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NOM and alkalinity interference in trace-level hexavalent chromium analysis

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ABSTRACT

Three analytical methods were evaluated for hexavalent and trivalent chromium analyses in the presence of natural organic matter (NOM) and alkalinity. Each method was tested using a simulated tap water with 1 μg L^{-1} Cr(VI) and 0.8 μg L^{-1} Cr(III) and several concentrations of NOM and/or alkalinity. An ion chromatograph with post column reaction cell conforming to USEPA Method 218.7 could accurately quantify Cr(VI) in the presence of up to 8 mg C L^{-1} NOM and up to 170 mg L^{-1} as $CaCO_3$ alkalinity, and no oxidation of chromium was observed when 0.8 μg L^{-1} Cr(III) was also present. A high-performance liquid chromatography coupled with inductively coupled plasma (HPLC–ICPMS) method and a field speciation method were also evaluated. Each of these methods was unaffected by the presence of alkalinity; however, the presence of NOM created issues. For the HPLC–ICPMS method, as the concentration of NOM increased the recovery of Cr(VI) decreased, resulting in a 'false negative' for Cr(VI). However, for the field speciation method, Cr(III) was complexed by NOM and carried through the ion exchange column, resulting in a 'false positive' for Cr(VI).

1. Introduction

In natural waters chromium typically exists in the trivalent [Cr(III)] or hexavalent [Cr(VI)] oxidation states. The current United States Environmental Protection Agency (USEPA) maximum contaminant level (MCL) for total chromium is 100 μg L^{-1} (0.1 mg L^{-1}) [1] but a new MCL for hexavalent chromium is under consideration pending a health assessment to be finalized in 2014 [2]. The State of California has established its own total chromium MCL of 50 μg L^{-1} (0.05 mg L^{-1}), a non-enforceable Public Health Goal (PHG) for Cr(VI) of 0.02 μg L^{-1} was issued in July 2011 [3], and as of August 22, 2013 the draft Cr(VI) MCL is 10 μg L^{-1} [4]. There is widespread public interest and concern related to detection of Cr(VI) in potable water above the PHG as evidenced by a recent high-profile non-peer-reviewed survey of U.S. drinking waters [5], prompting research carefully examining the accuracy of trace chromium analysis. There is particular concern about methods which cause false detection of Cr(VI) given that it is a suspected carcinogen in water and has a very low PHG.

1.1. Analytical techniques for Cr(VI)

The analysis of low level Cr(VI) concentrations is challenging due to the redox sensitivity of chromium. It is known that the presence of oxidizing or reducing agents, either naturally-occurring or added for drinking water treatment, may alter the oxidation state of chromium in the collected sample as a function of time. Unless a method immediately quantifies chromium species in the field, preservation is necessary to stop speciation changes until later sample analysis. pH also plays a major role in the redox chemistry of chromium, with Cr(III) thermodynamically favored at lower pH and Cr(VI) favored at higher pH. It has been a challenge to find appropriate methods of preservation that are applicable to a wide variety of waters, prompting parallel efforts to immediately speciate samples in the field to completely avoid problems with speciation issues caused by sample preservation.

None of the methods for Cr(VI) analysis are currently approved for compliance with the Safe Drinking Water Act (SDWA), since, at present, Cr(VI) is not a regulated chemical under the SDWA. However, the USEPA Method 218.7 is approved for Cr(VI) determination by the Unregulated Contaminant Monitoring Rule 3 [6]. This method is described below, along with an HPLC–ICPMS method and a field speciation method. These latter two methods might be beneficial in that one analytical instrument could be used to determine both total chromium and Cr(VI). Each of these methods has advantages and

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disadvantages. The field speciation method avoids concerns with speciation changes during storage, is simple to use, and only requires one analytical instrument to measure both total chromium and Cr(VI). The HPLC–ICPMS method likewise only requires one analytical instrument to measure both types of chromium but does require more expertise than the field speciation method. Finally, the USEPA Method 218.7 has the lowest detection capability for Cr(VI) but an additional instrument is required to measure total chromium.

