

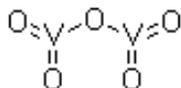
## Vanadium and Vanadium Compounds

Materials for the December 4-5, 2008 Meeting of the California Environmental Contaminant Biomonitoring Program (CECBP) Scientific Guidance Panel (SGP)

Agenda Item: "Consideration of Potential Designated Chemicals"

Vanadium, elemental (V) [CASRN: 7440-62-2]

Vanadium pentoxide (V<sub>2</sub>O<sub>5</sub>) [CASRN: 1314-62-1]



### **Exposure or potential exposure to the public or specific subgroups:**

Vanadium is an element found in the earth's crust, minerals, fossil fuels, and most living organisms. In the environment, vanadium exists in a range of oxidation states. Vanadium pentoxide (V<sub>2</sub>O<sub>5</sub>) is the major commercial form of vanadium. The primary use of vanadium is in the production of alloys. Vanadium pentoxide is used as a catalyst in industrial processes, in particular in the manufacture of sulfuric acid. The US Geological Survey (USGS 2008) estimated U.S. vanadium consumption at approximately 4,180 metric tons in 2007, which was a 4 percent increase from 2006. Vanadium pentoxide anhydride imports were estimated to be 2,240 metric tons in 2007 (USGS 2008). Vanadium production usually occurs as a byproduct of iron, titanium, phosphorus, and uranium ore processing (IARC 2006).

Vanadium is released into the environment by the combustion of vanadium-rich fuel oils and from petroleum processing. In 2006, almost 345,000 pounds of vanadium and vanadium compounds were disposed of on and off-site by industries in California (TRI 2006). Oil-combustion alone accounts for 91 percent of total atmospheric vanadium emissions worldwide (Mamane and Pirrone 1998, WHO 2001). Vanadium is found in almost all coals in concentrations up to 10 grams/kilogram (g/kg) (IARC 2006). Vanadium is present in crude oil in concentrations up to 1400 milligrams/kilogram (mg/kg) and released in coal fly ash in concentrations ranging from 0.1-1 milligrams/gram (mg/g) (Mamane and Pirrone 1998, IARC 2006). Vanadium is also present in residual (heavy) fuel oils, which when combusted release vanadium into the atmosphere at concentrations of 10-50 mg/g in fly ash particulates (Mamane and Pirrone 1998, IARC 2006). Marine distillate oil also contains vanadium (Nigam et al. 2007).

Vanadium is potentially an indicator of diesel exhaust emissions because of its presence in diesel fuel as well as its use in diesel engine catalysts, in particular selective catalytic reduction (SCR). There are two potential markets for vanadium catalyst technology in diesel engines: the original engine manufacturers (OEM) stock (i.e., new vehicles) and the retrofit market (older vehicles). According to the Manufacturers of Emission Controls Association, the projected SCR technology for 2010 model year heavy-duty

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diesel trucks will use a zeolite-based catalyst system (and not a vanadium-based system). However, there is interest among manufacturers in certifying vanadium-based SCR systems for the OEM off-road market (Joe DeVita, personal communication with Rachel Roisman). For the on-road retrofit market, manufacturers have been deploying both vanadium- and zeolite-based catalyst systems and it is unclear the extent to which vanadium will continue to be used. Over the next 10 years, about 180,000 off-road vehicles in California are expected to be retrofitted with diesel emission control systems as a result of off-road regulation (CARB 2007) and estimates are that not more than 5 percent of those systems would include NOx retrofits (Kim Heroy-Rogalski, personal communication with R. Roisman). It is unclear what percentage of NOx retrofits would be SCR and how many of the SCR systems would use vanadium. It is also unclear to what extent the on-road retrofit market will use vanadium-based SCR technology. Furthermore, several car and light-duty to medium-duty truck manufacturers plan to introduce SCR vehicles in the 2010-2011 model year timeframe; but it is unclear how many of these will use vanadium-based systems (J. DeVita, personal communication with R. Roisman).

Humans are exposed to  $V_2O_5$  in the workplace from the refining and processing of mineral ores, burning of fossil fuels, manufacture of chemicals using vanadium catalysts, and cleaning of oil-fired boilers and furnaces. Non-occupational exposures occur via inhalation of ambient air and consumption of contaminated food and water. Estimated daily intake from dietary sources in 1991 was 10–20 micrograms ( $\mu\text{g}$ ) per person per day (Byrne and Kucera, 1991). Air measurements of 31-32 nanograms/cubic meter ( $\text{ng}/\text{m}^3$ ) vanadium were observed in a variety of indoor and outdoor environments in Riverside County, California in 2001-2002 (Na et al. 2004). Assuming 20  $\text{m}^3$  air breathed per day, the measured air concentrations would correspond to an inhalation exposure of 600  $\text{ng}/\text{day}$ . Since vanadium is poorly absorbed from the gastrointestinal tract, inhalation exposures potentially pose the greatest risk. Recent research sponsored by the California Air Resources Board (CARB) found relatively high levels of vanadium emitted from a modern ocean-going container vessel powered by heavy fuel oil (Agrawal et al. 2008). In the Multiple Air Toxics Exposure Study (MATES III) conducted by the South Coast Air Quality Management District, the highest measurements of vanadium were seen in West Long Beach, where average levels of vanadium (26-28  $\text{ng}/\text{m}^3$ ) were more than double those seen in all other areas in the Los Angeles Basin except for North Long Beach (SCAQMD, 2008). These findings suggest the potential for higher vanadium exposure in communities near ports.

