses of Concern to Living Things Which Eat Wildlife, Domestic Animals, or Birds:

No information found.

B) Concentrations or Doses of Concern in Food Items Eaten by Wildlife, Birds, or Domestic Animals (Includes LD50 Values Which do not Fit Well into Other Categories, Includes Oral Doses Administered in Laboratory Experiments):

Oak Ridge National Lab, 1994: Risk Assessment Screening Benchmarks for Wildlife derived from No-Observed-Adverse-Effect (NOAEL) levels (mg contaminant per kg body weight per day). To be considered unlikely to represent an ecological risk, wet-weight field concentrations should be below the following (right column) benchmarks for each species present at the site [650]:

CAS 7440-62-2 VANADIUM (AS SODIUM METAVANADATE)

SPECIES	NOAEL (mg/kg/day)	FOOD CONCENTRATION (ppm)
Rat (test species)	0.2100	0.0000
Short-tailed Shrew	0.5380	0.8970
Little Brown Bat	0.6770	2.0300
White-footed Mouse	0.4740	3.0700
Meadow Vole	0.3770	3.3210
Cottontail Rabbit	0.1270	0.6420
Mink	0.1350	0.9830
Red Fox	0.0820	0.8200
Whitetail Deer	0.0360	1.1550

Dietary vanadium has been shown to suppress egg production of laying hens [57]. Dietary vanadium at levels as low as 0.5 mg/kg have been shown to alter metabolism in mallards [205].

The effect of vanadium on copper metabolism was studied in rats. Male Wistar rats were given single oral doses of sodium vanadate or vanadyl sulfate at concentrations corresponding to 12 and 15 mg/kg vanadium, respectively, or sodium vanadate or vanadyl sulfate six times weekly for 3 months in doses corresponding to 3 and 3.75 mg/kg vanadium, respectively. They were killed 1, 2, 4, or 24 hours after dosing in the acute study and at 2, 4, 6, 8, 10, or 12 weeks in the subchronic study. Active transport of copper in the proximal duodenal segment of the intestine using an everted gut/sac technique was determined. ... In the acute study, serum copper concentrations were significantly decreased 4 hours after dosing by both vanadyl salts, but significantly increased 24 hours after treatment. Serum ceruloplasmin was not affected. Copper transfer in the intestine was significantly inhibited by both salts in the acute and subchronic study, sodium vanadate having the greater inhibitory effect. Subchronic administration of either compound did not generally alter serum copper concentrations. Both compounds significantly reduced serum ceruloplasmin after 4 weeks and hepatic copper concentrations after 6 weeks (Witkowska D et al; Bull Environ Contam Toxicol 40 (2): 309-16, 1988) [940].

C) Body Burden Residues in Wildlife, Birds, or Domestic Animals: Typical, Elevated, or of Concern Related to the

Well-being of the Organism Itself:

Little comparative data are available for vanadium, but one composite sample of 5 softshell turtles from Castolon had a vanadium concentration of 0.20 mg/kg [65]. This value is close to the 0.15 mg/kg geometric mean of vanadium concentrations recorded for 26 softshell turtle samples from the lower Rio Grande Valley [202].

In cow milk, vanadium was found at levels from about 0.2 ug/kg (wet wt) /according to a 1978 report/ to 10 ug/kg (Friberg, L., Nordberg, G.F., Kessler, E. and Vouk, V.B. , eds,. Handbook of the Toxicology of Metals. 2nd ed. Vols I, II.: Amsterdam: Elsevier Science Publishers B.V., 1986.,p. V2 641) [940].

Vanadium in trace amounts, 0.5 ppm, in the livers of rabbits on high cholesterol diets reduces plasma cholesterol and liver phospholipids and diminishes the size of aortic plaques. Vanadium also reduces plasma cholesterol in normal males on ordinary diets. The mechanism by which this occurs is by inhibition of conversion of hydroxymethylglutaric to methylcrotonic acid and by prevention of the utilization of mevalonic acid, important steps in the preliminary stages of cholesterol synthesis. Lowered plasma cholesterol values appeared to be the rule among vanadium workers in the Colorado Plateau (Clayton, G. D. and F. E. Clayton (eds.). Patty's Industrial Hygiene and Toxicology: Volume 2A, 2B, 2C: Toxicology. 3rd ed. New York: John Wiley Sons, 1981-1982. 2027) [940].

Tis.Human:

A) Typical Concentrations in Human Food Survey Items:

In cow milk, vanadium was found at levels from about 0.2 ug/kg (wet wt) /according to a 1978 report/ to 10 ug/kg (Friberg, L., Nordberg, G.F., Kessler, E. and Vouk, V.B. , eds,. Handbook of the Toxicology of Metals. 2nd ed. Vols I, II.: Amsterdam: Elsevier Science Publishers B.V., 1986.,p. V2 641) [940].

Food Survey Results [940]:

Vanadium concn in food reported in the literature differ widely. In older studies, the values are usually considerably higher than in more recent ones. As an example ...

/in a 1963 report/ a colorimetric method ... /demonstrated/ 1.5 mg/kg (wet wt) in potatoes, whereas /reports published in the late seventies/ using AAS or NAA ... /gave/ concn ranging from 1 to 6 ug/kg. Similar variations exist for other vegetables & fruits, but are not so great. ... Concn in meat are approx 1 ug/kg. It is likely that vanadium concn in common food do not exceed a few ug/kg. [Friberg, L., Nordberg, G.F., Kessler, E. and Vouk, V.B. , eds,. Handbook of the Toxicology of Metals. 2nd ed. Vols I, II.: Amsterdam: Elsevier Science Publishers B.V., 1986.,p. V2 641].

Determination of vanadium content of selected foods showed that beverages, fats, oils, & fresh fruit & vegetables contained the least vanadium ranging from <0.001 to 0.005 mg/kg. Grains, seafood, meats, & dairy products were generally within the range of 0.005 to 0.03 mg/kg, prepared food within 0.011 to 0.093 mg/kg, while dill seed & black pepper contained 0.431 & 0.987 mg vanadium/kg, respectively. [Seiler, H.G., H. Sigel and A. Sigel (eds.). Handbook on the Toxicity of Inorganic Compounds. New York, NY: Marcel Dekker, Inc. 1988. 750].

