METHOD 218.7: DETERMINATION OF HEXAVALENT CHROMIUM IN DRINKING WATER BY ION CHROMATOGRAPHY WITH POST-COLUMN DERIVATIZATION AND UV–VISIBLE SPECTROSCOPIC DETECTION

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METHOD 218.7

DETERMINATION OF HEXAVALENT CHROMIUM IN DRINKING WATER BY ION CHROMATOGRAPHY WITH POST-COLUMN DERIVATIZATION AND UV–VISIBLE SPECTROSCOPIC DETECTION

1. SCOPE AND APPLICATION

1.1 METHOD – Method 218.7 provides procedures for the determination of hexavalent chromium Cr(VI) as the chromate anion CrO_4^{2-} in finished drinking water using ion chromatography. Samples are analyzed by direct injection. This method is intended for use by analysts skilled in the operation of ion chromatographic instrumentation and in the interpretation of the associated data.

Analyte	Chemical Abstracts Services Registry Number (CASRN)
Hexavalent chromium (as CrO_4^{2-})	13907-45-4

1.2 SUPPORTING DATA

1.2.1 Single-laboratory method performance data, presented in Section 17, were collected using 4-mm i.d. anion exchange chromatographic columns designed for use with ammonium hydroxide/ammonium sulfate eluent systems and 4-mm i.d. columns designed for use with carbonate/bicarbonate eluent systems.

1.2.2 Precision and accuracy data have been generated for the analysis of Cr(VI) in reagent water and finished drinking water from both ground water and surface water sources (Sect. 17, Tables 4, 5 and 6).

1.2.3 Single laboratory Lowest Concentration Minimum Reporting Levels (LCMRLs) for Cr(VI) ranged from 0.012 to 0.036 microgram per liter (μg/L) (Section 17, Table 3). The LCMRL is the lowest spiking concentration such that the probability of spike recovery in the 50% to 150% range is at least 99%. The procedure used to determine the LCMRL is described elsewhere.[1] Laboratories using this method are not required to determine LCMRLs, but they must demonstrate that the Minimum Reporting Level (MRL) for Cr(VI) meets the requirements described in Section 9.2.4.

1.2.4 Determining a detection limit (DL) for Cr(VI) is optional (Sect. 9.2.6). The DL is defined as the statistically calculated minimum concentration that can be measured with 99% confidence that the reported value is greater than zero.[2] DLs for Cr(VI) fortified into reagent water ranged from 0.0044 to 0.015 μg/L (Table 3).

1.3 METHOD FLEXIBILITY – The laboratory is permitted to modify chromatographic conditions including IC columns and eluent compositions different from those utilized in the method. Changes may not be made to sample collection and preservation (Sect. 8) or to the quality control (QC) requirements (Sect. 9). Method modifications should be considered

only to improve method performance. Modifications that are introduced in the interest of reducing cost or sample processing time, but result in poorer method performance, may not be used. In all cases where method modifications are proposed, the analyst must perform the procedures outlined in the Initial Demonstration of Capability (IDC, Sect. 9.2), and verify that all on-going QC acceptance criteria in this method (Section 9.3) are met, especially precision and accuracy in real sample matrixes.

2. SUMMARY OF METHOD[3-6]

Samples are preserved with a combined buffer/dechlorinating reagent which complexes free chlorine and increases the pH to a value greater than eight. A measured volume (usually 1 mL) of the sample is introduced into an ion chromatograph. CrO_4^{2-} is separated from other matrix components on an anion exchange column. CrO_4^{2-} is derivatized with 1,5-diphenylcarbazide in a post-column reactor and is detected spectrophotometrically at a wavelength of 530 nm. Cr(VI) is qualitatively identified via retention time, and the concentration of CrO_4^{2-} in the sample is calculated using the integrated peak area and the external standard technique. Results are reported in units of µg/L of Cr(VI).

3. DEFINITIONS

3.1 ANALYSIS BATCH – A set of samples that is analyzed on the same instrument during a 24-hour period that begins and ends with the analysis of the appropriate Continuing Calibration Check (CCC) standards. Additional CCCs may be required depending on the length of the Analysis Batch and the number of field samples.

3.2 CALIBRATION STANDARD – A solution of Cr(VI), which includes the method preservative, prepared from the Primary Dilution Standards. The calibration standards are used to calibrate the instrument response with respect to analyte concentration.

3.3 CONTINUING CALIBRATION CHECK (CCC) – A calibration standard that is analyzed periodically to verify the accuracy of the existing calibration.

3.4 DETECTION LIMIT (DL) – The minimum concentration of Cr(VI) that can be identified, measured, and reported with 99% confidence that the concentration is greater than zero. This is a statistical determination (Sect. 9.2.6), and accurate quantitation is not expected at this level.

3.5 FIELD REAGENT BLANK (FRB) – An aliquot of reagent water that is placed in a sample container in the laboratory and treated as a sample in all respects, including shipment to the sampling site, exposure to sampling site conditions, storage, preservation, and all analytical procedures. The purpose of the FRB is to determine if Cr(VI) or other interferences are introduced into the samples during sampling, transport, and storage.

3.6 LABORATORY DUPLICATES (LDs) – Two sample aliquots (LD_1 and LD_2) taken in the laboratory from a single sample bottle, and analyzed separately with identical procedures. By cancelling variation contributed from sample collection, preservation, and storage

procedures, Laboratory Duplicates provide an estimate of precision associated specifically with the analytical determination.

3.7 LABORATORY FORTIFIED BLANK (LFB) – An aliquot of reagent water, containing the method preservative, to which a known quantity of Cr(VI) is added. The LFB is used during the IDC to verify method performance for precision and accuracy.

3.8 LABORATORY FORTIFIED SAMPLE MATRIX (LFSM) – An aliquot of a field sample to which a known quantity of Cr(VI) is added. The LFSM is processed and analyzed as a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results.

3.9 LABORATORY FORTIFIED SAMPLE MATRIX DUPLICATE (LFSMD) – A second aliquot of the field sample used to prepare the LFSM which is fortified and analyzed identically to the LFSM. The LFSMD is used instead of the Laboratory Duplicate to assess method precision if Cr(VI) is absent from the sample matrix.

3.10 LABORATORY REAGENT BLANK (LRB) – An aliquot of reagent water that contains the method preservative. The LRB is used to determine if Cr(VI) or other interferences are introduced from the laboratory environment, the reagents or glassware, and to test for cross contamination.

