24 Determine hexavalent chromium according to EPA Method 218.7

Hexavalent chromium released into nature ends up in drinking water, causing significant contamination: even minute doses are harmful to the environment and to health. This article reveals how hexavalent chromium can enter the environment and how it can be analyzed.

Metrohm USA, working closely with the U.S. Environmental Protection Agency (EPA), has developed a highly sensitive ion chromatographic method for determining hexavalent chromium that is now part of the latest EPA Method 218.7. The analysis is explained in detail on the web page info.metrohmusa.com/hexachrome/latest-news.html, where you can also download the latest EPA Method 218.7 free of charge.

Uses and properties of chromium and its salts

In the environment, chromium is encountered primarily in the two forms Cr(III) and Cr(VI). Whereas Cr(III) compounds pose no major risk (and are essential for humans), hexavalent chromium (also called hexachrome, chrome-6, and Cr(VI)) is harmful. The strong oxidizing agent Cr(VI) is classified as carcinogenic, mutagenic, and damaging to the DNA. Acute chromium(VI) poisoning leads to renal damage. Chronic Cr(VI) exposure can lead to changes in the gastrointestinal tract. If inhaled, it can cause lung cancer. Because hexavalent chromium dissolves very readily in water, the result is high bioavailability and mobility.

Chromium is used in the production of steel (added to give greater hardness and resistance to corrosion), in the electroplating industry (surface treatment by means of chromium plating; passive films by means of chromatization), in leather production (chrome tanning), and as a pigment in dyes and coatings. Chromium was also used as an impregnating agent for wood. Limestone and clay, the starting materials for cement, also contain chromium in the form of Cr(III), some of which oxidizes to Cr(VI) during the production of cement.

Examples of the release of hexavalent chromium into the environment

A study by the «Environmental Working Group» (EWG), an American environmental organization, in 2010 revealed that more than 74 million Americans in 42 U.S. states consume drinking water that is contaminated with hexavalent chromium. Cr(VI) was detected in 31 of 35 drinking water samples from throughout America; 25 samples even contained a worryingly high dose. In the mid-1990s there was a hexachrome scandal, when legal assistant Erin Brockovich discovered that the company «Pacific Gas and Electric» in Hinkley, California, had discharged hexavalent chromium into the groundwater over a period of several years. Numerous people became ill at that time and some even died.

In China, too, there are problems with hexavalent chromium in drinking water. A chemical plant in Qujing, a city in Yunnan province, had to be shut down by the authorities in 2011 after it was revealed that it had dumped more than 5,000 metric tons of toxic chromium waste into a nearby river and the surrounding area and deposited 140,000 metric tons of chromium waste in its own dump close to the river.

Worldwide, the leather industry uses chrome tanning with Cr(III) salts (e.g., chromium sulfate) as the most common tanning process. Cr(VI) can result from improper tanning conditions, or even be contained already as an impurity in the tanning chemicals. Even the smallest quantities of Cr(VI) in the leather trigger inflammatory skin reactions when they come into contact with the skin (contact allergen). This chromate allergy ("bricklayer's itch") can, incidentally, also be brought on by cement-containing building materials. Conventional leather tanning requires a very large quantity of water; the wastewater contains readily water-soluble hexavalent chromium. Inadequate wastewater purification and illegal dumping (e.g., of leather waste) lead to pollution of the groundwater. This can be seen, for example, in the Indian city of Kanpur on the Ganges. In 2006, the «Blacksmith Institute», an environmental organization, included Kanpur among the ten most polluted places on earth.

Hexavalent chromium is also an issue in Europe. In Switzerland, it is estimated that up to ten metric tons of chromium(VI) pigments were used for decades after 1970 in the form of coatings with a heavy-metal content to protect bridges, vertical tanks, pressurized pipelines etc. As a result of (improper) remediation work, it is reckoned that up to 300 kilograms of Cr(VI) enters the environment annually across Switzerland. This is evident from a report of Empa, the Swiss Federal Laboratories for Materials Science and Technology.

The purpose of this article is not to point the finger at individual countries. Hexavalent chromium and its release into the environment is a global problem that affects millions of people, especially through the consumption of drinking water. Access to clean drinking water has been a human right since 2010 according to a UN declaration!

Regulations on the use of hexavalent chromium in the EU

The RoHS Directive severely restricts the use of Cr(VI) compounds in Europe: from 1 July 2006, new electrical and electronic equipment that is put on the market is no longer allowed to contain any Cr(VI), mercury, cadmium, lead, or brominated flame retardants. The EU End-of-Life Vehicles Directive prohibits (with a few exceptions) the use of lead, Cr(VI), cadmium, and mercury in the automotive sector.

Limits for hexavalent chromium

The drinking water standard of the U.S. EPA provides for a maximum concentration of total chromium in drinking water (including Cr(III), Cr(VI), and other forms) of 100 µg/L or 100 ppb. The state of California applies stricter limits: since 31 December 2010, the public health goal for hexavalent chromium has been 0.02 µg/L. The EU limit for total chromium, which is the same as that of the World Health Organization (WHO) and the German Drinking Water Ordinance (Trinkwasserverordnung), is 50 µg/L. The Swiss limit for hexavalent chromium is 20 µg/L.

Metrohm method is used by EPA to monitor limits

Extremely sensitive measuring methods are required to monitor compliance with the limits. Working closely with the U.S. EPA, Metrohm developed an extremely sensitive ion chromatographic method for detecting Cr(VI) that is now part of the most recent EPA Method 218.7. The achievable detection limit with this method is lower than the very strict Californian limit of 0.02 µg/L for hexavalent chromium.

Valuable tips on how hexavalent chromium can be determined using ion chromatography are revealed by Metrohm USA on the web page **info.metrohmusa.com/hexachrome/latestnews.html.** There you can download the Application Work AW IC US6-0152-012011 «Determination of Hexavalent Chromium in drinking water, ground water and surface water by Ion Chromatography followed by Post Column Reaction (PCR) and UV/Vis detection (conforming to USEPA method 218.7)» and the EPA Method 218.7 that is based on it. In addition to further background information, the web page also shows you how you can determine Cr(VI) voltammetrically. It's worth a look!

Here you can find out all you need to know about Cr(VI) determination according to EPA 218.7: **info.metrohmusa.com/hexachrome/latestnews.html**

Are you interested in other Metrohm applications? On the web page **www.metrohm.info** you will find information on further applications for downloading.