1.1.1. USEPA method 218.7 (ion chromatography coupled with a post-column reactor)

Ion chromatography coupled with a post-column reactor (IC-PCR) has become the industry standard for low level Cr(VI) analysis. Hexavalent chromium will react with 1,5-diphenylcarbazide to form a pink complex whose color intensity is proportional to the Cr(VI) concentration in the original solution (Standard Method 3500-Cr D) [7]. This solution can be analyzed using a spectrophotometer set at 540 nm to determine the Cr(VI) concentration. When this method was coupled with ion chromatography (IC) in USEPA Method 218.6 [8] the detection limit improved substantially. In this method, filtered water samples are preserved at pH 9 using a 2500 mM ammonium sulfate plus 1000 mM ammonium hydroxide buffer. The IC column (Dionex IonPac AS7 or equivalent) is able to separate the Cr(VI), which exists as chromate (CrO_4^{2-}) at this pH, from other anionic species. The 1,5-diphenylcarbazide is added using a post-column mixing coil and the pink complex formed is measured with a spectrophotometer (as described above). The method detection limit (MDL) for this method is listed as 0.3 $\mu g\,L^{-1}$ for potable water analysis [9], while the minimum reporting level (MRL) is 0.4 $\mu g\,L^{-1}$ [10].

USEPA Method 218.6 has been modified several times over the years to improve the detection limit [11,12,13], and in 2011 the USEPA released Method 218.7, "Determination of Hexavalent Chromium in Drinking Water by Ion Chromatography with Post-Column Derivatization and UV–Visible Spectroscopic Detection," to update Method 218.6 [14]. The method describes two separate IC systems that can be used for analysis. Operating conditions for each of these systems are described, including eluents (either ammonium sulfate/ammonium hydroxide or sodium carbonate/sodium bicarbonate), column and reaction coil sizes, and flow rates. For USEPA Method 218.7 the MDL ranges from 0.0044 to 0.015 $\mu g\,L^{-1}$, depending on the preservative and eluent system used, while the MRL is 0.02 $\mu g\,L^{-1}$ [14].

1.1.2. HPLC–ICPMS

Many researchers have utilized high-performance liquid chromatography (HPLC) coupled with inductively coupled plasma mass spectrometry (ICPMS) to conduct a speciation analysis for chromium [15–24]. Soluble Cr(III) typically exists as Cr^{3+}, $CrOH^{2+}$, or $Cr(OH)_2^+$ in natural waters while Cr(VI) exists as $HCrO_4^-$ or CrO_4^{2-}. Since the Cr(III) species are positively charged ions and the Cr(VI) species are negatively charged ions, they can be separated using either anion or cation exchange. After separation, ICPMS can be used to quantify the concentration of one or both of the chromium species.

In order to achieve low detection limits, both the HPLC and the ICPMS portions of the analysis must be optimized. Depending on the type of column used, HPLC–ICPMS may quantify only Cr(VI) or it may be able to quantify both Cr(III) and Cr(VI). In the latter case HPLC must achieve a good separation between the Cr(III) and Cr(VI) peaks with a high signal-to-noise ratio. Column type, eluent composition and pH, and injection volume must be optimized for best results.

1.1.3. Field speciation method

Another technique for determining Cr(VI) is based on a field method using a cation exchange column [25]. In theory, passing water through this column will remove all the Cr(III) (a cation) but not the Cr(VI) (an anion). This method has a reported MDL of 0.05 $\mu g\,L^{-1}$ for Cr(VI) when the collected sample is analyzed with graphite furnace atomic absorption spectrometry (GFAAS). However, rigorous testing in the presence of constituents such as natural organic matter (NOM) has not been conducted. Previous work suggests that NOM can form complexes with Cr(III), converting it into an anion that can pass through the column and give a "false positive" of Cr(VI) in samples [26,27,28,29], and the authors include a caveat that waters with organic carbon greater than 5–10 $mg\,L^{-1}$ should be tested for this type of "false positive" by adding a known concentration of Cr(III) to a duplicate and checking for higher Cr(VI) concentrations [25]. On the other hand, other work has suggested that NOM found in soil organic matter may reduce Cr(VI) to Cr(III) to give a "false negative" [30,31,32,33,34] although at least one researcher has reported that NOM does not participate in redox reactions with chromium (tested at a pH of 7.35 ± 0.11) [35].

1.2. Summary of possible interferences with chromium analysis from carbon

ICPMS is the most sensitive USEPA approved analytical method for determining low-μg/L levels of total chromium [Cr(III)+Cr(VI)] [36] but there are potential drawbacks. Prior to analysis, total chromium samples are collected in plastic or glass bottles and preserved with HNO_3, and have a maximum 6 month holding time [37]. Past work by MWH Laboratories conducted a study in which more than 1500 drinking water samples were analyzed for both Cr (VI) and total chromium using IC and ICPMS, respectively [38]. This study found that nearly half of the 770 samples with total chromium greater than 1 $\mu g\,L^{-1}$ had Cr(VI) concentrations measured by IC to be greater than the total chromium measured by ICPMS. Eaton et al later noted that operating the ICPMS in a 'collision cell' or 'dynamic reaction cell' mode where the argon plasma was supplemented with ammonia fixed most of this problem [39]. This 'collision cell technology' or 'CCT' is a technique that attempts to eliminate the formation of polyatomic interferences that can occur when using ICPMS for total chromium measurement [40]. These interferences occur at the most abundant isotopes of chromium, ^{52}Cr and ^{53}Cr, when carbon or chlorine is present (e.g., $^{40}Ar^{12}C$, $^{35}Cl^{16}O^{1}H$, $^{37}Cl^{16}O$). This means waters with high alkalinity, high carbon content, or high chloride content will result in more background noise and higher detection limits.