3.11 LOWEST CONCENTRATION MINIMUM REPORTING LEVEL (LCMRL) – The single laboratory LCMRL is the lowest spiking concentration such that the probability of spike recovery in the 50% to 150% range is at least 99%.[1] LCMRL determinations from multiple laboratories can be used to develop a statistically derived MRL (Sect. 3.13).

3.12 MATERIAL SAFETY DATA SHEETS (MSDS) – Written information provided by vendors concerning a chemical's toxicity, health hazards, physical properties, fire and reactivity data, storage instructions, spill response procedures, and handling precautions.

3.13 MINIMUM REPORTING LEVEL (MRL) – The minimum concentration that can be reported by a laboratory as a quantified value for Cr(VI). This concentration must meet the criteria defined in Section 9.2.4 and must be no lower than the concentration of the lowest calibration standard. A laboratory may be required to demonstrate a specific MRL by a regulatory body if this method is being performed for compliance purposes.

3.14 POST-COLUMN REACTOR – For this method, the post-column reactor consists of a reagent delivery pump, a mixing tee, and a reaction coil.

3.15 PRIMARY DILUTION STANDARD (PDS) – An aqueous solution containing Cr(VI), which is prepared from a Stock Standard Solution. The PDS solution is diluted to prepare calibration standards and sample fortification solutions.

3.16 PROCEDURAL CALIBRATION – A calibration technique in which calibration standards are processed through the entire method, including sample preparation and addition of preservative.

3.17 QUALITY CONTROL SAMPLE (QCS) – A solution containing Cr(VI) at a known concentration that is obtained from a source external to the laboratory and different from the source of calibration standards. The purpose of the QCS is to verify the accuracy of the primary calibration standards.

3.18 REAGENT WATER – Purified water that does not contain any measurable quantity of Cr(VI) or interfering compounds at or above one-third the MRL.

3.19 STOCK STANDARD SOLUTION – A concentrated standard solution that is prepared in the laboratory using assayed reference materials, or that is purchased from a commercial source with a certificate of analysis.

4. INTERFERENCES

4.1 LABWARE – The stability of Cr(VI) was demonstrated for this method using high-density polyethylene (HDPE) sample bottles. Polypropylene copolymer bottles are also acceptable. Aliquots of the PDS and sample fortification solutions were transferred using polypropylene pipette tips. Other types of sample bottles may be used; however, the laboratory must confirm the stability of Cr(VI) in these materials over 14 days by formal experiment.

4.2 REAGENTS AND EQUIPMENT – Method interferences may be caused by contaminants in reagents (including the method preservative) and in the ion chromatographic system. All laboratory reagents and instruments must be routinely demonstrated to be free from interferences, and to contribute less than one-third the MRL for Cr(VI), under the conditions of the analysis. This may be accomplished by analyzing LRBs, as described in Section 9.3.1.

4.3 MATRIX INTERFERENCES – Matrix interferences are caused by contaminants that are present in the sample. The extent of matrix interferences will vary considerably from source to source, depending upon the nature of the water. Matrix components may directly interfere by producing a signal at or near the retention time of the Cr(VI) peak; however, the method is extremely selective due to the chromatographic separation of the analyte from matrix components, coupled with the discrimination of the post-column reagent for the chromate anion. Sample ionic strength may enhance or suppress Cr(VI) response; however, the 4-mm column systems used during method development tolerate typical concentrations of common anions in drinking water in combination with method preservative. 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. The analysis of Laboratory Fortified Sample Matrix (Sect. 9.3.4) provides the user of the method with evidence for the presence (or absence) of matrix effects.

4.4 OXIDATION-REDUCTION (REDOX) CONCERNS – To ensure sample integrity, Cr(VI) must be protected from reduction, and Cr(III), if present, must not oxidize to Cr(VI) during

sample storage. Within the normal pH range in drinking water, Cr(VI), present as a result of pollution or oxidation of Cr(III) in source water during treatment, forms oxyanions, which are typically represented as $HCrO_4^-$ and CrO_4^{2-}. The very stable CrO_4^{2-} anion dominates above pH 7[8]; therefore, the method preservative is designed to buffer samples to at least pH 8. Chromate compounds are quite soluble, mobile and stable, particularly in an oxidizing environment.[8] In contrast, soluble Cr(III) species oxidize to Cr(VI) in the presence of free chlorine[9], although natural organic matter in surface water sources may complex Cr(III), slowing its oxidation even in a highly oxidizing environment.[7] The rate of Cr(III) oxidation increases with chlorine concentration and is pH-dependent.[7] For these reasons, both preservation options prescribed in this method include ammonium ions to complex free chlorine. The resulting formation of chloramines minimizes, but does not completely prevent, the oxidation of Cr(III).[7] 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. Representative study results for a surface water source are presented in Section 17, Table 7.

5. SAFETY

5.1 Each chemical should be treated as a potential health hazard and exposure to these chemicals should be minimized. Each laboratory is responsible for maintaining an awareness of OSHA regulations regarding safe handling of chemicals used in this method. A reference file of MSDSs should be made available to all personnel involved in the chemical analysis. Hexavalent chromium in solid form presents an inhalation hazard, is toxic and a suspected carcinogen. All forms of hexavalent chromium should be handled with appropriate precautions. A fact sheet on the health effects of hexavalent chromium in the workplace is available on the OSHA website @ www.osha.gov.

5.2 Preparation of the post-column reagent and the ammonium hydroxide preservative require the use of concentrated acid and concentrated base. These reagents should be prepared in a hood, adding acid to water, and wearing splash goggles with chemical resistant gloves. Gloves and splash goggles should be worn when transferring the post-column reagent to the instrument reservoir.

6. EQUIPMENT AND SUPPLIES

References to specific brands or catalog numbers are included as examples only and do not imply endorsement of the product. Such reference does not preclude the use of other vendors or suppliers.

6.1 SAMPLE CONTAINERS – 125-ml, wide-mouth, high-density polyethylene (HDPE) (Fisher Scientific Cat. No. 02-911-958 or equivalent); 125-mL polypropylene copolymer (Fisher Scientific Cat. No. 02-893-A or equivalent).

6.2 AUTOSAMPLER VIALS – Size and material meeting vendor specification for the ion chromatograph. Polypropylene and polystyrene are commonly used for ion chromatography.

6.3 AUTOMATIC PIPETTE – (Eppendorf Research Pro or equivalent). An automatic pipette with polypropylene tips is recommended for preparing all standard solutions and for fortifying QC samples.