B) Concentrations or Doses of Concern in Food Items Eaten by Humans (Includes Allowable Tolerances in Human Food, FDA, State and Standards of Other Countries):

EPA 1996 IRIS database information [893]:

No information given on vanadium in general. The following information given on vanadium pentoxide:

Crit. Dose: 0.89 mg/kg-day [Study 1 NOAEL(adj)] UF: 100 MF: 1

RfD: 9E-3 mg/kg-day Confidence: Low

RfD for vanadium in general: 7E-3 mg/kg-day [952].

RfD for vanadium sulfate: 2E-2 mg/kg-day [952].

EPA Region III Risk Based Concentration (RBC) for fish tissue: 9.5 mg/kg [903].

Average Daily Intake [940]:

Estimated average daily dietary intake of the metal is 20 ug. [Baselt RC; Biological Monitoring Methods for Industrial Chemicals p. 275 (1980)].

The 2 mg ... estimated to be the daily average intake of vanadium is probably incorrect. ... /Other studies have been conducted which/ provide reasonable suggestions concerning the typical daily dietary intake by humans. ... The vanadium content of nine institutional diets /were ascertained/ and ... /it was/ found that they would supply 12.4 to 30.1 ug of vanadium daily (average, 20 ug). ... /from these studies it is concluded that/ "It can be estimated that the daily dietary intake is of the order of a few tens of micrograms, though it may vary over wide limits". [National Research Council. Drinking Water and Health. Volume 3. Washington, DC: National Academy Press, 1980. 350].

Assuming that 20 cu m is inhaled daily, ambient air would contribute 0.2% to 6% to the total daily intake of vanadium in some regions & cities in the USA. In some eastern cities, ambient air would contribute as much or more vanadium as the typical diet. However, in regions other than the eastern US, ambient air would contribute probably less than 0.1% to the total daily intake of vanadium. /Vanadium/ [National Research Council. Drinking Water and Health. Volume 3. Washington, DC: National Academy Press, 1980. 351].

Assuming a daily intake of 2 liters of water, data indicate that typical drinking water sources would contribute between negligible amounts & 140 ug of vanadium daily. The average contribution is probably near 8 ug of vanadium daily which would be 40% of the amount of vanadium derived from usual dietary source. In some instances, the contribution of drinking water to the daily intake of vanadium may be much greater than the contribution of the diet. For example, if the drinking water contained 33 ug of vanadium per liter, it would contribute 3 times as much vanadium as a typical diet. [National Research Council. Drinking Water and Health. Volume 3. Washington, DC: National Academy Press, 1980. 354].

C) Body Burden Residues in Humans: Typical, Elevated, or of Concern Related to the Well-being of Humans:

Information from HSDB [940]:

It is/ estimated that the total body content of vanadium in healthy, adults humans is approx 100 ug. [National Research Council. Drinking Water and Health. Volume 3. Washington, DC: National Academy Press, 1980. 352].

The vanadium concentration in lung, pulmonary lymph nodes, blood, and urine of coal miners (USA) all show values well elevated above corresponding samples from resident nonminers, and far above those from individuals living away from such sources. Content in coal miners lungs ranged from 9.9 to 99 ug vanadium/g; pulmonary lymph nodes values were from 20 to 43 ug/g, compared to lungs of nonminers residing in the area of 0.7 to 11 ug/g, and with the highest lung values among residents of USA cities, less than 0.01 to 0.95 ug vanadium/g. [Clayton, G. D. and F. E. Clayton (eds.). Patty's Industrial Hygiene and Toxicology: Volume 2A, 2B, 2C: Toxicology. 3rd ed. New York: John Wiley Sons, 1981-1982. 2024].

The concentration of vanadium in human milk was determined to be 0.1-0.2 ng/g. An infant ingesting 1 liter of milk per day would thus have a daily intake of 0.1-0.2 ug vanadium (assumes 1 l milk weighs 1 kg). [Nat'l Research Council Canada; Effects of Vanadium in the Canadian Environment p.49 (1980) NRCC No. 18132].

A survey was made in five countries of the levels of 21 trace elements in human fingernails. More than 500 samples from Japan, India, Poland, Canada, and the United States were analyzed, and possible geographic, age, or sex differences were explored. Trace elements included, ... vanadium. ... Only trace or subtrace levels (0.05 to 5 ppm) were found for /some elements including vanadium/. ... Vanadium levels decreased with increasing age in both males and females. ... Use of tin coated iron and aluminum cookware was probably responsible for higher levels of aluminum and iron in Indian samples. Nonsmokers had higher levels of manganese in Japan and of selenium in Canada, Poland, and the United States. /Results suggest/ that significant differences occur in trace element distributions for populations of different origin, and a survey such as this can be useful in establishing the impact of dietary and living habits on trace element distribution in devitalized human tissues. [Takagi Y et al; Bull Environ Contam Toxicol 41 (5): 690-5 (1988)].

Urine vanadium concentrations appear to correlate reasonably well with the degree of absorption of the metal. Normal urine concentrations were found to average 12 ug/l in control subjects and 47 ug/l in workers exposed to 0.1-0.9 mg/cu m of vanadium as the pentoxide. [Lewis CE, Arch Ind Health 19: 497-503 (1959) as cited in Baselt RC; Biological Monitoring Methods for Industrial Chemicals p. 276 (1980)].

Vanadium is a natural component of fuel oil, and workers have developed vanadium poisoning during cleaning operations on oil-fired furnaces. Several of the most severely affected men were found to have urine vanadium concentrations of 43-380 ug/l. [Baselt RC; Biological Monitoring Methods for Industrial Chemicals p. 270 (1980)].

Using an indirect colorimetric method, blood vanadium concentrations in normal subjects were found to be generally less than 10 ug/l, reported serum vanadium concentrations averaging 420 ug/l (range 350-480) in normal subjects; no vanadium was found in erythrocytes. [Baselt RC; Biological Monitoring Methods for Industrial Chemicals p. 275 (1980)].