While total carbon can result in a false positive for total chromium on the ICPMS as described above, organic carbon can contribute to either a false positive or a false negative for Cr(VI) measurements. For example, the IC method uses anion exchange to capture Cr(VI), and then elutes it in a peak for the measurement. In this instance there would be a false negative if any organic carbon present complexes the Cr(VI) and carries it through the anion exchange column. False positives for Cr(VI) can result when using HPLC–ICPMS or the field speciation method described above, since in these methods the Cr(III) is supposed to be captured within the ion exchange media so that all the chromium measured is assumed to be Cr(VI). Any Cr(III) that passes through because of complexation with organic carbon would therefore be falsely categorized as Cr(VI).

1.3. Objective of study

This study was conducted to evaluate the measurement of hexavalent chromium using these three analytical techniques in a simulated drinking water containing varying levels of alkalinity

and NOM to determine whether there are any analytical issues when inorganic or organic carbon co-occurs with chromium.

2. Materials and methods

In this study three analytical methods for the determination of low level Cr(VI) were compared. These included USEPA Method 218.7 [14], an HPLC–ICPMS method modified from a protocol previously described by Seby et al. [23], and a field speciation method developed by Ball and McClesky [25]. The analytical procedures associated with each method are described below in further detail. Preliminary experiments were conducted to estimate the MRL for each analytical method used in the study. Simulated Blacksburg (VA) tap water was formulated and varying amounts of alkalinity and/or NOM were added along with a 1 μ L^{-1} spike of Cr(VI). A 0.8 μg L^{-1} Cr(III) spike was also added to some test conditions so that each method could be evaluated on its effectiveness in preventing oxidation of Cr(III) to Cr(VI). Standard calibration solutions obtained from High-Purity Standards (Charleston, SC) were used as the spiking solutions.

2.1. Simulated tap water preparation

Simulated tap water was prepared by adding calcium chloride, potassium chloride, sodium silicate, and magnesium silicate to distilled water to obtain a water chemistry with approximately 11 mg L^{-1} calcium, 4 mg L^{-1} magnesium, 4 mg L^{-1} silicon, and 1.5 mg L^{-1} potassium. The resulting chloride and sulfate concentrations were 21 mg L^{-1} and 16 mg L^{-1}, respectively. Alkalinity was added by dosing an appropriate amount of 20 g L^{-1} sodium bicarbonate solution. In this study various levels of alkalinity were evaluated, including 0, 40, and 170 mg L^{-1} as $CaCO_3$. Natural organic matter (NOM) was added at 0, 2, 4, and 8 mg C L^{-1} by dosing an appropriate amount of Suwanee River Fulvic Acid II (International Humic Substances Society, Saint Paul, MN). The pH of each simulated tap water was adjusted to 7.7 with 0.1 N sodium hydroxide or 0.1 N hydrochloric acid prior to any chromium addition to avoid speciation changes which might be caused by changing pH. The Suwanee River Fulvic Acid II stock solution did contain 0.08 μg Cr per mg C (as measured by atomic absorption spectroscopy) so this amount was deducted from each result as appropriate. Alkalinity was measured using standardized sulfuric acid titration according to Method 2320 [7]. TOC was measured using the combustion catalytic oxidation/NDIR method with a Shimadzu TOC-VCSN (Columbia, MD) [7]. The MRL for this analysis was 0.25 mg C L^{-1}.

