Trace Level Hexavalent Chromium Occurrence and Analysis [Project #4404]

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OBJECTIVES:
This project had three main objectives: (1) conduct a state-of-the-science (SOS) summary on hexavalent chromium in drinking water, (2) investigate the analytical methods for hexavalent chromium, and (3) perform a preliminary evaluation of chromium behavior in selected drinking water treatment facilities.

BACKGROUND:
Chromium is an inorganic contaminant that has recently received increased attention from the drinking water community and the public at large. In aqueous systems, chromium typically exists in two different oxidation states: the trivalent form [Cr(III)], and the potentially carcinogenic hexavalent form [Cr(VI)]. The EPA currently has a maximum contaminant level (MCL) for total chromium species (Cr(III) plus Cr(VI)) of 100 µg/L (0.1 mg/L). In September 2010, EPA released a draft toxicological review of effects of ingestion of hexavalent chromium, which is due to be finalized in 2014. EPA has also mandated monitoring of both total chromium and hexavalent chromium under the third round of the Unregulated Contaminant Monitoring Rule (UCMR3), scheduled to begin in 2013. Using the health assessment and monitoring results from UCMR3, EPA will then determine if a new MCL should be set specifically for hexavalent chromium. The State of California has established its own total chromium MCL of 50 µg/L (0.05 mg/L), and a non-enforceable Public Health Goal (PHG) for hexavalent chromium of 0.02 µg/L was issued in July 2011. California will now proceed with setting an MCL for hexavalent chromium.

While much is known about the behavior of chromium in drinking water, gaps remain related to treatment and analysis at the very low levels (i.e., sub-µg/L) related to the California PHG.

APPROACH:
The research team first completed a detailed literature review related to hexavalent chromium in drinking water. Then, a series of laboratory experiments were conducted to evaluate preservation and analysis of chromium, using laboratory and real waters. Finally, samples were collected at various water treatment systems and analyzed to evaluate the behavior of chromium through the treatment and distribution infrastructure.
RESULTS/CONCLUSIONS:

Chromium Analysis

The newest low-level detection method for hexavalent chromium (EPA Method 218.7) should be used for sample analysis, although possible interferences from particulate forms of chromium must be investigated. Preservation of chromium speciation prior to analysis is critical. The ammonia buffer specified in Method 218.7 is capable of maintaining chromium speciation even in the presence of free chlorine, NOM, and biological activity, at 4 °C, for up to 14 days. Two other buffers — the carbonate buffer used in the National Chrome and Boron Occurrence Survey and the borate buffer recommended by California Department of Public Health — are not effective when chlorine is present. Both of these buffers were designed for raw water samples and should not be used for finished drinking water sample preservation.

In contrast to hexavalent chromium analysis, which is accurate at levels down to the PHG of 0.02 µg/L, analytical methods for total chromium are at least an order of magnitude less sensitive. When using ICP-MS for total chromium analysis, samples must be digested to eliminate an interference from carbon present in water samples (as now specified for UCMR3 monitoring). Other speciation techniques such as a field ion-exchange and HPLC-ICPMS show promise and should be further investigated, although interference from NOM can be significant.

Chromium Behavior in Water Treatment Plants

While the full extent of low-level chromium occurrence is unknown, detectable chromium was found at all of the water utilities sampled in this project. Utilities participating in the chromium profiles all had levels of total and hexavalent chromium at less than 2% of the current federal MCL of 100 µg/L. Cr(VI) concentrations were < 2 µg/L in the source water and < 0.6 µg/L in finished water, while Total Cr was < 2 µg/L in the source water and < 1.1 µg/L in finished water. Although hexavalent chromium levels were very low, changes were discernible as water moved through the treatment facilities and distribution system. In some cases, there appears to be a small amount of chromium added during treatment due to chemical addition or contact with plant infrastructure (e.g., stainless steel, cement). However, in nearly all cases, this chromium was removed by subsequent treatment such as coagulation or softening.

APPLICATIONS/RECOMMENDATIONS:

Chromium Analysis

Utilities need to be aware that analytical methods for Cr(VI) and Total Cr have very different levels of sensitivity and interferences, and continue to evolve. The analytical method for hexavalent chromium (EPA Method 218.7) is much more sensitive than in the past, and samples previously listed as “below detection” may now be detectable at the low levels (sub-µg/L) now of interest. Moreover, the analytical method for Total
Chromium is much less sensitive than methods for hexavalent chromium, so it is not likely sufficient to use a Total Chromium measurement as a surrogate to see if hexavalent chromium levels are of concern. When collecting samples for Cr(VI) analysis by Method 218.7, the EPA ammonium buffer should be used to preserve samples.

An ion-exchange chromium field speciation method shows promise, and allows determination of Cr(VI) in speciated samples by ICP or graphite furnace, without the use of the (more expensive) EPA Method 218.7 ion chromatography method. This may be useful for utilities who are doing internal process monitoring. However, this method is still not as sensitive as Method 218.7 and NOM will interfere with the method.

**Chromium Behavior in Water Treatment Plants**

Utilities who are concerned about chromium should monitor their raw water as well as within their treatment process to determine the source of chromium in finished water and effectiveness of treatment processes. Monitoring should include both Cr(VI) and Total Cr, and since Cr(III) and Cr(VI) can easily interconvert, redox conditions and sample preservation must be considered. Utilities may also consider collecting filtered samples to evaluate particulate versus soluble forms of chromium. Results must be interpreted carefully in light of the detection capabilities of each analytical method used.