Tis.Misc. (Other Tissue Information):

Toxicity to plants: moderate, and at least one astragalus plant is used as a vanadium indicator [951]. Many of the astragalus plants are also selenium indicators.

Bio.Detail: Detailed Information on Bioconcentration, Biomagnification, or Bioavailability:

Preliminary data suggests the potential for bioaccumulation or bioconcentration of vanadium is low or limited for the following biota: mammals, birds, and fish. It appears to be high to very high for mollusks, crustacea, and lower animals and moderate for higher plants, mosses, lichens, and algae [83]. It has a much higher bioconcentration potential in mollusks than in fish [83]. The best potential mediums for biological monitoring (including gradient monitoring) appear to include higher plants, clams, mosses, and lichens [83].

Plants take up vanadium from soil, groundwater, surface water, and air pollution [83]. Animals take up vanadium from contaminated air, contaminated water, and contaminated food [83].

Presumably, man & animals do not store or accumulate vanadium in hazardous amount (National Research Council. Drinking Water & Health Volume 1. Washington, DC: National Academy Press, 1977. 296) [366].

The mean elemental concentration of this metal in plants was

1 ppm in the same areas where rocks were 150 ppm [951].

Interactions:

Vanadium toxicity is intensified by high dietary zinc, & is reduced by ascorbic acid, high protein, chromium, & manganese (Luckey, T.D. and B. Venugopal. Metal Toxicity in Mammals, 1. New York: Plenum Press, 1977. 180) [940].

See: interactions with iron in Soil.Plant section above.

Uses/Sources:

Vanadium, with a mean crustal abundance of 150 mg/kg, is placed fourteenth in the order of geochemical abundance. Although vanadium ranks alongside elements such as cobalt, copper, molybdenum, and zinc, it is more widely dispersed, thus having a higher accessibility to plants than elements that tend to concentrate in discrete bodies [983].

Among the 65 or so minerals in which vanadium occurs, the more important sources of the metal include carnotite, patronite, roscoelite, and vanadinite [254]. Vanadium is found in soil and is deposited in water as a result of fallout from air pollution [83] and is often found in ore along with uranium [190]. Other sources of vanadium are in phosphate rock, certain iron ores, and some crude oils in the form of organic complexes [254]. It is a byproduct of petroleum refining [494]. Vanadium is present in all fuel oils and it remains in the residue after the more volatile fractions have been distilled [940]. Vanadium pentoxide is used in ceramics and as a catalyst [254].

Because the metal has good structural strength and a low fission neutron cross-section, it finds extensive application in the nuclear industry [254]. The metal is also used in forming rust-resistant spring and high-speed tool steels; about 80% of the production of vanadium is used to make ferrovanadium or as a steel additive [254].

Major Uses [940]:

The principal use of vanadium is as an alloying addition to iron & steel, particularly in high strength steels &, to a lesser extent, in tool steels & castings. [Kirk-Othmer Encyclopedia of Chemical Technology. 3rd ed., Volumes 1-26. New York, NY: John Wiley and Sons, 1978-1984.,p. 23(83) 673].

In the production of aerospace titanium alloys ... [Bureau of Mines. Mineral commodity summaries P.176 (1989)].

Target material for x-rays, vanadium cmpd, especially catalysts for synthetic rubber [Sax, N.I. and R.J. Lewis, Sr. (eds.). Hawley's Condensed Chemical Dictionary. 11th ed. New York: Van Nostrand Reinhold Co., 1987. 1214].

In producing rust resistant, spring, & high speed tool steels.

It is an important carbide stabilizer in making steels. Vanadium foil is used as a bonding agent in cladding titanium to steel. [Weast, R.C. (ed.) Handbook of Chemistry and Physics. 69th ed. Boca Raton, FL: CRC Press Inc., 1988-1989.,p. B-40].

Component of microstructure & gas content controller in copper alloys; strength enhancer & heat resistor in aluminum alloys; component of other alloys-eg, permanent magnet alloys; catalyst in certain petrochemical reactions; component of instruments for experimental programs [SRI].

Interest in the intermetallic compound V_3Ga for superconductor applications could lead to expanded use /of vanadium/ in the future. During the 1970s, vanadium alloys were considered for use as cladding material for the fuel in liquid metal cooled fast reactors. However, most development programs involving vanadium for this purpose have been reduced because of insufficient funding. [Kirk-Othmer Encyclopedia of Chemical Technology. 3rd ed., Volumes 1-26. New York, NY: John Wiley and Sons, 1978-1984.,p. 23(83) 673].

Major Uses [366]:

Component of ferrovanadium alloy (an additive to steels), titanium-aluminum-vanadium alloy for aircraft; bonding agent in cladding titanium to steel; microstructure & gas content controller in copper alloys; strength enhancer & heat resistor in aluminum alloys; component of other alloys-eg, permanent magnet alloys; catalyst in certain petrochemical reactions; component of instruments for experimental programs

Natural Sources [940]:

It usually occurs in some oxidized form usually as a metal vanadate. Vanadium can also be found in trace amounts in fossil fuels. ... Vanadium does not occur in highly concentrated forms. This is true despite the fact that it is as abundant in the earth's crust as zinc & nickel & occurs in at least 50 different mineral species. [National Research Council. Drinking Water & Health Volume 1. Washington, DC: National Academy Press, 1977. 296].

Although ores containing small amounts of vanadium are rather widely distributed throughout the world, the most important ones are found in the Western Hemisphere. During the 1970s domestic USA sources (mine production & recovery) have been largely confined to four states, Colorado, Arkansas, Idaho, & Utah. The chief vanadium ores in uranium bearing sandstones are carnotite ($K_2O.2UO_3.V_2O_5.3H_2O$), roscoelite ($CaO.3V_2O_5.9H_2O$), & vanadinite ($Pb(PbCl)(V_2O_4)$). In all, more than 65 vanadium ores have been described, but all except 5 or 6 are of secondary origin formed by oxidation or weathering. Other potential sources are weathered shale, 1% vanadium pentoxide, & oil crudes, up to 3.72 ug vanadium/ml. [Clayton, G. D. and F. E. Clayton (eds.). Patty's Industrial Hygiene and Toxicology: Volume 2A, 2B, 2C: Toxicology. 3rd ed. New York: John Wiley Sons, 1981-1982. 2013].