2.2. USEPA Method 218.7 (ion chromatography coupled with a post-column reactor)

Triplicate samples from each experimental condition were analyzed using USEPA Method 218.7 [14]. Five mL samples were immediately preserved with 0.05 mL of 250 mM ammonium sulfate plus 100 mM ammonium hydroxide buffer/dechlorinating solution upon collection. Samples were analyzed within 14 days of collection using a Dionex ICS1000 ion chromatograph (Sunnyvale, CA) with a variable wavelength detector (VWD). The eluent was also a 250 mM ammonium sulfate and 100 mM ammonium hydroxide solution. The sample injection loop had a volume of 1 mL. Hexavalent chromium was separated from the rest of the matrix using a Dionex IonPac AG7 guard (2 mm ID × 50 mm) in conjunction with an IonPac AS7 analytical (2 mm ID × 150 mm) anion exchange column and then derivatized with 1,5-diphenylcarbazide in a post-column reactor (PCR). Cr(VI) was detected spectrophotometrically at a wavelength of 530 nm. Calibration standards were prepared by diluting a Cr(VI) solution obtained from High-Purity Standards (Charleston, SC). Quality control check standards and blanks were analyzed after every 10 samples. Samples were also randomized prior to analysis to minimize effects of instrument variability.

2.3. HPLC–ICPMS method

Triplicate aliquots from each experimental condition were also analyzed using HPLC in conjunction with ICPMS. No preservative was used since samples were analyzed within one day of collection. For each sample, 1 mL was injected onto a Dionex CG5 guard (4 mm ID × 50 mm) in conjunction with a CS5 analytical (4 mm ID × 150 mm) cation exchange column using a 1 mL sample loop. The sample was then transferred to a Thermo Electron X-Series ICPMS (Waltham, MA) using 350 mM nitric acid eluent delivered by a Dionex Advanced Gradient Pump at a flow rate of 1 mL per minute. The ICPMS was operated in collision cell technology (CCT) mode with helium gas to minimize the interference from the polyatomic $^{40}Ar^{12}C$ dimer. Mass 52 was monitored for a period of 300 seconds and the area under the chromium peak was calculated by the PlasmaLab software. A calibration curve was constructed using low-level Cr(VI) calibration standards prepared by diluting from a 1 mg L^{-1} solution obtained from High-Purity Standards (Charleston, SC). Quality control check standards and blanks were analyzed after every 10 samples. Samples were also randomized prior to analysis to minimize effects of instrument variability.

2.4. Field speciation method

Samples were also collected in triplicate using a field speciation method developed by Ball and McClesky (2003) [25]. In this method a sample is passed through a cation exchange cartridge with a volume of 1.5 mL (IC-H, Alltech). The first 3 mL of each sample is passed through the column to waste. Then 5–10 mL is collected in a plastic tube for subsequent analysis by ICPMS. After collection and prior to analysis the sample is preserved with nitric acid to 2% v/v. As with the HPLC–CPMS method, the ICPMS analysis was conducted in CCT mode with helium gas to minimize interference from the polyatomic $^{40}Ar^{12}C$ dimer on the ^{52}Cr isotope. If the method is functioning properly, any total chromium measured by ICPMS is actually Cr(VI) since the Cr(III) should be retained on the cation exchange column. As in the case of the two previous analytical methods, quality control check standards and blanks were analyzed after every 10 samples and samples were randomized to minimize effects of instrument variability.

2.5. Minimum reporting level (MRL) determination

Prior to running tests on waters containing Cr(VI), an MRL for Cr(VI) was determined for each analytical method used in this study per the protocol detailed in USEPA Method 218.7 [14]. Results indicate that the IC-PCR method has the lowest MRL

Table 1
Summary of MRLs for Cr(VI) analytical methods.

Method	Sample matrix	Date	MRL (μg/L)
ICP-MS	DDW	May 2012	0.1
ICP-MS	DDW	July 2012	0.2
ICP-MS	DDW	October 2012	0.2
ICP-MS	Simulated tap	August 2012	0.5
ICP-MS	Simulated tap	October 2012	0.5
HPLC–ICPMS	DDW	July 2012	0.2
USEPA Method 218.7	DDW	May 2012	0.02

for Cr(VI) of the three methods tested (Table 1). Using distilled deionized water (DDW) as the sample matrix the MRL for the IC-PCR method was 0.02 μg L^{-1}, which was an order of magnitude lower than the MRL for either the ICPMS or HPLC–ICPMS methods. The effect of water chemistry on MRL was also evaluated for the ICPMS method. During the initial testing and using DDW an MRL of 0.1 μg L^{-1} was obtained; however, during repeat tests this could not be duplicated. When the simulated tap water was used (including an alkalinity of 40 mg L^{-1} as $CaCO_3$) an MRL of 0.5 μg L^{-1} was obtained. Therefore, for all subsequent tests a Cr(VI) concentration of approximately 1 μg L^{-1} was used to insure that it exceeded the MRL for all analytical methods studied.

2.6. Statistical analysis

Student's *t* tests with an alpha of 0.05 were conducted to establish statistical significance. However, due to the small standard deviations of some of the analytical methods, consideration was used when assessing whether values were 'practically' different based on measurement error. In this study, values were deemed 'not significantly different' even if they had a *t*-test *p*-value less than 0.05 if the difference between means was less than or equal to 0.2 μg L^{-1}.