### **Known or suspected health effects:**

In 2005,  $V_2O_5$  (orthorhombic crystalline form) was added to the Proposition 65 list of chemicals known to the state of California to cause cancer.  $V_2O_5$  is mutagenic in mice and interferes with enzymes involved in DNA synthesis and repair (IARC 2006).  $V_2O_5$  can pass the blood–placenta barrier and is teratogenic in rodents (IARC 2006). Eye, skin and respiratory tract irritation have been associated with human exposure to elemental vanadium and  $V_2O_5$ .

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### **Need to assess efficacy of public health actions:**

Vanadium is a potential marker for exposures to diesel engine exhaust and possibly a better marker for port exposures from use of heavy fuels in ocean-going vessels. Biomonitoring vanadium could help evaluate the efficacy of CARB's regulatory efforts to reduce exposures to air contaminants associated with use of certain fuels.

### **Potential to biomonitor:**

*Physical and chemical properties (V<sub>2</sub>O<sub>5</sub>):*

Vapor pressure: 0 mm Hg

Water solubility: Slightly soluble in water (0.1–0.8 g/100 cm<sup>3</sup>)

Bioaccumulation: Bioconcentration factors (BCFs) of 365-630 were found in fish (Sadiq and Zaidi 1985, Heit et al. 1984, Tsui and McCart 1981).

*Previous biomonitoring studies:* Vanadium levels have been measured in humans in occupational (Hauser et al. 1998, Kucera et al. 1998) and non-occupational (Sabbioni et al. 1996, Kucera and Sabbioni 1998, Versieck and Cornelis 1980, Zenz and Berg 1967) settings. The American Conference of Industrial Hygienists has established a Biological Exposure Index for vanadium and recommends weekly urine monitoring in exposed workers. Blood and serum levels of non-exposed worker populations range from 0.02 to 0.1 micrograms/liter (µg/L), while levels in urine range from 0.2 to 0.8 µg/L (IARC 2006).

The Centers for Disease Control and Prevention (CDC) considered biomonitoring for vanadium as part of the National Health and Nutrition Examination Survey (NHANES). CDC developed a method for measuring vanadium in serum, but concerns about distinguishing among sources of vanadium, determining background levels, and analytical interference resulted in CDC's not designating vanadium as a priority for biomonitoring (Dr. Robert Jones, CDC, personal communication with R. Roisman). New Mexico initially planned to test for vanadium as part of the Rocky Mountain Biomonitoring Consortium, but later decided against including it, consistent with the CDC's decisions (Len Flowers, New Mexico Department of Public Health, personal communication with R. Roisman).

### **Availability of analytical methods:**

Vanadium has been measured by various methods (Atomic Absorption, Graphite Furnace Atomic Absorption) and inductively coupled plasma mass spectroscopy (ICP-MS). A critical aspect of analysis is resolution of the interference problem - vanadium has the same mass (51) as the compound ClO that is formed from matrix ions. Both collision cell and dynamic reaction cell (DRC) technology result in removing ClO and permit analysis of vanadium. The CDC has a method for measuring vanadium in serum using ICP-DRC-MS. The California Department of Public Health (CDPH) laboratory has an Agilent ICP-MS that uses Collision/Reaction Cells. The limit of detection depends on the equipment used. The Agilent ICP-MS is expected to give a detection limit for vanadium in the sub parts per billion range.

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### **Availability of adequate biospecimens:**

Long-term exposure causes vanadium to accumulate in the bone, from which it is slowly released into the blood. Vanadium can be detected in urine, whole blood, and serum. Urine levels provide information about recent exposures and whole blood and serum levels represent long-term exposure (Kucera et al. 1998). In addition to the consideration of biomonitoring for vanadium itself, vanadium is also discussed as a component of a three-pronged biomonitoring approach to measure diesel exhaust exposure (see “Diesel Exhaust” for more information).

**Incremental analytical cost:** Vanadium cannot be measured in the same panel with other metals. The vanadium assay can be run on the Agilent ICP-MS. The incremental analytical cost of adding vanadium to a metal screen is similar to mercury and cadmium. Addition of each element involves an individual method development (one time) cost and a continuing quality control/quality assurance cost.

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