Most of the approximately 20 primary vanadium-bearing minerals have been found in Canada while only a few of the secondary minerals occur. The primary minerals are generally associated with basic igneous rock, basic alkaline igneous rock, carbonatite complexes, titaniferous magnetite complexes and chromite, uranium, iron and manganese deposits. Vanadium, ... is present in coal and crude oil. Six samples of Albertan coal from various locations had an average vanadium content of 0.01% (100 mg/kg). One sample of Nova Scotia coal contained 0.08% (800 mg/kg) vanadium while the ash from six British Columbia coal samples contained an average of 0.04% (400 mg/kg) vandium. The weighted average of vanadium in USA coal is 25 mg/kg. In contrast, natural gas contains less than 50 mg V/kg. [Nat'l Research Council Canada; Effects of Vanadium in the Canadian Environment p.13-16 (1980) NRCC No. 18132].

Petroleum & other naturally occurring hydrocarbons such as asphaltite contain appreciable quantities of vanadium. [National Research Council. Drinking Water and Health. Volume 3. Washington, DC: National Academy Press, 1980. 351].

Vanadium does not occur naturally in highly concentrated forms. This is true despite the fact that it is as abundant in the earth's crust as zinc & nickel & occurs in at least 50 different mineral species. It usually occurs in some oxidized form usually as a metal vanadate. Vanadium can also be found in trace amounts in fossil fuels. [National Research Council. Drinking Water & Health Volume 1. Washington, DC: National Academy Press, 1977. 296].

Although ores containing small amounts of vanadium are rather widely distributed throughout the world, the most important ones are found in the Western Hemisphere. During the 1970s domestic USA sources (mine production & recovery) have been largely confined to four states, Colorado, Arkansas, Idaho, & Utah. The chief vanadium ores in uranium bearing sandstones are carnotite ($K_2O.2UO_3.V_2O_5.3H_2O$), roscoelite ($CaO.3V_2O_5.9H_2O$), & vanadinite ($Pb(PbCl)(V_2O_4)$). In all, more than 65 vanadium ores have been described, but all except 5 or 6 are of secondary origin formed by oxidation or weathering. Other potential sources are weathered shale, 1% vanadium pentoxide, & oil crudes, up to 3.72 ug vanadium/ml. [Clayton, G. D. and F. E. Clayton (eds.). Patty's Industrial Hygiene and Toxicology: Volume 2A, 2B, 2C: Toxicology. 3rd ed. New York: John Wiley Sons, 1981-1982. 2013].

A principal ore is patronite. [Sax, N.I. and R.J. Lewis, Sr. (eds.). Hawley's Condensed Chemical Dictionary. 11th ed. New York: Van Nostrand Reinhold Co., 1987. 1215].

Natural Sources [366]:

Abundance in earth's crust: 0.01% By weight. Widespread in nature; over 65 minerals known including patronite...Vanadinite...Roscoelite... And carnotite... [The Merck Index. 10th ed. Rahway, New Jersey: Merck Co., Inc., 1983. 1417].

Artificial Sources [940]:

The major point sources of atmospheric emission are metallurgical works (30 kg vanadium/ton vanadium produced), & oil & coal burning (0.2 to 2 kg/1000 tons & 30-300 kg/1X10+6 liters, respectively). Fossil fuel combustion is the largest source of air pollution by vanadium, partly as a result of the limited use of efficient flue gas cleaning. [Friberg, L., Nordberg, G.F., Kessler, E. and Vouk, V.B. , eds,. Handbook of the Toxicology of Metals. 2nd ed. Vols I, II.: Amsterdam: Elsevier Science Publishers B.V., 1986.,p. V2 642].

One kind of pollution from vanadium must be noted when considering water. Residues from the milling & mining of vanadium are often heaped on the ground or used as landfills, thus being exposed to rainfall & groundwater drainage, which could result in water pollution for many miles around. [National Research Council. Drinking Water & Health Volume 1. Washington, DC: National Academy Press, 1977. 296].

A relatively large amount of vanadium (some 30,000 metric tons/yr) enters the environment from man's activities, but no widespread detrimental effects have been identified. [National Research Council. Drinking Water & Health Volume 1. Washington, DC: National Academy Press, 1977. 297].

Artificial Sources [366]:

Urban air contains some vanadium...Due to use of petroleum products or from refineries... [Doull, J., C.D. Klaassen, and M. D. Amdur (eds.). Casarett and Doull's Toxicology. 2nd ed. New York: Macmillan Publishing Co., 1980. 460].

Residues from milling & mining of vanadium are often heaped on ground or used as landfills, thus being exposed to rainfall & groundwater drainage, which could result in water pollution for many miles around. [National Research Council. Drinking Water & Health Volume 1. Washington, DC: National Academy Press, 1977. 296].

Forms/Preparations/Formulations:

Information from HSDB [940]:

Grade: 99.99% pure (electrolytic process), single crystals

[Sax, N.I. and R.J. Lewis, Sr. (eds.). Hawley's Condensed Chemical Dictionary. 11th ed. New York: Van Nostrand Reinhold Co., 1987. 1214].

The majority of vanadium is used/ as a ferrovanadium alloy, which is produced commercially by the reduction of vanadium ore, slag or technical grade oxide with carbon, ferrosilicon, or aluminum. The product grades, which may contain 35-80% (by wt) vanadium, are classified according to their vanadium content. The consumer use & grade desired dictate the choice of reductant. [Kirk-Othmer Encyclopedia of Chemical Technology. 3rd ed., Volumes 1-26. New York, NY: John Wiley and Sons, 1978-1984.,p. 23(83) 677].

Chem.Detail: Detailed Information on Chemical/Physical Properties:

Solubilities [940]:

INSOL (sic, actually "relatively insoluble") IN WATER [The Merck Index. 10th ed. Rahway, New Jersey: Merck Co., Inc., 1983. 1418].