3. Results and discussion

3.1. Effect of NOM on analytical method performance

As discussed in Sections 1.1.3 and 1.2, NOM may affect analytical method performance in a variety of ways. For ICPMS, the carbon component of NOM can lead to false positives for chromium even when operating in CCT mode. Also, NOM may oxidize any Cr(III) that is present to Cr(VI), resulting in false positives for the IC-PCR, HPLC–ICPMS, and field speciation methods. In this study three levels of NOM were added to the simulated tap water to evaluate the effect on each analytical method. These included nominal values of 2, 4, and 8 mg L^{-1} as C (Table 2). The effect of the NOM addition on each of the analytical methods is detailed in the sections that follow.

3.1.1. ICPMS (total chromium)

Total chromium for each NOM test condition was analyzed by ICPMS in CCT mode. Total chromium measured in the simulated tap water was 1.0 μg L^{-1} and the total chromium measured in each of the waters with NOM ranged between 0.8 and 0.9 μg L^{-1} (Fig. 1). There was no statistical or practical difference between these values. As expected, when 0.8 μg/L Cr(III) was added to the simulated tap water the total chromium measured was 1.8 μg L^{-1}. Total chromium measured in the waters with NOM ranged from 1.6 to 1.7 μg L^{-1} (Fig. 1). There was also no statistical or practical difference between these concentrations.

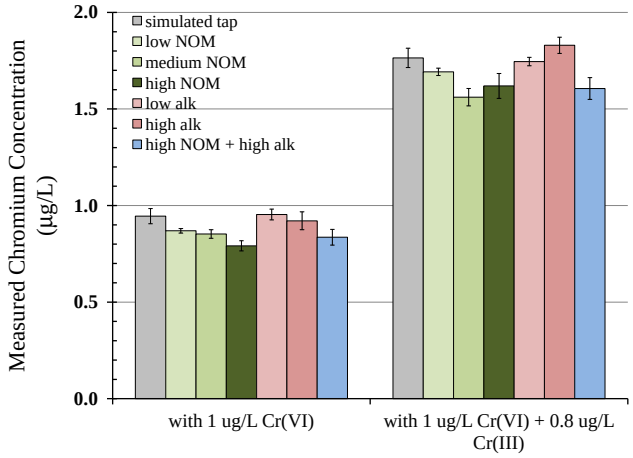

Fig. 1. Total chromium concentration in seven water chemistries as analyzed by ICPMS. Either 1 μg L^{-1} Cr(VI) or 1 μg L^{-1} Cr(VI)+0.8 μg L^{-1} Cr(III) was added to each water chemistry prior to analysis. Error bars denote ±1 standard deviation.

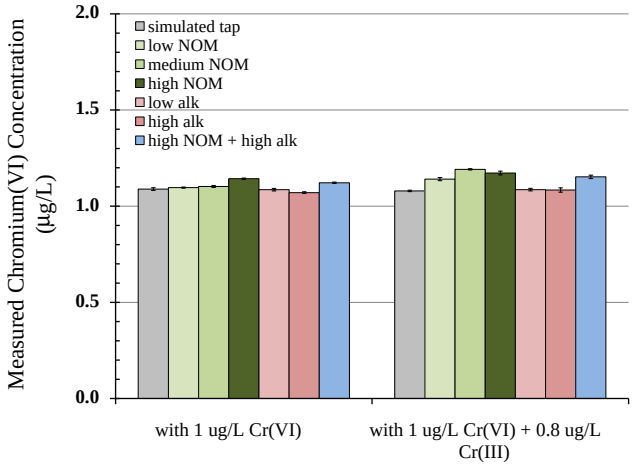

Fig. 2. Cr(VI) concentration in seven water chemistries as analyzed by IC-PCR. Either 1 μg L^{-1} Cr(VI) or 1 μg L^{-1} Cr(VI)+0.8 μg L^{-1} Cr(III) was added to each water chemistry prior to analysis. Error bars denote ±1 standard deviation.

Table 2
pH, alkalinity, and TOC measurements for the seven study conditions.

