Changes from EPA Method 218.6 to 218.7 Yield Improved Detection Limits for Hexavalent Chromium

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Introduction

Chromium is a naturally occurring metal that is widely used in steel making, plating, tanning, paints, dyes, and wood preservation. The most common environmental forms are trivalent Cr(III), hexavalent Cr(VI), and the metallic form Cr. The trivalent form is a nutrient and sold as a nutritional supplement, while Cr(VI) is a highly toxic carcinogen and regulated by the US EPA in drinking water and certain waste waters.[1, 2] Cr(VI) is also monitored in soils, sludges, sediments, concrete, and leather to prevent exposure. In the US, the Criteria for Maximum Concentration is 0.016 μg/L for surface waters. Many countries also have discharge regulations, including Argentina, Russia, and Italy (0.2 mg/L); Brazil, Mexico and Poland (0.5 mg/L), and Hungary (0.1 mg/L). Some countries have set a range for their discharge limits depending on the type of water, such as Chile (0.05–0.2 mg/L) and Tunisia (0.01–0.5 mg/L).

In 1999, the state of California established a public health goal (PHG) of 0.2 μg/L, parts-per-billion (ppb), for Cr(VI) and 2.5 μg/L for total chromium.[3] The PHG was based on an estimated one-in-one-million lifetime cancer risk level. The US Environmental Protection Agency (EPA) conducted a comprehensive review of the health effects of chromate based on toxicity studies performed by the US National Toxicology Program in 2008.[4] In 2009, the Office of Environmental Health Hazard Assessment (OEHHA) at the California EPA proposed to lower the PHG for Cr(VI) to 0.06 ppb.[5] In September 2010, the EPA released the *Toxicological Review of Hexavalent Chromium* which was opened for public comment.[6] The EPA is expected to release the results of this assessment in 2011/2012. Based on the EPA's 2010 toxicological review, the OEHHA issued a new PHG for chromate at 0.02 μg/L in drinking water. In 2011 the EPA recommended enhanced monitoring for Cr(VI); drinking water intake, well locations and entry points to and within distribution systems are to be sampled quarterly and ground water sources semi-annually. This recommendation came from an independent survey of drinking water from 35 major cities in the US, who reported that a vast majority exceeded the regulatory limits for Cr(VI). Current prevalence data suggests that the incidence of Cr(VI) is more dependent on the concentration being measured; the higher the concentration chosen, the less will be found. Conversely, if concentrations chosen are close to the minimum detection limits (MDLs), then Cr(VI) will be found to be virtually everywhere. Though federally regulated, the EPA method 200.8 measures total chromium, with the assumption being that this amount be treated as Cr(VI). At typical water pH, most chromium will be in the Cr(VI) form. However, California uses the more specific EPA 218.6 that uses anion exchange separation followed by postcolumn derivatization and visible detection to specifically determine Cr(VI). It remains to be seen if the more specific methods mentioned below will be accepted for compliance monitoring at a national level. Finally, the EPA is proposing to add Cr(VI) to its Unregulated Contaminant Monitoring Rule 3, which will require analysis using a new method EPA 218.7.

Detection

Cr(VI) species are oxyanions (e.g., CrO_4^{2-}, $Cr_2O_7^{2-}$) and are thus amenable to separation by anion-exchange chromatography. Anion-exchange chromatography with postcolumn derivatization and visible detection has proven to be a robust method for the analysis determination of Cr(VI) from in a wide variety of sources and validated as EPA method 218.6. This method was developed in 1991 for drinking water, groundwater, and industrial water effluents. The MDLs for this method are 0.3 to 0.4 μg/L depending on the water matrix. This method uses a Thermo Scientific Dionex IonPac AS7 column (4 × 250 mm) for separation followed by detection after postcolumn reaction with diphenylcarbazide, which yields a compound with visible absorbance at 530 nm. Samples are collected and pH adjusted to 9–9.5 using an ammonium hydroxide/ammonium sulphate based preservation buffer and stored at 4 °C for 24 h to prevent reduction to Cr(III). Filtering is required prior to injection.