6.4 ANALYTICAL BALANCE – Capable of weighing to the nearest 0.0001 gram (g).

6.5 ION CHROMATOGRAPHY SYSTEM WITH POST-COLUMN REACTOR

6.5.1 IC SYSTEM – An analytical system consisting of an autosampler, pump module with vacuum degassing option, sample loop, guard column, anion separator column, post-column reagent addition capability, post-column reaction coil, UV–Vis absorbance detector set to monitor a wavelength of 530 nm, and a data acquisition and management system. The system must not contain any metal parts in the sample, eluent and reagent flow paths.

6.5.2 SAMPLE LOOP – Polyetheretherketone (PEEK) construction and sized for the column system. One- and 1.25-mL sample loops were used to generate the performance data presented in this method. Smaller or larger injection volumes may be used as long as the Initial Demonstration of Capability (Sect. 9.2), calibration, and sample analyses are performed using the same injection volume. The laboratory must be able to meet the MRL verification criteria (Section 9.2.4) using the selected injection volume.

6.5.3 GUARD COLUMN – Size and resin per vendor specification; capable of removing strongly adsorbing organic compounds and particles that could damage the analytical column.

6.5.4 ANALYTICAL COLUMN – Anion exchange column capable of resolving the chromate anion from matrix components. Any column that provides adequate resolution, peak shape, capacity, accuracy and precision (Sect. 9), and does not result in suppression or enhancement of analyte response (Sect. 4.3) may be used.

6.5.5 COLUMN COMPARTMENT – Temperature controlled recommended.

6.5.6 POST-COLUMN REACTOR– Pneumatic or mechanical reagent pump capable of pulse-free operation, mixing tee, and reaction coil (sized and configured per vendor specifications).

6.5.7 DATA SYSTEM – An interfaced data system is required to acquire, store, and output data. The computer software must have the capability of processing stored data by recognizing and integrating a chromatographic peak within a given retention time window. The software must be able to construct a linear regression or quadratic regression calibration curve and calculate the Cr(VI) concentration using the external standard technique.

7. REAGENTS AND STANDARDS

7.1 REAGENTS AND SOLVENTS – Reagent grade or better chemicals must be used. Unless otherwise indicated, it is intended that all reagents will conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society (ACS), where such specifications are available. Other grades may be used if the reagent is demonstrated to be free of Cr(VI) and other interferences, and all requirements of the IDC are met when using these reagents.

7.1.1 AMMONIUM HYDROXIDE (NH_4OH, CASRN 1336-21-6) – 28-30% NH_3 w/w (Fisher Cat. No. AC42330 or equivalent). For preparing $NH_4OH/(NH_4)_2SO_4$ (liquid) preservative and IC eluent.

7.1.2 AMMONIUM SULFATE [$(NH_4)_2SO_4$, CASRN 7783-20-2] (Sigma-Aldrich Cat. No. A4915 or equivalent). For preparing $NH_4OH/(NH_4)_2SO_4$ (liquid) preservative, $CO_3^{-2}/HCO_3^-/(NH_4)_2SO_4$ (solid) preservative, and IC eluent.

7.1.3 METHANOL (CH_3OH, CASRN 67-56-1) – (Fisher Optima® LC/MS grade or equivalent). For preparing the post-column reagent.

7.1.4 SODIUM BICARBONATE ($NaHCO_3$, CASRN 144-55-8) – for preparing $CO_3^{-2}/HCO_3^-/(NH_4)_2SO_4$ (solid) preservative and IC eluent.

7.1.5 SODIUM CARBONATE (Na_2CO_3, CASRN 497-19-8) – Anhydrous. For preparing $CO_3^{-2}/HCO_3^-/(NH_4)_2SO_4$ (solid) preservative and IC eluent.

7.1.6 REAGENT WATER – Distilled or deionized water. For preparing calibration standards and reagents.

7.1.7 1,5-DIPHENYLCARBAZIDE ($C_{13}H_{14}N_4O$, CASRN 140-22-7) – for preparing the post-column reagent.

7.1.8 SULFURIC ACID (H_2SO_4, CASRN 7664-93-9) – 93 to 98 percent, trace metal grade (Fisher Cat. No. A510 or equivalent). For preparing the post-column reagent.

7.1.9 PREPARATION OF POST-COLUMN REAGENT – 2-mM 1,5-diphenylcarbazide, 10% methanol and 0.5 M (1 N) sulfuric acid. Add 28 mL of sulfuric acid to approximately 500 mL of reagent water in a 1-liter volumetric flask or suitably sized bottle. Mix and cool to room temperature in a water bath. While this solution is cooling, weigh 0.50 gram of 1,5-diphenylcarbazide into a 100-mL beaker, add 75 mL of methanol, and sonicate for five minutes to dissolve the solid. Transfer this solution to a 100-mL volumetric flask; bring to volume with methanol and mix. Add the entire contents of the volumetric flask to the sulfuric acid solution and dilute to 1.0 L with reagent water. Mix and transfer the solution to the post-column reagent reservoir. Method 218.7 was developed adhering to a schedule for replacing post-column reagent five days after the

original date of preparation. Users of this method must determine when this reagent should be replaced based on the recommendations of the instrument manufacturer, and on the ability to meet the QC requirements in Section 9.

7.1.10 PREPARATION OF $CO_3^{-2}/HCO_3^-/(NH_4)_2SO_4$ (SOLID) PRESERVATIVE – Nominally 13.3 mg Na_2CO_3, 10.5 mg $NaHCO_3$ and 33 mg $(NH_4)_2SO_4$. These are the appropriate amounts for a 100-mL sample. Weigh 1–1.25 times these values and transfer to a dry, 125-mL sample bottle.

7.1.11 PREPARATION OF $NH_4OH/(NH_4)_2SO_4$ (LIQUID) PRESERVATIVE –Dissolve 3.3 g $(NH_4)_2SO_4$ in 75 ml of reagent water. Add 6.5 mL ammonium hydroxide and dilute to 100-mL final volume. During method development, the stability of the concentrated preservative was verified for one month when stored at ambient temperature. Laboratories using this method are required to determine when this reagent should be replaced.

7.1.12 PREPARATION OF COLUMN ELUENTS – Representative column eluent systems are listed in Section 17, Tables 1 and 2. Eluent solutions of these types should be prepared on a weekly basis or at intervals recommended by the instrument manufacturer.

7.2 STANDARD SOLUTIONS – Solution concentrations listed in this section were used to develop this method and are included only as examples. Guidance on the storage stability of Primary Dilution Standards and calibration standards is provided in the applicable sections below. Although estimated stability times for standard solutions are given, laboratories should use standard QC practices to determine appropriate storage conditions and when standards need to be replaced.