Test Condition	pH		Alkalinity, mg/L as $CaCO_3$		TOC, mg/L as C	
	With 1 μg/L Cr (VI)	With 1 μg/L Cr (VI)+ 0.8 μg/L Cr(III)	With 1 μg/L Cr (VI)	With 1 μg/L Cr (VI)+ 0.8 μg/L Cr(III)	With 1 μg/L Cr (VI)	With 1 μg/L Cr (VI)+ 0.8 μg/L Cr(III)
Baseline	7.8	7.9	5.2	5.0	0.2	0.1
Low NOM	7.7	7.8	6.2	5.6	1.9	1.8
Medium NOM	7.8	7.8	6.6	6.2	4.4	4.4
High NOM	7.8	7.6	7.5	6.6	8.2	8.4
Low alk	7.6	7.7	37	41	0.1	0.1
High alk	7.8	7.9	179	167	0.2	0.3
High NOM+high alk	7.9	7.8	174	175	8.7	8.4

3.1.2. IC-PCR

Based on the MRL data (Table 1) the IC-PCR method is the most sensitive method for Cr(VI) tested in this study. The simulated tap water had a Cr(VI) concentration of 1.1 μg L^{-1} using this method (Fig. 2) and NOM addition did not affect the Cr(VI) concentration. Likewise, there was no difference in Cr(VI) recovery when 0.8 μg L^{-1} Cr(III) was present (Fig. 2). While most researchers seem to agree (see Section 1.1.3) that NOM can reduce Cr(VI) to Cr(III), the results of this study indicate that the presence of up to 8 mg L^{-1} NOM does not affect Cr(VI) for this analytical method. More study might be needed to ascertain the effect of NOM at other pH levels. Extra work performed in our laboratory appears to indicate that NOM might have mixed effects on chromium speciation at lower or higher pH than that used in this study. At pH 5.2–5.9 the presence of NOM tended to reduce Cr(VI), while at pH 9.2–9.4 NOM tended to oxidize Cr(III).

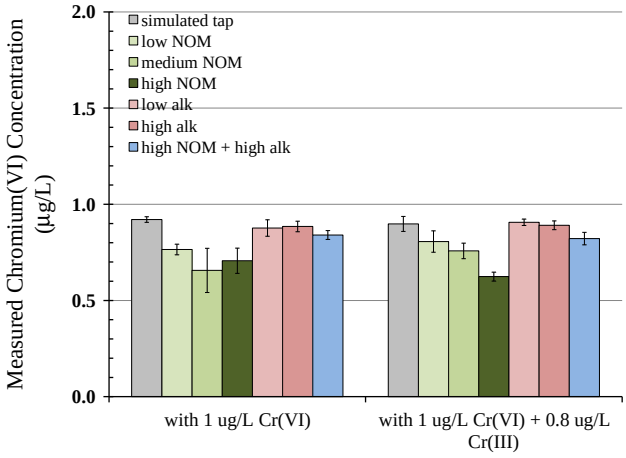

Fig. 3. Cr(VI) concentration in seven water chemistries as analyzed by HPLC–ICPMS. Either 1 µg L^{-1} Cr(VI) or 1 µg L^{-1} Cr(VI)+0.8 µg L^{-1} Cr(III) was added to each water chemistry prior to analysis. Error bars denote ±1 standard deviation.

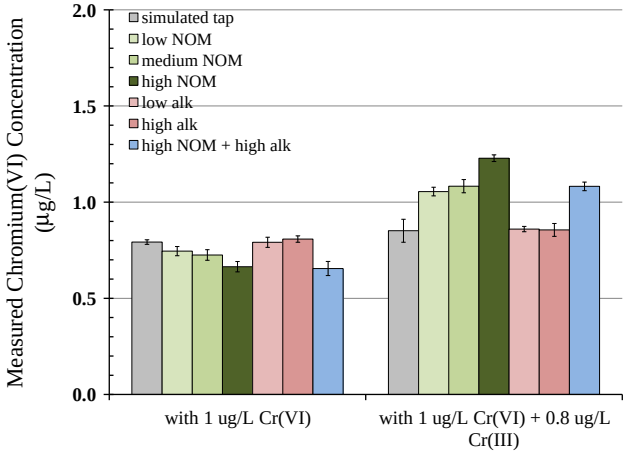

Fig. 4. Cr(VI) concentration in seven water chemistries as analyzed by the field speciation method. Either 1 µg L^{-1} Cr(VI) or 1 µg L^{-1} Cr(VI)+0.8 µg L^{-1} Cr(III) was added to each water chemistry prior to analysis. Error bars denote ±1 standard deviation.