Density/Specific Gravity [940]:

6.11 AT 18.7 DEG C [The Merck Index. 10th ed. Rahway, New Jersey: Merck Co., Inc., 1983. 1418].

Molecular Weight [940]:

50.9415 [The Merck Index. 10th ed. Rahway, New Jersey: Merck Co., Inc., 1983. 1417].

Boiling Point [940]:

3380 DEG C [Weast, R.C. (ed.) Handbook of Chemistry and Physics. 69th ed. Boca Raton, FL: CRC Press Inc., 1988-1989.,p. B-142].

Melting Point [940]:

1917 DEG C [The Merck Index. 10th ed. Rahway, New Jersey: Merck Co., Inc., 1983. 1418].

Color/Form [940]:

Light gray or white lustrous powder, fused hard lumps or body-centered cubic crystals [The Merck Index. 10th ed. Rahway, New Jersey: Merck Co., Inc., 1983. 1418].

Pure vanadium is a bright white metal [Weast, R.C. (ed.) Handbook of Chemistry and Physics. 69th ed. Boca Raton, FL: CRC Press Inc., 1988-1989.,p. B-40].

Other Chemical/Physical Properties [940]:

Two naturally occurring isotopes: (51)V (99.75%): (50)V (0.25%); the latter is radioactive: T1/2 6X10+15 years; artificial isotopes: 46-49; 52-54 [The Merck Index. 10th ed. Rahway, New Jersey: Merck Co., Inc., 1983. 1418].

Precipitates gold, silver & platinum from their salts; reduces mercuric salts to mercurous, ferric salts to ferrous; not attacked by bromine water, or by cold sulfuric acid [The Merck Index. 10th ed. Rahway, New Jersey: Merck Co., Inc., 1983. 1418].

Vanadium is resistant to attack by hydrochloric or dilute sulfuric acid & to alkali solutions. It is also quite resistant to corrosion by seawater but is reactive toward nitric, hydrofluoric, or concn sulfuric acids. Galvanic corrosion tests run in simulated seawater indicate that vanadium is anodic with respect to stainless steel & copper but cathodic to aluminum & magnesium. Vanadium exhibits corrosion resistance to liquid metals, eg, bismuth & low oxygen sodium. [Kirk-Othmer Encyclopedia of Chemical Technology. 3rd ed., Volumes 1-26. New York, NY: John Wiley and Sons, 1978-1984.,p. 23(83) 675].

Forms an alloy with fe (ferrovanadium) in which there is complete liquid solubility; forms a very hard and stable carbide, v4c3 in carbon and most alloy steels. [Clayton, G. D. and F. E. Clayton (eds.). Patty's Industrial Hygiene and Toxicology: Volume 2A, 2B, 2C: Toxicology. 3rd ed. New York: John Wiley Sons, 1981-1982. 2015].

Acts as metal or nonmetal; VALANCES 2, 3, 4, 5 [Sax, N.I. and R.J. Lewis, Sr. (eds.). Hawley's Condensed Chemical Dictionary. 11th ed. New York: Van Nostrand Reinhold Co., 1987. 1214].

When heated in air at different temperatures, it oxidizes to a brownish black trioxide, a blue black tetraoxide, or a reddish orange pentoxide. It reacts with chlorine at fairly low temperatures (180 deg C) forming vanadium tetrachloride & with carbon & nitrogen at high temperatures forming VC & VN, respectively. The pure metal in massive form is relatively inert toward oxygen, nitrogen, & hydrogen at room temperature. [Kirk-Othmer Encyclopedia of Chemical Technology. 3rd ed., Volumes 1-26. New York, NY: John Wiley and Sons, 1978-1984.,p. 23(83) 675].

Lattice constant, 0.3026 nm; specific heat, 0.50 J/g at 20-100 deg C; latent heat of fusion, 16.02 kJ/mol; enthalpy, 5.27 kJ/mol at 25 deg C; entropy, 29.5 kJ/mol deg C at 25 deg C; thermal conductivity, 0.31 W/cm deg K at 100 deg C; electrical resistance, 24.8-26.0 microohm cm at 20 deg C; recrystallization temp, 800-1000 deg C; modulus of elasticity, (1.2-1.3)X10+5 MPa [Kirk-Othmer Encyclopedia of Chemical Technology. 3rd ed., Volumes 1-26. New York, NY: John Wiley and Sons, 1978-1984.,p. 23(83) 675].

Pure vanadium is soft & ductile [Weast, R.C. (ed.) Handbook of Chemistry and Physics. 69th ed. Boca Raton, FL: CRC Press Inc., 1988-1989.,p. B-40].

Vanadium has good structural strength & a low fission neutron cross section, making it useful in nuclear applications [Weast, R.C. (ed.) Handbook of Chemistry and Physics. 69th ed. Boca Raton, FL: CRC Press Inc., 1988-1989.,p. B-40].

Fate.Detail: Detailed Information on Fate, Transport, Persistence, and/or Pathways:

Absorption, Distribution and Excretion [940]:

Concentrations of...Vanadium...In the lung increase up to age 40; these increases are due to the accumulation of insoluble particles. [Doull, J., C.D. Klaassen, and M. D. Amdur (eds.). Casarett and Doull's Toxicology. 2nd ed. New York: Macmillan Publishing Co., 1980. 409].

Most ingested vanadium remains unabsorbed by the gastrointestinal tract and is excreted in the feces. [National Research Council. Drinking Water and Health. Volume 3. Washington, DC: National Academy Press, 1980. 354].

The rate of absorption of vanadium which is present naturally in food is unknown but is assumed to be about 0.5%. [Nat'l Research Council Canada; Effects of Vanadium in the Canadian Environment p.47 (1980) NRCC No. 18132].

In humans, ingested vanadium is absorbed poorly by the gastrointestinal tract. Only 0.1-1.0% of a 100 and 125 mg dose of diammonium oxytartarovanadate was absorbed gastrointestinally, and 60% of the absorbed dose was excreted by the kidneys within 24 hr. Only 2.6 + or - 1.6% of the radioactivity from a 0.3 mg/kg dose of vanadium from (48)V vanadium pentoxide administered by gavage was absorbed by 70 day old female Fischer rats. [Curan GL et as; J Clin Invest 38: 1251-61 (1959) as cited in USEPA, Office of Drinking Water; Criteria Document (Draft): Vanadium p.4 (1987) EPA 600/8-88/061].