7.2.1 ANALYTE STOCK STANDARD SOLUTION (1000 µg/mL) – Prepare from neat material (ACS reagent grade, >99% purity) in reagent water or obtain Cr(VI) as a certified solution in water (e.g., Ultra Cat. No. ICP-024A, AccuStandard Cat. No. WC-HEX-10X-1 or equivalent). For $K_2Cr_2O_7$ starting material, dry the salt at 100 °C to a constant weight; weigh 0.283 g, dissolve in reagent water, and dilute to 100 mL. Store stock standards at room temperature.

7.2.1.1 ANALYTE PRIMARY DILUTION STANDARD (Analyte PDS) (1000 µg/L) – Prepare the Analyte PDS by diluting the Analyte Stock Standard solution (1:1000) into reagent water. Include the same preservative used for field samples. An example preparation of Analyte PDS solutions (those used to collect data presented in Section 17) is provided in the table below. Store the PDS in a 125-mL HDPE or polypropylene bottle. The Analyte PDS is used to prepare calibration standards and to fortify QC samples with Cr(VI).

Stock Concentration	Aliquot of Stock Standard Solution (7.2.1, 1000 µg/mL)	Preservative Amounts	Volume Reagent Water	PDS Concentration
1000 µg/mL with $NH_4OH/(NH_4)_2SO_4$ (liquid) preservative	0.10 mL	1 mL preservative (Sect. 7.1.11)	0.10 L	1000 µg/L
1000 µg/mL with solid preservative	0.10 mL	13.3 mg Na_2CO_3, 10.5 mg $NaHCO_3$ 33 mg $(NH_4)_2SO_4$	0.10 L	1000 µg/L

Storage stability of the Analyte PDS was verified during method development. The Analyte PDS was stable for at least 14 days when stored at room temperature.

7.2.2 CALIBRATION STANDARDS (CALs) – Prepare a series of calibration standards (at least six levels) by diluting the Analyte PDS into reagent water. Include the same preservative used for field samples. The lowest calibration standard must be at or below the concentration of the MRL (Sect. 9.2.4). The calibration standards may also be used as CCCs. An example preparation of calibration standards (starting with the Analyte PDS) used to collect method performance data is provided in the table below.

Dilution Aliquot	Starting Concentration (µg/L)	Final Volume (L)	Final Concentration (µg/L)
0.50 mL Analyte PDS	1000	0.10	5.0
0.10 mL Analyte PDS	1000	0.10	1.0
10 mL 5.0 µg/L CAL	5.0	0.10	0.50
5.0 mL 5.0 µg/L CAL	5.0	0.10	0.25
2.0 mL 5.0 µg/L CAL	5.0	0.10	0.10
1.0 mL 5.0 µg/L CAL	5.0	0.10	0.050
0.4 mL 5.0 µg/L CAL	5.0	0.10	0.020

Storage stability of the calibration standards was evaluated during method development at concentrations between 0.020 µg/L and 1.0 µg/L. The calibration solutions were stable for at least 14 days when stored at 4 °C.

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1 ADDITION OF PRESERVATIVE –The samples are preserved with a combined buffer/dechlorinating reagent. Either the liquid formulation or the solid formulation of the preservative described in the following sections may be used. Only one preservative formulation should be used (liquid or solid) to prepare the sample bottles.

8.1.1. LIQUID FORMULATION - $NH_4OH/(NH_4)_2SO_4$ – The liquid preservative may be added to sample bottles prior to shipment. Apply the concentrated preservative (Sect. 7.1.11) at the rate of 1 mL per 100 mL of sample. Sample bottles prepared in advance may be stored for one month prior to use.

8.1.2. SOLID FORMULATION - $CO_3^{-2}/HCO_3^-/(NH_4)_2SO_4$ – The solid preservative may be added to sample bottles prior to shipment. Add 13.3 mg Na_2CO_3, 10.5 mg $NaHCO_3$ and 33 mg $(NH_4)_2SO_4$ to each bottle following the instructions in Section 7.1.10.

8.2 SAMPLE COLLECTION – Open the tap and allow the system to flush for approximately 5 minutes. Fill sample bottles with 100-mL of sample, taking care not to flush out the preservative. Invert the bottle several times to mix the sample with the preservative.

8.3 SAMPLE SHIPMENT AND STORAGE – Storage stability studies have demonstrated that samples are stable for at least 14 days at both ambient temperature (25 °C) and chilled temperature (6 °C). If the anticipated shipping conditions would expose the samples to temperature extremes, samples may be chilled during shipment. Standard quality control practices should be put in place to confirm that the shipping conditions do not adversely affect sample stability. A laboratory fortified sample that is shipped with the sample kit can aid in making this determination. Upon sample receipt, measure the free chlorine and sample pH. The free chlorine concentration must be less than 0.1 mg/L and the pH must be >8 for the sample to be valid. In the laboratory, it is recommended that the samples are stored at or below 6 °C until analysis.

8.4 SAMPLE HOLDING TIMES – Results of the sample storage stability study (Table 7) indicate that Cr(VI) is stable for at least 14 days when collected, preserved, shipped and stored as described in Sections 8.1 to 8.3. Samples should be analyzed as soon as possible, but must be analyzed within 14 days.

9. QUALITY CONTROL

9.1 QC requirements include the IDC and ongoing QC requirements. This section describes each QC parameter, its required frequency, and the performance criteria that must be met. The QC criteria discussed in the following sections are summarized in Section 17, Tables 8 and 9. These QC requirements are considered the minimum acceptable QC program. Laboratories are encouraged to institute additional QC practices to meet their specific needs.

9.2 INITIAL DEMONSTRATION OF CAPABILITY (IDC) – The IDC must be successfully performed prior to analyzing any field samples. The IDC must be repeated if changes are made to analytical parameters not previously validated during the IDC, for example, changing from $NH_4OH/(NH_4)_2SO_4$ preservative to the $CO_3^{-2}/HCO_3^-/(NH_4)_2SO_4$ preservative or translating the method to a 2-mm column system. Prior to conducting the IDC, the analyst must meet the calibration requirements outlined in Section 10.2.

9.2.1 DEMONSTRATION OF LOW SYSTEM BACKGROUND – Analyze an LRB after the analysis of the highest concentration calibration standard. Confirm that the blank is free of contamination as defined in Section 9.3.1.