3.1.3. HPLC–ICPMS

The simulated tap water had a 0.9 µg L^{-1} Cr(VI) concentration as measured by the HPLC–ICPMS method. However, the addition of NOM slightly decreased the amount of Cr(VI) measured (Fig. 3) although the difference was not statistically different. Similar results were noted for the conditions with 0.8 µg L^{-1} Cr(III) added, except that the difference between the simulated tap water and the water with high NOM was statistically and practically different (0.9 versus 0.6 µg L^{-1}, respectively) (Fig. 3). A possible reason for this phenomenon might be that the NOM is complexing some of the chromium and then adsorbing to the HPLC column since the IC-PCR results do not indicate that the NOM is reducing the Cr(VI). The fact that no extraneous chromatographic peaks were observed lends some credence to this hypothesis and additional testing using the method of standard addition could identify and correct for most errors associated with matrix effects.

3.1.4. Field speciation

For the field speciation method the simulated tap water had a measured Cr(VI) concentration of 0.8 µg L^{-1}. For the test conditions with low NOM, medium NOM, and high NOM conditions the Cr(VI) concentration measurements were 0.8, 0.7, and 0.7 µg L^{-1}, respectively (Fig. 4) indicating that NOM had no effect on Cr(VI) concentration when Cr(III) is absent. When 0.8 µg L^{-1} Cr(III) was added to each of these test conditions an upward trend in measured chromium was also observed with the Cr(VI) concentration increasing from 0.8 µg L^{-1} (at 0.1 mg C L^{-1}) to 1.1 µg L^{-1} (at 1.8 mg C L^{-1}) and 1.1 µg L^{-1} (at 4.4 mg C L^{-1}) to 1.2 µg L^{-1} (at 8.4 mg C L^{-1}) (Fig. 4). This increased signal indicates that NOM is responsible for the apparent increase in Cr(VI) concentration. There are two hypotheses for why this might be the case. This recovery of Cr(VI) from the Cr(III) spike could be occurring as a result of the complexation of Cr(III) with NOM and subsequent travel through the speciation column or by the oxidation of Cr(III) to Cr(VI) by the NOM.

A second experiment was conducted with the same simulated tap water; however a condition was included with 1 µg L^{-1} Cr(III) and no Cr(VI). This water contained 170 mg L^{-1} as $CaCO_3$ alkalinity and either 0 or 7.4 mg L^{-1} NOM. In this experiment, for waters with no NOM, the addition of 1.0 µg L^{-1} Cr(III) did not affect the Cr(VI) concentration measurement. However, when 7.4 mg L^{-1} NOM was present, 0.5 µg L^{-1} of the 1.0 µg L^{-1} Cr(III) added was incorrectly recovered as Cr(VI) (data not shown but also corroborated by IC-PCR measurement). This result, in conjunction with the IC-PCR results described above (Section 3.1.2), indicate that the NOM is not oxidizing the Cr(III) to Cr(VI), but that it is complexing the Cr(III) and carrying it through the ion exchange column. This result can also explain the upward trend in Cr(VI) measurements when no Cr(III) was added (Fig. 4). As explained in Section 2.1, there was a small amount of chromium (0.08 µg L^{-1}) present in the NOM stock. The majority of this chromium was in the Cr(III) oxidation state as indicated by IC-PCR results. In all likelihood, this chromium was complexed by the NOM and carried through the field column, resulting in the false positives described earlier in this section.

3.2. Effect of alkalinity on analytical method performance

Alkalinity may also affect analytical method performance. For ICPMS, the carbon component of alkalinity can lead to false positives for chromium even when operating in CCT mode. In this study two levels of alkalinity were added to the simulated tap water: "low" (~40 mg L^{-1} as $CaCO_3$) and "high" (~170 mg L^{-1} as $CaCO_3$) (Table 2). The high level of alkalinity was also added to the simulated tap water with a high level of NOM. The effect of the alkalinity addition on each of the analytical methods is detailed in the sections that follow.

3.2.1. ICPMS (total chromium)

Total chromium for each alkalinity test condition was analyzed by ICPMS in CCT mode. For the simulated tap water, low alkalinity, and high alkalinity conditions, the total chromium concentration measurement was 1.0 µg L^{-1}, 1.0 µg L^{-1}, and 0.9 µg L^{-1}, respectively (Fig. 1), indicating that carbon did not give a false positive for chromium for alkalinity up to 170 mg L^{-1} as $CaCO_3$. When 0.8 µg L^{-1} Cr(III) was added to each of these test conditions the total chromium concentrations were 1.8 µg L^{-1} for each condition (Fig. 1). Additionally, one test was conducted with both high NOM (8.7 mg C L^{-1}) and high alkalinity (174 mg L^{-1} as $CaCO_3$). Total chromium measured for this test condition was practically identical to the total chromium measured in the test condition with just high NOM (0.8 µg L^{-1}) and in the test condition with 0.8 µg L^{-1} Cr(III) added (1.6 µg L^{-1}). From these results it is apparent that the CCT mode of operation is sufficient to eliminate any inorganic carbon interference on total chromium measurements.