Vanadium compounds and metallic vanadium, when absorbed, are rapidly excreted and exhibit low degrees of toxicity, as indicated by minor irritation and lack of systemic effects. The action level is therefore defined as equal to the recommended environmental limit for each of the two proposed categories of vanadium. /Vanadium metal and cmpd/ [NIOSH; Criteria Document: Vanadium p.101 (1977) DHEW Pub. NIOSH 77-

222].

The deposition of vanadium particles in the respiratory tract is expected to follow the general pattern of increasing pulmonary deposition with decreasing particle size. Absorption from the respiratory tract is dependent on the solubility of the vanadium species deposited. When (48)VOCl2 (a water-soluble vanadium compound) was given to rats by intratracheal injection, 60% of the material remained in the lung after 15 minutes and 33.5% remained after 9 weeks. The lung, unlike other organs, appears to accumulate vanadium with increasing age, reaching approximately 6.5 ug V/g (wet weight) in persons over age 65. /Vanadium and its soluble cmpd/ [Nat'l Research Council Canada; Effects of Vanadium in the Canadian Environment p.47 (1980) NRCC No. 18132].

Laboratory and/or Field Analyses:

Many laboratory methods are available for vanadium [861,943]. Standard methods used in the past have included EPA 289.1, 289.2, and ICP methods 200.7 and 200.8 (40 CFR, Part 136.3, Table 1B, page 386, 1994) [1005,1006].

Certain low concentration criteria or benchmarks may require relatively rigorous methods (ICP/MS/SIM for example), while routine applications may require only routine ICP analyses. Detection limits should be no higher than comparison benchmarks or criteria for various media (water, sediments, soil, tissues, etc), some of which are low (see sections above).

Water detection limits need to be lower than 30 ug/L to match lowest water benchmarks (see W.General section above). EPA ICP/MS method 200.8 has an instrument detection limit of 0.006 ug/L in the SIM mode [1006].

Otherwise, the detection limits should usually not exceed the following default concentrations often recommended by the Fish and Wildlife Service and the National Park Service: 0.50 ppm dry weight in tissues and 1.0 ppm in sediments and soils (Roy Irwin, National Park Service, Personal Communication, 1996).

In data interpretation, it is important to understand that contaminants data from different labs, different states, and different agencies, collected by different people, are often not very comparable (see also, discussion in the disclaimer section at the top of this entry).

As of 1997, the problem of lack of data comparability (not only for water methods but also for soil, sediment, and tissue methods) between different "standard methods" recommended by different agencies seemed to be getting worse, if anything, rather than better. The trend in quality assurance seemed to be for various agencies, including the EPA and others, to insist on quality assurance plans for each project. In addition to quality control steps (blanks, duplicates, spikes, etc.), these quality assurance plans call for a step of insuring data comparability [1015,1017]. However, the data comparability step is often not given sufficient consideration. The tendency of agency guidance (such as EPA SW-846 methods and some other new EPA methods for bio-concentratable substances) to allow more and more flexibility to select options at various points along the way, makes it harder in insure data comparability or method validity. Even volunteer monitoring programs are now strongly encouraged to develop and use quality assurance project plans [1015,1017].

At minimum, before using contaminants data from diverse sources, one should determine that field collection methods, detection limits, and lab quality control techniques were acceptable and comparable. The goal is that the analysis in the concentration range of the comparison benchmark concentration should be very precise and accurate.

It should be kept in mind that quality control field and lab blanks and duplicates will not help in the data quality assurance goal as well as intended if one is using a method prone to false negatives. Methods may be prone to false negatives due to the use of detection limits that are too high, the loss of contaminants through inappropriate handling, or the use of inappropriate methods.

Additional information on variability in contaminants data:

> The way one person collects, filters, and acidifies in the field may be different than the way another does it. Sources of potential variation include the following:
>
> > 1) "As soon as practical." Different situations can change the elapsed time considered by the field collector to be "as soon as practical." It may take different amounts of time to get to a safe or otherwise optimum place to filter and acidify. In one case precipitation and other changes could be going on in the collection bottle while the bottle in on the way to filtration and acidification, while in another case the field collector filters and acidifies the samples within minutes. Weather, safety concerns, and many other factors could play a role.
> >
> > 2) "Normally 3 mL of (1+1) of nitric acid per liter should be sufficient to preserve the sample." Sometimes it is not, depending on alkalinity and other factors. What field collectors sometimes (often?) do is just use pop tabs of 3 mL of nitric acid and hope for the best rather than checking to see that the acidity has been lowered to below a pH of two. EPA CFR guidelines just call for a pH of below two, whereas samples meant to be "acid soluble" metals call for a pH of 1.5 to 2.0 [25]. See also, various USEPA 1984 to 1985 Ambient Water Quality Criteria Documents for individual metals.
> >
> > 3) One person might use triple distilled concentrated nitric acid rather than reagent grades of acid to avoid possible contamination in the

acid, while another may not. When using very low detection limits, some types of acid may introduce contamination and influence the results (Pat Davies, Colorado Division of Wildlife, personal communication, 1997).

4) Holding times can strongly influence the results and there can be quite a bit of variation even within EPA recommended limits (see Silver entry for details). Holding times previously recommended for EPA for NPDES water samples of metals other than mercury or Chromium VI have been as long as 6 months (Federal Register, Volume 49, No. 209, Friday, October 28, 1984, page 43260). In the 1994 version of the CFR, NPDES holding times for mercury and Chromium VI are the same ones listed in 1984, but no EPA holding times are given for other metals (40 CFR, Part 136.3, Table 2, page 397, 1994).