9.2.2 DEMONSTRATION OF PRECISION – Prepare and analyze seven replicate LFBs. Fortify these samples near the midrange of the initial calibration curve. The method

preservative must be added to the LFBs as described in Section 8. The percent relative standard deviation (%RSD) of the concentrations of the replicate analyses must be ≤15%.

$$\%\ \text{RSD} = \frac{\text{Standard Deviation of Measured Concentrations}}{\text{Average Concentration}} \times 100$$

9.2.3 DEMONSTRATION OF ACCURACY – Using the same set of replicate data generated for Section 9.2.2, calculate the average percent recovery. The average percent recovery for Cr(VI) must be within ±15% of the true value.

$$\%\ \text{Recovery} = \frac{\text{Average Measured Concentration}}{\text{Fortified Concentration}} \times 100$$

9.2.4 MINIMUM REPORTING LEVEL (MRL) CONFIRMATION – Establish a target concentration for the MRL based on the intended use of the method. Analyze an initial calibration following the procedures in Section 10. The lowest calibration standard used to establish the initial calibration (as well as the low-level CCC) must be at or below the concentration of the MRL. Establishing the MRL concentration too low may cause repeated failure of ongoing QC requirements. Confirm the MRL following the procedure outlined below.

9.2.4.1 Fortify and analyze seven replicate LFBs at or below the proposed MRL concentration. The LFBs must contain the method preservative as specified in Section 8. Calculate the mean (*Mean*) and standard deviation for these replicates. Determine the Half Range for the Prediction Interval of Results (HR_{PIR}) using the equation

$$HR_{PIR} = 3.963S$$

where *S* is the standard deviation and 3.963 is a constant value for seven replicates.[1]

9.2.4.2 Confirm that the Upper and Lower limits for the Prediction Interval of Results ($PIR = Mean \pm HR_{PIR}$) meet the upper and lower recovery limits as shown below.

The Upper PIR Limit must be ≤150 percent recovery.

$$\frac{Mean + HR_{PIR}}{Fortified\,Concentration} \times 100 \leq 150\%$$

The Lower PIR Limit must be ≥50 percent recovery.

$$\frac{Mean - HR_{PIR}}{Fortified\,Concentration} \times 100 \geq 50\%$$

9.2.4.3 The MRL is valid if both the Upper and Lower PIR Limits meet the criteria described above. If these criteria are not met, the MRL has been set too low and must be confirmed again at a higher concentration.

NOTE: These equations are only valid for seven replicate samples.

9.2.5 QUALITY CONTROL SAMPLE (QCS) – Analyze a mid-level Quality Control Sample (Sect. 9.3.6) to confirm the accuracy of the primary calibration standards.

9.2.6 DETECTION LIMIT DETERMINATION *(optional) – While DL determination is not a specific requirement of this method, it may be required by various regulatory bodies associated with compliance monitoring. It is the responsibility of the laboratory to ascertain whether DL determination is required based upon the intended use of the data.*

The DL, as defined for this method, is an MDL^2 with the additional requirement that the analyses for the procedure must be performed over at least three days. Prepare at least seven replicate LFBs at a concentration estimated to be near the DL. This concentration may be estimated by selecting a concentration at two to five times the noise level. The method preservative must be added to the samples as described in Section 8. Process the seven replicates through all steps of Section 11. Do not subtract blank values when performing DL calculations.

NOTE: If an MRL confirmation data set meets these requirements, a DL may be calculated from the MRL confirmation data, and no additional analyses are necessary.

Calculate the DL using the following equation:

$$DL = s \times t_{(n-1,1-\alpha = 0.99)}$$

where

$t_{(n-1,1-\alpha = 0.99)}$ = Student's *t* value for the 99% confidence level with n-1 degrees of freedom (for seven replicate determinations, the Student's *t* value is 3.143 at a 99% confidence level),
n = number of replicates, and
s = standard deviation of replicate analyses.

9.3 ONGOING QC REQUIREMENTS – This section describes the ongoing QC elements that must be included when processing and analyzing field samples.

9.3.1 LABORATORY REAGENT BLANK (LRB) – Analyze an LRB during the IDC and with each Analysis Batch. Prepare the LRB by adding reagent water to a sample bottle representative of those used to collect the samples, preferably from the same sample kit. The LRB must contain the sample preservative. Cr(VI), or contaminants that produce a signal overlapping with the Cr(VI) peak, must be less than one-third the MRL. If Cr(VI) is detected in the LRB at concentrations equal to or greater than this level, then all

samples analyzed in the corresponding Analysis Batch are invalid. Subtracting blank values from sample results is not permitted.

9.3.2 CONTINUING CALIBRATION CHECK (CCC) – Analyze CCC standards at the beginning of each Analysis Batch, after every ten field samples, and at the end of the Analysis Batch. See Section 10.3 for concentration requirements and acceptance criteria for CCCs. Additional guidance on sequencing proper Analysis Batches is provided in Section 11.2.

9.3.3 LABORATORY FORTIFIED BLANK (LFB) – Because this method utilizes procedural calibration standards, which are fortified reagent waters, there is no difference between the LFB and the Continuing Calibration Check standard. Consequently, the analysis of a separate LFB is not required as part of the ongoing QC; however, the term "LFB" is used for clarity in the IDC.

9.3.4 LABORATORY FORTIFIED SAMPLE MATRIX (LFSM) – Within each Analysis Batch, analyze a minimum of one LFSM. The background concentration of Cr(VI) in the sample matrix must be determined in a separate aliquot and subtracted from the measured value in the LFSM. If various sample matrixes are analyzed regularly, for example, drinking water processed from ground water and surface water sources, performance data should be collected for each source.

9.3.4.1 Prepare the LFSM by fortifying a sample with an appropriate amount of the Analyte PDS (Sect. 7.2.1.1). Generally, select a spiking concentration that is greater than or equal to the native concentration of Cr(VI). If the native concentration does not allow this criterion to be met without exceeding the calibration range, dilution with reagent water containing the method preservative is permitted. Selecting a duplicate aliquot of a sample that has already been analyzed aids in the selection of an appropriate spiking level. If this is not possible, use historical data when selecting a fortifying concentration.

9.3.4.2 Calculate the percent recovery (%R) using the equation:

$$\%R = \frac{(A - B)}{C} \times 100$$

where
A = measured concentration in the fortified sample,
B = measured concentration in the unfortified sample, and
C = fortification concentration.

9.3.4.3 Cr(VI) recovery for samples fortified at concentrations near or at the MRL (within a factor of two times the MRL concentration) must be within $\pm$50% of the true value. Recovery for samples fortified at all other concentrations must be within $\pm$15% of the true value. If the accuracy falls outside the designated range, and the laboratory performance is shown to be in control in the CCCs, the recovery is judged matrix biased. Report the result in the unfortified sample as "suspect/matrix."