3.2.2. IC-PCR

In this study the simulated tap water had a Cr(VI) concentration of 1.1 μg L^{-1} using IC-PCR (Fig. 2) and the addition of low or high alkalinity had no effect. The addition of 0.8 μg L^{-1} Cr(III) also did not affect the Cr(VI) measurements. Cr(VI) concentrations were 1.1 μg L^{-1} at each level of alkalinity tested after the addition of 0.8 μg L^{-1} Cr(III) (Fig. 2). Likewise, the test condition with both high NOM and high alkalinity showed that Cr(VI) was equivalent to the Cr(VI) measured in the high NOM only test condition (1.1 μg/L) and in the test condition with 0.8 μg L^{-1} Cr(III) added (1.2 μg L^{-1}).

3.2.3. HPLC–ICPMS

As in the case of the IC-PCR method, the addition of alkalinity had no effect on the measurement of Cr(VI) with or without the addition of 0.8 μg L^{-1} Cr(III) (Fig. 3). A comparison of each test condition with and without the addition of 0.8 μg L^{-1} Cr(III) shows that in each case there is a maximum of 0.1 μg L^{-1} difference in the Cr(VI) concentration measured. An interesting observation, however, is that the high level of alkalinity appears to counteract the effect of NOM in decreasing the Cr(VI) recovery. That is, when 170 mg/L alkalinity is present, 8 mg/L NOM does not result in a large decrease in Cr(VI) recovery (Fig. 3). We speculate that this might be an effect of the increasing ionic strength as alkalinity is increased.

3.2.4. Field speciation

The addition of alkalinity had no effect on the measurement of Cr(VI) by the field speciation method (Fig. 4). Cr(VI) in the simulated tap water, water with low alkalinity, and water with high alkalinity all measured 0.8 μg L^{-1}. Results were similar in the test conditions with 0.8 μg L^{-1} Cr(III) added. The simulated tap, low alkalinity, and high alkalinity waters each had Cr(VI) measurements of 0.9 μg L^{-1}. The test condition with both high NOM and high alkalinity and no Cr(III) added showed that Cr(VI) was the same as the Cr(VI) measured in the high NOM only test (0.7 μg L^{-1}). Likewise, in the test with both high NOM and high alkalinity plus 0.8 μg L^{-1} Cr(III) added, the Cr(VI) measurement was similar to the condition with high NOM only (1.1 μg L^{-1} versus 1.2 μg L^{-1}).

4. Conclusions

Low-level chromium measurement can be difficult and maintaining speciation of Cr(VI) while measuring ultra-low concentrations is especially important. Additionally, the presence of alkalinity and/or NOM can lead to false positives or false negatives for Cr(VI) evaluated. USEPA Method 218.7 utilizes IC-PCR and proved to be an extremely reliable method; the addition of up to 8 mg C L^{-1} NOM and up to 170 mg L^{-1} as $CaCO_3$ alkalinity had no significant effect on the recovery of Cr(VI). When Cr(III) was added to the simulated tap water, it was not oxidized to Cr(VI) by either the addition of NOM or alkalinity as evidenced by results from this method. Note that the NOM used in this study was a fulvic acid and that other types of organic carbon may produce different results.

More work needs to be conducted on the HPLC–ICPMS method to precisely identify the cause of decreasing Cr(VI) signal as the concentration of NOM increased. In the absence of NOM and in the presence of up to 170 mg L^{-1} alkalinity this method worked well and was able to accurately quantify Cr(VI) even in the presence of a 0.8 μg L^{-1} Cr(III) spike.

The field speciation method worked well in waters with alkalinity, but the presence of 8.2 mg C L^{-1} NOM resulted in a 0.3 μg L^{-1} false positive for Cr(VI) when 0.8 μg L^{-1} Cr(III) was present, indicating that NOM may have been complexing some of the Cr(III) and allowing it to pass through the speciation column. Even a modest amount of NOM (1.9 mg C L^{-1}) resulted in a 0.2 μg L^{-1} false positive for Cr(VI) when 0.8 μg L^{-1} Cr(III) was present.

When attempting to quantify Cr(VI) in water, care must be taken to adequately preserve the speciation upon sample collection. Furthermore, special attention needs to be paid to the amount of organic carbon present as this may result in a 'false positive' in Cr(VI) concentration if Cr(III) is present in the water being tested and one is using the field speciation method. Alkalinity, on the other hand, does not appear to affect ICPMS performance (as long as CCT is used) or the other chromatographic analytical methods evaluated in this study.

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