As more information became available

concerning Cr(VI) toxicity and subsequent lower regulatory limits established by the OEHHA, it soon became apparent that 218.6 did not meet the more stringent sensitivity requirements. Therefore, several modifications were made to improve the detection limits to 0.02 µg/L. These modifications included lower flow-rates, a larger reaction coil and a larger injection volume. Lower flow-rates combined with a larger reaction coil, from 375 µL to 750 µL, provides a longer residence time to ensure that the reaction of Cr(VI) anion with diphenylcarbazide go to completion. The larger injection loop allows more mass (total anions) to be loaded onto the anion-exchange column. Greater sensitivity can be gained by increasing the volume of sample injected, but too large a sample can cause retention time shifts or loss of efficiency when column overloading leads to excessive peak distortion. In addition to Cr(VI), other common anions (e.g., Cl^-, SO_4^{2-}) in the sample and sample buffer compete with Cr(VI) for the anion-exchange sites on the column. Thus a balance between maximum loading without overloading needs to be determined. To avoid matrix effects, the concentration of the sample buffer used for pH adjustment was lowered 10-fold. In most cases this was more than sufficient to adjust the pH of the sample and allowed a larger loop injection for increased mass loading and ultimately greater sensitivity. The capacity of the anion-exchange column used was more than enough for the binding and separation of competing anions from the matrix and sample preservation buffer. Peak heights more than doubled with these adjustments, yielding MDLs of 0.02 µg/L, as described in Thermo Fisher Scientific Application Update 144 and elsewhere.[7, 8] However, when the OEHHA further lowered the PHG to 0.02 µg/L in 2011, the sensitivity improvements in AU 144 were once again insufficient.

Further improvements were developed and are summarized in Thermo Fisher Scientific Application Update 179.[9] In AU 179, a 2-mm column format was used and options for postcolumn reagent delivery were incorporated into the method. Results show greatly improved sensitivity with a 2-mm column format, and that there was no difference in sensitivity using a pneumatic delivery system, auxiliary pump or system pump for postcolumn reagent delivery. Figure 1 shows a chromatogram of a 0.1 µg/L Cr(VI) as CrO_4^{2-} standard in deionized water (DI) and in high-ionic water (HIW) using a DP pump for PCR delivery and a semi-micro flow cell. The elution time for chromate was about 7 min. A slight shift (0.05 min) in the retention time for chromate in the HIW matrix was observed. However, the peak shape and the peak area response were similar to standards in DI water. In the concentration range 0.005–1 µg/L, the peak response recovery ranged from 89–103% in the presence of 100 mg/L chloride, sulphate and carbonate.

The MDLs for Cr(VI) as CrO_4^{2-} are summarized in Table 1. MDL is a measure of the precision of replicate injections of a low-level standard and is defined as the minimum concentration of an analyte that can be

Figure 1: Determination of a 0.1 µg/L Cr(VI) standard in (a) DI water and (b) HIW. Column: Dionex IonPac AG7 (2 × 50 mm) and AS7 (2 × 250 mm) column set; eluent: 250 mM $(NH_4)_2SO_4$/100 mM NH_4OH; flow-rate: 0.36 mL/min; injection volume: 1 mL; postcolumn reagent: 2 mM diphenylcarbazide/10% methanol/1 N sulphuric acid; reaction coil: 125 µL; flow cell: semi-micro. Peak: 1 = Cr(VI).

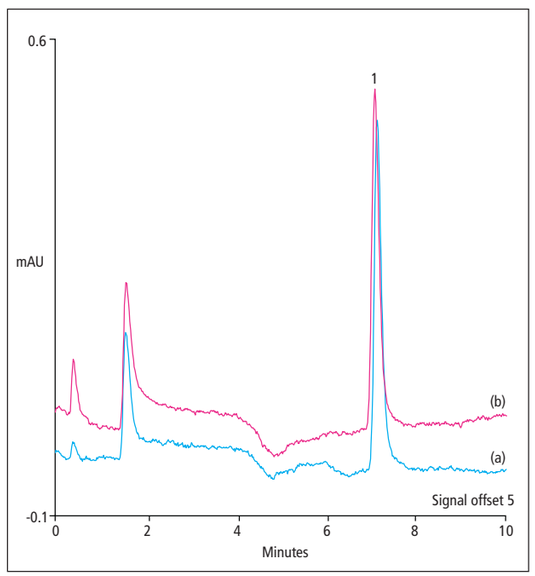

Figure 2: Determination of Cr(VI) in (a) a DI water blank, (b) a 0.007 µg/L Cr(VI) standard in DI water and (c) a municipal tap water sample, yielding a measured value of 0.05 µg/L of Cr(VI). Column: Dionex IonPac AG7 (2 × 50 mm) and AS7 (2 × 250 mm) column set; eluent: 250 mM $(NH_4)_2SO_4$/100 mM NH_4OH; flow-rate: 0.36 mL/min; injection volume: 1 mL; postcolumn reagent: 2 mM diphenylcarbazide/10% methanol/1 N sulphuric acid; reaction coil: 125 µL; flow cell: standard PEEK. Peak: 1 = Cr(VI).