NOTE: In order to obtain meaningful percent recovery results, correct the measured value in the LFSM and LFSMD for the native level in the unfortified samples, even if the native value is less than the MRL. This is the only time that values below the MRL may be used for calculations.

9.3.5 LABORATORY DUPLICATE OR LABORATORY FORTIFIED SAMPLE MATRIX DUPLICATE (LD or LFSMD) – Within each Analysis Batch, analyze a minimum of one Laboratory Duplicate or one Laboratory Fortified Sample Matrix Duplicate. If Cr(VI) is not routinely observed in field samples, analyze an LFSMD rather than an LD.

9.3.5.1 Calculate the relative percent difference (RPD) for duplicate measurements (LD1 and LD2) using the equation:

$$\text{RPD} = \frac{\left|\text{LD}_1 - \text{LD}_2\right|}{\left(\text{LD}_1 + \text{LD}_2\right)/2} \times 100$$

9.3.5.2 RPDs for Laboratory Duplicates must be ≤15%. Greater variability may be observed when Laboratory Duplicates have Cr(VI) concentrations that are near or at the MRL (within a factor of two times the MRL concentration). At these concentrations, Laboratory Duplicates must have RPDs that are ≤50%. If the RPD falls outside the designated range, and the laboratory performance is shown to be in control in the CCC, the precision is judged matrix influenced. Report the result in the unfortified sample as "suspect/matrix."

9.3.5.3 If an LFSMD is analyzed instead of a Laboratory Duplicate, calculate the RPD for the LFSM and LFSMD using the equation:

$$\text{RPD} = \frac{\left|\text{LFSM} - \text{LFSMD}\right|}{\left(\text{LFSM} + \text{LFSMD}\right)/2} \times 100$$

9.3.5.4 RPDs for duplicate LFSMs must be ≤15%. Greater variability may be observed when the matrix is fortified near or at the MRL (within a factor of two times the MRL concentration). LFSMs at these concentrations must have RPDs that are ≤50%. If the RPD falls outside the designated range, and the laboratory performance is shown to be in control in the CCC, the precision is judged matrix influenced. Report the result in the unfortified sample as "suspect/matrix."

9.3.6 QUALITY CONTROL SAMPLE (QCS) – A QCS must be analyzed during the IDC, and then each time new calibration standards are prepared. Prepare the QCS near the midpoint of the calibration range. The acceptance criterion for the QCS is 85 to 115% of the true value. If the accuracy for Cr(VI) fails the recovery criterion, prepare fresh standard dilutions and repeat the QCS evaluation.

10. CALIBRATION AND STANDARDIZATION

Demonstration and documentation of initial analyte calibration are required before performing the IDC and prior to analyzing field samples. The initial calibration must be repeated each time a major instrument modification or maintenance is performed.

10.1 OPTIMIZATION

10.1.1 ION CHROMATOGRAPHY INSTRUMENT CONDITIONS – IC operating conditions and columns used to collect method performance data are given in Section 17, Tables 1 and 2. Conditions different from these (e.g., IC columns and eluent systems) may be used if the QC criteria in Sections 9.2 and 9.3 are met, and chromatographic precision and accuracy is demonstrated within each Analysis Batch and for representative sample matrixes.

10.1.2 POST-COLUMN REAGENT DELIVERY CONDITIONS – Representative conditions for reaction coil volume and post-column reagent flow rates are provided in Section 17, Tables 1 and 2. Select conditions that provide the best signal-to-noise values for Cr(VI) at concentrations near the MRL.

10.1.3 UV–Vis DETECTOR – Monitor wavelength 530 nm.

10.2 INITIAL CALIBRATION

10.2.1 CALIBRATION STANDARDS – Prepare a set of calibration standards (at least six levels) as described in Section 7.2.2. The Cr(VI) concentration in the lowest calibration standard must be at or below the MRL. Field samples must be quantified using a calibration curve that spans the same concentration range used to collect the IDC data (Sect. 9.2); i.e., analysts are not permitted to use a restricted calibration range to meet the IDC criteria and then use a larger dynamic range during analysis of field samples.

10.2.2 CALIBRATION – Calibrate the IC system using the Cr(VI) peak area and the external standard technique. Fit the calibration points with either a linear regression or quadratic regression (response vs. concentration). Weighting may be used. Forcing the calibration curve through the origin is not recommended. The IC instruments used during method development were calibrated using inverse concentration-weighted linear curves.

10.2.3 CALIBRATION ACCEPTANCE CRITERIA – Validate the initial calibration by calculating the concentration of Cr(VI) using the regression equations for each of the standard runs used to generate the calibration curve. For calibration levels that are ≤MRL, the result should be within $\pm$50% of the true value. Cr(VI) concentrations in other calibration levels should calculate to be within $\pm$15% of the true value. If these criteria cannot be met, the analyst may have difficulty meeting ongoing QC criteria. Corrective action is recommended, such as reanalyzing the calibration standards, restricting the range of calibration, or performing instrument maintenance.

10.3 CONTINUING CALIBRATION CHECKS (CCCs) – Analyze a CCC to verify the initial calibration at the beginning of each Analysis Batch, after every tenth field sample, and at the end of each Analysis Batch. The beginning CCC for each Analysis Batch must be at or below the MRL. This CCC verifies instrument sensitivity prior to the analysis of samples. Alternate subsequent CCCs between the remaining calibration levels.

10.3.1 Calculate the concentration of Cr(VI) in the CCC. Calibration standards fortified at a level ≤MRL must calculate to be within ±50% of the true value. The calculated concentration in CCCs fortified at all other levels must be within ±15%. If these limits are exceeded, then all samples analyzed since the last acceptable CCC are invalid. Re-analyze these samples, providing they are still within holding time, after an acceptable calibration has been restored.

10.4 REMEDIAL ACTION – Failure to meet CCC QC performance criteria requires remedial action. Acceptable method performance may be restored simply by preparing fresh post-column reagent and eluent followed by flushing the column and reaction coil for an extended period. Following this and other minor remedial action, check the calibration with a mid-level CCC and a CCC at the MRL, or alternatively recalibrate according to Section 10.2. If calibration failures persist, maintenance may be required such as replacing the guard column, analytical column or reaction coil. These latter measures constitute major maintenance, and the analyst must return to the initial calibration step (Sect. 10.2) and verify sensitivity by analyzing a CCC at or below the MRL.

11. PROCEDURE

This section describes the procedures for sample preparation and analysis. Important aspects of this analytical procedure include proper sample collection and storage (Sect. 8), ensuring that the instrument is properly calibrated (Sect. 10), and that all required QC elements are included (Sect. 9). All field, QC, and calibration samples including the LRB must be preserved as described in Section 8.