Differences in the details of the method used can drastically change the results. Some cold, wet, hurried, or fire ant-bitten collectors might decide that it is not "practical" to filter and acidify quite so immediately in the field, and may decide the shore, a vehicle, a motel room, or even a remote lab are more "practical" locations. Filtering and acidifying in the field immediately is a better option for consistency (see copper entry for an example of what can happen if there is a delay). If one field filters and acidifies, one may be changing metals and colloidal content. Acidifying effects microbial changes. If one holds the samples a while before filtering and acidifying, the situation changes. In collection bottles there are potential aging effects: temperature changes, changes in basic water chemistry as oxygen and other dissolved gasses move from the water into the headspace of air at the top, potential aggregation of colloidal materials, precipitation of greater sizes with time, development of bigger and more colloids, and more sorption (Roy Irwin, NPS, personal communication, 1997).

The bottom line: since standard EPA methods for holding times and field preservations change, updates are not always convenient to obtain, since the wording is somewhat imprecise, and since field collectors may actually do different things in different situations, variation in metals concentrations may sometimes be due to differences in how individual investigators treat samples in the field and lab (Roy Irwin, National Park Service, Personal Communication, 1997).

Notes on total vs. acid soluble vs. dissolved metals:

Although most of the lab tests done to develop water quality criteria and other benchmarks were originally based on "total" values rather than "dissolved" values, the lab settings were typically fairly clean and the numbers generated by the lab tests are therefore often even more comparable to field "dissolved" values than to field "total" values (Glen Suter, Oak Ridge National Lab, Personal Communication, 1995). As of January 1995, the U.S. EPA was recommending that states use dissolved measurements in water quality standards for metals, in concert with recommendations EPA previously made for the Great Lakes [672]. However, generic conversion factors may not hold up for many areas. Both total and dissolved concentrations should be checked at new locations before relying on this conversion factor (Pat Davies, Colorado Division of Wildlife, personal communication, 1997).

Filtration and Holding Times:

For ICP water samples for metals for NPDES permits, EPA recommends the following (40 CFR Part 136, Appendix C, 1994 edition of CFR Part 40, page 642):

1) For samples of "total or total recoverable elements," samples should be acidified to a pH of two or less at the time of collection or as soon as possible thereafter.

2) For determination of dissolved elements, the samples must be filtered through a 0.45 micron membrane filter as soon as soon as practical after collection, using the first 50-100 ml to rinse the filter flask. Acidify the filtrate with nitric acid to a pH of 2 or less. Normally 3 mL of (1+1) of nitric acid per liter should be sufficient to preserve the sample.

3) For determination of suspended elements, the samples must be filtered through a 0.45 micron membrane filter as soon as soon as practical after collection. The filter is then transferred to a suitable container for storage and shipment, with no preservation required.

Other information on vanadium analytical methods from the ATSDR [943] (see ATSDR for embedded reference information):

BIOLOGICAL MATERIALS [943]: A number of analytical techniques have been used to determine ppm to ppt levels of vanadium in biological materials. These include neutron activation analysis (NAA), graphite furnace atomic absorption spectrometry (GFAAS), spectrophotometry, isotope dilution thermal ionization-mass spectrometry (IDMS), and inductively coupled plasma atomic emission spectrometry (ICP-AES). In general, biological and environmental samples may be prepared prior to quantification of vanadium by acid digestion with nitric acid. Sample dilution with nitric acid or other agents to solubilize vanadium from the sample matrix can also be employed. If the concentration of vanadium in the dissolved sample is very low, preconcentration techniques such as chelation or extraction may be used. Chelation and extraction efficiency will vary with the technique used. Owing to its high sensitivity, the NAA technique has been widely used to measure trace elements (including vanadium) in biological samples (Allen and Steinnes 1978; Lavi and Alfassi 1988; Mortin and Chasteen 1988; Mousty et al. 1984). The NAA technique is based on the interaction of the nuclei of vanadium atoms in the sample with thermal neutrons, resulting in the emission of photons (gamma rays). The resultant gamma ray is detected with a high-resolution lithium-drifter germanium detector. The concentration of vanadium is determined through its short-lived (half-life = 3.75 minutes) radionuclide 52V. Detection limits of low- to sub-ppb (ug/L) levels of vanadium in blood and urine samples were obtained (Allen and Steinnes 1978; Lavi and Alfassi 1988; Mousty et al. 1984). The advantages of the NAA technique are its sensitivity and multi-elemental capability. The disadvantages of this technique include its high cost and the limited availability of nuclear facilities for NAA analysis [943].

Abbreviations [943]: BTA = benzoyl-N-(o-tolyl)hydroxyl amine; CPCHA = chlorophenylcinnamohydroxamic acid; GFAAS = graphite furnace atomic absorption spectrometry; ICP-AES = inductively coupled plasma atomic emission spectrometry; IDMS = isotope mass spectrometry; MIBK = methyl isobutyl ketone; NAA = neutron activation analysis [943].

GFAAS has also been used for measuring trace levels of vanadium in the serum and urine of humans and animals (Ishida et al. 1989; Mousty et al. 1984). Detection limits of 0.08 ug/L in serum and 0.06 ug/L in urine were achieved (Ishida et al. 1989). The GFAAS technique is as sensitive as NAA, and is also rapid, simple, relatively free from interference, and relatively inexpensive (Ishida et al. 1989; Krishnan et al. 1976). Spectrophotometry has been extensively used to measure vanadium in environmental and biological samples (Abbasi 1981 and 1987; Agrawal 1975; Gupta and Tandon 1973; Jha 1979; Paul and Gupta 1982). The method typically involves dry or wet ashing of the sample, followed by preconcentration via an extraction procedure using chloroform and a chelating agent specific for vanadium. The spectrophotometric technique is convenient, rapid, selective, and sensitive for measuring ppm (mg/L) levels of vanadium in blood and urine samples (Paul and Gupta 1982). A procedure has been developed for the determination of vanadium in biological materials using IDMS. In this procedure, the vanadium isotope 50V in the sample was increased by adding a 50V-enriched spike solution, and ion counting detection was employed (Fassett and Kingston 1985). Isobaric interferences caused by chromium and titanium in the matrix require efficient dissolution and clean-up procedures prior to mass spectrometric measurements. These include wet digestion and dry-ashing of the sample matrix, followed by separation of vanadium from the matrix by chelation on an ion-exchange chromatography column. Detection limits of 2.6 ug of vanadium/L of serum and 0.0987 ug of vanadium/g of liver were obtained (Fassett and Kingston 1985). Although the sensitivity for measuring vanadium by the IDMS technique is in the ppb range in biological and environmental samples, it is a time-consuming and expensive technique [943].