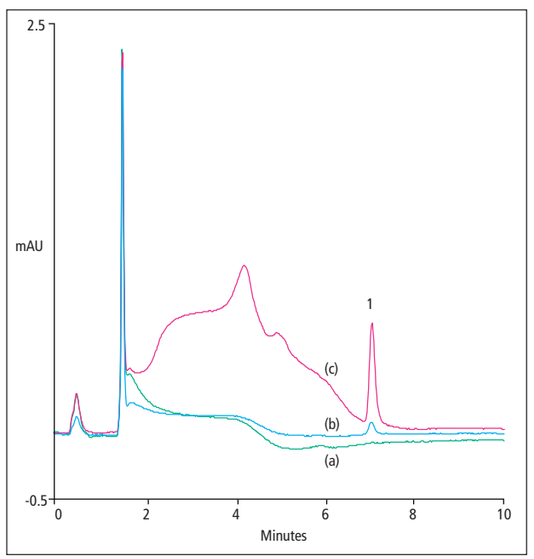

Table 1: Method detection limits for chromate in HIW based on a 1000 µL injection, 2 mm format.

Chromate Conc. (µg/L)	Std. Dev. (µg/L)	RSD (%)	MDL (µg/L)
0.001	0.0003	10.03	0.0009
0.005	0.0004	6.62	0.0013

identified, measured and reported with 99% confidence that the analyte concentration is greater than zero. In this application, the MDL for chromate Cr(VI) as CrO_4^{2-} was determined by analysing seven replicate injections of HIW fortified with Cr(VI) as CrO_4^{2-} at two concentration levels of 0.001 and 0.005 µg/L (i.e., approximately 3–5× the estimated instrument detection limit). Both levels produced a calculated MDL value of 0.001 µg/L. This will enable a minimum quantification limit of 0.003 µg/L for Cr(VI) as CrO_4^{2-}, which will be adequate for routine analysis at the proposed California PHG of 0.02 µg/L. Comparable results were obtained for seven replicate injections of DI water fortified with Cr(VI) as CrO_4^{2-}. Figure 2 shows (a) a DI water blank, (b) a 0.007 µg/L Cr(VI) as CrO_4^{2-} standard in DI water and (c) a municipal tap water sample with a measured concentration of 0.05 µg/L Cr(VI).

New EPA Method 218.7

Due to the same toxicity and regulatory developments, the EPA Office of Ground Water and Drinking Water incorporated these improvements to update method 218.6 to a new method, EPA 218.7. Though this method uses a 4-mm column format, a 2-mm format can easily be used while still complying with the acceptable criteria for the EPA's method flexibility rule. Using a 4-mm format column, single laboratory Lowest Concentration Minimum Reporting Levels (LCMRLs) for Cr(VI) ranged from 0.012 to 0.036 µg/L. DLs for Cr(VI) fortified into reagent water ranged from 0.0044 to 0.015 µg/L. Within the normal pH range in drinking water, Cr(VI) anion dominates above pH 7; therefore, the method preservative is designed to buffer samples to at least pH 8. This lowering of the pH from 9–9.5 to 8 makes sample adjustment easier as well as practical. Chromate compounds are soluble, mobile and stable in an oxidizing environment. In contrast, soluble Cr(III) species oxidize to Cr(VI) in the presence of free chlorine, although natural organic matter in surface water sources may complex Cr(III), slowing its oxidation even in a highly oxidizing environment. The rate of Cr(III) oxidation increases with chlorine concentration and is pH-dependent. For these reasons both preservation options prescribed in EPA 218.7 include ammonium ions to complex free chlorine. The resulting formation of chloramines minimizes but does not completely prevent, the oxidation of Cr(III). During method development, experiments were conducted that demonstrated the ability of the method preservative to minimize the oxidation of Cr(III) and to prevent the reduction of Cr(VI) for at least 14 days in drinking water from ground and surface water sources. Acceptable method performance has been demonstrated for samples with hardness up to 350 mg/L as $CaCO_3$ and total organic carbon content of 3 mg/L.

Conclusion

This testing presents modifications to the existing US EPA method 218.6 to allow sufficient sensitivity for determining hexavalent chromium (i.e., Cr(VI) as CrO_4^{2-}) at the proposed California PHG level of 0.02 µg/L and have been incorporated into EPA method 218.7 for drinking water. The use of 2-mm guard and analytical columns resulting in an MDL for Cr(VI) at 0.001 µg/L will allow a minimum quantification limit of 0.003 µg/L, which is more than sufficient for the proposed California PHG of 0.02 µg/L.

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