11.1 SAMPLE ANALYSIS

11.1.1 Establish IC operating and post-column reagent delivery conditions per the guidance in Section 10.1.

11.1.2 Flush the column, start the post-column reagent delivery pump, warm up the UV–Vis detector, and take other steps necessary to stabilize the IC system prior to beginning each analysis sequence. This step is especially important if the system has been idle for an extended period.

11.1.3 Establish a valid initial calibration following the procedures in Section 10.2 or confirm that the existing calibration is still valid by analyzing a low-level CCC (Sect. 10.3). Analyze field and QC samples in a properly sequenced Analysis Batch as described in Section 11.2.

11.2 THE ANALYSIS BATCH – An Analysis Batch is a sequence of samples, analyzed within a 24-hour period of no more than 20 field samples that includes all required QC samples (LRB, CCCs, LFSMs and LFSMDs or LDs). The required QC samples are not included in counting the maximum field sample total of 20. Dilutions are counted as samples. The purpose of the 20-sample limit is to ensure that a low-level CCC and an LRB are repeated on a regular and frequent basis. Analytical conditions for the Analysis Batch must be the same as those applied during calibration.

11.2.1 After a valid calibration curve is established, begin every Analysis Batch by analyzing an initial low-level CCC at or below the MRL. This initial CCC must be within ±50% of the true value. Continue the Analysis Batch by analyzing an LRB, followed by field and QC samples at appropriate frequencies (Section 9.3). Analyze and rotate between a mid- and a high-level CCC after every ten field samples and at the end each Analysis Batch. Do not count QC samples (LRBs, LDs, LFSMs, LFSMDs) when calculating the required frequency of CCCs. After 20 field samples or 24 hours, the low-level CCC and LRB must be repeated to begin a new Analysis Batch.

11.2.2 The close-out CCC completes the Analysis Batch. The acquisition start time of the closeout CCC must be within 24 hours of the acquisition start time of the low-level CCC at the beginning of the Analysis Batch. More than one Analysis Batch within a 24-hour period is permitted.

12. DATA ANALYSIS AND CALCULATIONS

12.1 For each Analysis Batch, establish an appropriate retention time window to identify Cr(VI). Base this assignment on measurements of actual retention time variation for Cr(VI) in standard solutions over the course of time. The suggested variation is plus or minus three times the standard deviation of the retention time for a series of injections. The injections from the initial calibration and from the IDC (Sect. 9.2) may be used to calculate the retention time window. However, the experience of the analyst should weigh heavily on the determination of an appropriate range.

12.2 At the conclusion of data acquisition, use the same software settings established during the calibration procedure to identify Cr(VI) in the predetermined retention time window. Confirm the identity by comparison of the retention time with that of the corresponding Cr(VI) peak in an initial calibration standard or CCC.

12.3 Calculate the Cr(VI) concentration using the multipoint calibration established in Section 10.2. Report only those values that fall between the MRL and the highest calibration standard.

12.4 Calculations must use all available digits of precision, but final reported concentrations should be rounded to an appropriate number of significant figures (one digit of uncertainty), typically two, and not more than three significant figures.

12.5 Prior to reporting the data, the chromatograms must be reviewed for incorrect peak identification or improper integration. The laboratory is responsible for ensuring that QC requirements have been met and that any appropriate qualifier is assigned.

12.6 The analyst must not extrapolate beyond the established calibration range. If the Cr(VI) result exceeds the range of the initial calibration curve, the sample may be diluted using reagent water containing the method preservative. Re-inject the diluted sample. Incorporate the dilution factor into final concentration calculations. The resulting data must be annotated as a dilution, and the reported MRL must reflect the dilution factor.

13. METHOD PERFORMANCE

13.1 PRECISION, ACCURACY AND DETECTION LIMITS – Single laboratory method performance data are presented in Section 17. LCMRLs and DLs for both $NH_4OH/(NH_4)_2SO_4$ preservative and the $CO_3^{-2}/HCO_3^-/(NH_4)_2SO_4$ preservative are presented in Table 3. Precision and accuracy data are presented for Cr(VI) fortified into reagent water and preserved with $NH_4OH/(NH_4)_2SO_4$ (Table 4). These data were collected using columns designed for use with an ammonium hydroxide/ammonium sulfate eluent system and columns designed for use with a carbonate/bicarbonate eluent system. Precision and accuracy data are presented for Cr(VI) fortified into two sources of chlorinated ground water, a chlorinated surface water finished with granular activated carbon (GAC) filtration, and a chlorinated surface water finished without GAC filtration. These data were collected using columns designed for an ammonium hydroxide/ammonium sulfate eluent system (Table 5) and columns designed for a carbonate/ bicarbonate eluent system (Table 6). All precision and accuracy data were collected for samples preserved with $NH_4OH/(NH_4)_2SO_4$. Figures 1 through 4 are chromatograms of Cr(VI) in reagent water and drinking water obtained under the conditions employed during method development.

13.2 SECOND LABORATORY EVALUATION – Four independent laboratories demonstrated acceptable method performance using 2- and 4-mm column systems with ammonium hydroxide/ammonium sulfate eluent, and one independent laboratory demonstrated acceptable method performance using a 4-mm column system with carbonate/bicarbonate eluent. The authors wish to acknowledge the Utah Water Research Laboratory (Logan, UT), Aqua Pennsylvania, Inc. (Bryn Mawr, PA), Metrohm USA, Inc. (Riverview, FL), Thermo Fisher Scientific/Dionex (Sunnyvale, CA), and MWH Laboratories (Monrovia, CA) for their contribution to the method development effort.

13.3 STORAGE STABILITY STUDY - Chlorinated surface water samples were preserved as required in Section 8 and stored over a 21-day period. Experimental conditions included samples fortified at 1.0 µg/L Cr(VI), samples fortified with 1.0 µg/L Cr(III), and unfortified samples (~0.060 µg/L Cr(VI)). Unfortified samples (to study the storage stability of low-level Cr(VI) concentrations) were held under refrigerated and ambient storage temperatures. Both preservative systems were studied for each of the preceding conditions. Samples fortified with Cr(III), and samples fortified with Cr(III) plus an additional 3-mg/L chlorine were studied to confirm the ability of the method preservative to prevent oxidation of dissolved Cr(III). The percent recovery (based on the mean concentration at day zero) and precision of two replicate analyses for each condition conducted after 0, 1, 2, 7, 14, and 21

days of storage are presented in Section 17, Table 7. For samples fortified with Cr(III), results are expressed as the percent conversion of Cr(III) to Cr(VI) using the mean concentration of Cr(VI) at day zero as the baseline.