ENVIRONMENTAL SAMPLES [943]: Many of the analytical methods for detecting vanadium in biological samples have also been used to measure vanadium in environmental samples...These include GFAAS, spectrophotometry, IDMS, and ICP-AES. Other techniques employed for measuring vanadium in environmental samples are flame atomic absorption spectrometry (FAAS) and direct current plasma-atomic emission spectrometry (DCP-AES). The most widely used methods utilize some modification of atomic absorption spectrometry (AAS). In general, similar methods are employed for preparation and clean up of environmental and biological samples prior to quantification of vanadium. Both AAS and AES methods are commonly used to detect vanadium in air. Trace levels of vanadium (as vanadium pentoxide) have been detected in air samples by GFAAS (Quickert et al. 1974). A detection limit of 0.25 ng of vanadium/m3 of sample for an air sample of 2,000 m3 was achieved. A method for the determination of vanadium in workplace air using DCP-AES was reported by Pyy et al. (1983). A detection limit of 4 ug of vanadium/m3 of sample and a practical working range of 0.01-100 ug of vanadium/m3 of sample were obtained. DCP-AES was shown to have a sensitivity and precision equal to or greater than commonly used AAS techniques. No limitations of this method were noted by the authors. NIOSH has recommended ICP-AES (Method 7300) for detecting vanadium and other elements in air. A working range of 5-2,000 ug of vanadium/m3 of sample in a 500-L air sample was obtained (NIOSH 1984b) [943].

GFAAS and FAAS are the techniques (Methods 7911 and 7910) recommended by EPA's Office of Solid Waste and Emergency Response for measuring low levels of vanadium in water and waste water (EPA 1986a). Detection limits of 4 ug of vanadium/L of sample and 200 ug of vanadium/L of sample were achieved using GFAAS and FAAS techniques, respectively. Spectrophotometry has also been employed to measure ppm levels of vanadium in aqueous media (Abbasi 1981; Jha 1979). Spectrophotometry is the method commonly employed to analyze for the presence of vanadium in soil. Detection of low ppm concentrations in the soil have been reported (Abassi 1981; Paul and Gupta 1982). IDMS and spectrophotometry have been used for measuring low ppm (ug/g) levels of vanadium in plant and marine animal tissues (Abbasi 1981; Fassett and Kingston 1985; Paul and Gupta 1982) [943].

Data Needs [943]: Methods for Determining Biomarkers of Exposure and Effect. AAS methods are the most widely used to measure low-to sub-ppb (ug/L) levels of vanadium in blood, urine, tissues, and other biological media (Ishida et al. 1989; Krishnan et al. 1976; Mousty et al. 1984). Other methods include NNA (Allen and Steinnes 1978; Lavi and Alfassi 1988; Morten and Chasteen 1988; Mousty et al. 1984), AES (Kawai et al. 1989), and ITDI-MS (Fassett and Kingston 1985). These methods have all been demonstrated to be sensitive, precise, and reliable methods to measure metals as long as sample preparation procedures are rigidly followed and cleanliness and purity of all vessels and reagents are maintained. Background levels of vanadium have been reported with these techniques, but discrepancies and problems have occurred because of the extremely low levels of vanadium found in many samples. Contamination from reagents and containers used in analyses can approach background levels and interfere with results. All of these techniques provide sensitive and reliable measures of exposure with the capability of correlating environmental levels with tissue and urinary levels of vanadium. Improvements in sample preparation techniques that simplify sample preparation while maintaining or increasing reliability of analyses would be advantageous. Since there are no well- documented biomarkers of effect specific for vanadium, it is difficult to assess the sensitivity and reliability of these methods for measuring levels associated with health effects. A decreased level of cystine (or cysteine) in hair and fingernails has been historically linked to vanadium exposure and suggested as a monitor of exposure (Mountain 1955). Accurate and precise methods exist for measuring these amino acids, but their depletion in hair and fingernails is not specific for vanadium exposure. More recent research did not indicate a correlation between cystine (or cysteine) depletion and vanadium exposure. There does not appear to be a need for additional research on this topic. Methods for Determining Parent Compounds and Degradation Products in Environmental Media. AAS methods are the most widely used to measure levels of vanadium in environmental media (EPA 1986a; Quickert et al. 1974). In addition, AES techniques (NIOSH 1984b; Pyy et al. 1983), IDTI-MS (Fassett and Kingston 1985), and spectrophotometry (Abbasi 1981; Jha 1979) are available to measure vanadium in air, water, wastewater, soil, plants, and marine tissues. As with biological material, these methods are sensitive and reliable as long as sample preparation and cleanup are carefully done. Since the most significant exposure to vanadium occurs in workers occupationally exposed to airborne vanadium, and significant absorption occurs by the inhalation route, air is the media of concern for potential human exposure. The GFAAS technique has sufficient accuracy and precision to measure background levels of vanadium in air as well as levels at which health effects might occur (Quickert et al. 1974). At hazardous waste sites, exposure is mostly likely to occur by ingestion of contaminated water, soil, or plants, although absorption via this route is small. The techniques recommended by EPA, GFAAS and FAAS (Methods 7910 and 7911), provide sensitive and reliable measures of ppb levels of vanadium in water and waste water (EPA 1986a). Spectrophotometry is commonly used to detect vanadium in soil accurately (Abbasi 1981; Paul and Gupta 1982). IDTI-MS and spectrophotometry are used to measure low-ppm levels of vanadium in plants as well as marine tissues (Abbasi 1981; Fassett and Kingston 1985; Paul and Gupta 1982). No additional methods for detecting vanadium in environmental media appear to be necessary at this time; however, improvements in sample preparation could increase sensitivity and reliability. 6.3.2 On-going Studies No on-going studies regarding methods for measuring vanadium in biological and environmental samples were located [943].

EPA 1996 IRIS database information [893]:

No information given on lab and field methods.