14. POLLUTION PREVENTION

14.1 For information about pollution prevention applicable to laboratory operations described in this method, consult: *Less is Better, Guide to Minimizing Waste in Laboratories*, a web-based resource available from the American Chemical Society at http://www.acs.org.

15. WASTE MANAGEMENT

15.1 The Agency requires that laboratory waste management practices be consistent with all applicable rules and regulations, and that laboratories protect the air, water, and land by minimizing and controlling all releases from fume hoods and bench operations. In addition, compliance is required with any sewage discharge permits and regulations, particularly the hazardous waste identification rules and land disposal restrictions.

16. REFERENCES

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17. REFERENCES, TABLES, DIAGRAMS, FLOWCHARTS, AND VALIDATION DATA

TABLE 1. ION CHROMATOGRAPHIC CONDITIONS USED TO COLLECT METHOD PERFORMANCE DATA: AMMONIUM HYDROXIDE/AMMONIUM SULFATE ELUENT

Parameter	Conditions		
Ion chromatograph	Dionex ICS 5000 with AS Autosampler and PC10 Post-column Pneumatic Delivery Package		
Guard Column	Dionex NG1 (4 x 35 mm)		
Anion Separator Column	Dionex IonPac® AS7 (4 x 250 mm)		
Column compartment temperature	30 ºC	Autosampler tray temperature	Ambient
Eluent	Isocratic: 250 mM ammonium sulfate, 100 mM ammonium hydroxide		
Eluent flow rate	1.0 mL/min		
Post-column flow rate	0.33 mL/min		
Sample volume	1000µL		
Post-column reagent	2 mM 1,5-diphenylcarbazide, 10% methanol, 1 N sulfuric acid		
Reaction coil, temperature	750-µL knitted polytetrafluoroethylene reaction coil, 30 °C		
Detector, wavelength	UV–Vis absorbance, 530 nm		

TABLE 2. ION CHROMATOGRAPHIC CONDITIONS USED TO COLLECT METHOD PERFORMANCE DATA: CARBONATE/BICARBONATE ELUENT

Parameter	Conditions		
Ion chromatograph	Metrohm IC Professional 850, Model 887 UV–Vis Detector, Model 858 Autosampler, Model 800 Dosino post-column reagent delivery system		
Guard Column	Metrohm RP2 Guard/3.5		
Anion Separator Column	Metrohm Metrosep A SUPP 5-150/4		
Column compartment temperature	45 ºC	Autosampler tray temperature	Ambient
Eluent	Isocratic: 12.8 mM sodium carbonate, 4.0 mM sodium bicarbonate		
Eluent flow rate	0.70 mL/min		
Post-column flow rate	0.22 mL/min		
Sample volume	1250µL		
Post-column reagent	2 mM 1,5-diphenylcarbazide, 10% methanol, 1 N sulfuric acid		
Reaction coil, temperature	375-µL knitted polytetrafluoroethylene reaction coil, ambient		
Detector, wavelength	UV–Vis absorbance, 530 nm		

TABLE 3. LOWEST CONCENTRATION MINIMUM REPORTING LEVELS (LCMRL) and DETECTION LIMITS (DL) for Cr(VI)

Conditions	Preservative	Calculated LCMRL, µg/L	DL Fortification Level, µg/L	DL
Ammonium hydroxide/ammonium sulfate eluent system	Liquid [a]	0.012	0.0125	0.0054
	Solid [b]	0.012	0.0125	0.0044
Carbonate/bicarbonate eluent system	Liquid [a]	0.036	0.050	0.010
	Solid [b]	0.023	0.020	0.015

[a] $NH_4OH/(NH_4)_2SO_4$ (liquid) preservative.
[b] $CO_3^{-2}/HCO_3^-/(NH_4)_2SO_4$ (solid) preservative.

TABLE 4. SINGLE LABORATORY PRECISION AND ACCURACY RESULTS FOR Cr(VI) IN REAGENT WATER (n=7); $NH_4OH/(NH_4)_2SO_4$ (LIQUID) PRESERVATIVE

	Mean % Recovery	% Relative Standard Deviation	Mean % Recovery	% Relative Standard Deviation	Mean % Recovery	% Relative Standard Deviation
Fortification:	**0.020 µg/L**		**0.20 µg/L**		**1.0 µg/L**	
Ammonium hydroxide/ammonium sulfate eluent system	90.9	4.2	93.5	1.5	94.4	1.8
Fortification:	**0.0625 µg/L**		**0.20 µg/L**		**1.0 µg/L**	
Carbonate/bicarbonate eluent system	98.5	8.0	96.9	4.9	96.2	0.93

TABLE 5. SINGLE LABORATORY PRECISION AND ACCURACY RESULTS FOR Cr(VI) IN DRINKING WATER MATRIXES USING AMMONIUM SULFATE/AMMONIUM HYDROXIDE ELUENT SYSTEM AND $NH_4OH/(NH_4)_2SO_4$ (LIQUID) PRESERVATIVE (n=7 unless noted)

	Native matrix µg/L	Mean % Recovery[e]	% Relative Standard Deviation	Mean % Recovery[e]	% Relative Standard Deviation
Fortification:	-	**0.060 µg/L**		**1.0 µg/L**	
Well water treated only by chlorination [a]	None detected	87.1	3.5	96.6	0.82
Fortification:	-	**0.050 µg/L**		**1.0 µg/L**	
Finished groundwater [b]	0.023	96.2	1.3	100	1.0
Finished surface water [c]	0.060 (n=3)	95.5	2.9	99.8	1.2
Finished surface water with GAC filtration [d]	0.048 (n=3)	94.4	2.4	98.3	0.75

[a] Well water parameters: pH = 7.94; total hardness = 252 mg/L as $CaCO_3$; free chlorine = 0.03 mg/L; total chlorine = 0.64 mg/L.
[b] Ground water parameters: pH = 7.66; total hardness = 322 mg/L as $CaCO_3$; free chlorine = 0.84 mg/L; total chlorine = 0.84 mg/L.
[c] Surface water parameters: TOC = 3.1 mg/L C; pH = 6.77; total hardness = 120 mg/L as $CaCO_3$; free chlorine = 1.2 mg/L; total chlorine = 1.52 mg/L.
[d] Surface water parameters: total hardness = 96 mg/L as $CaCO_3$; free chlorine = 1.12 mg/L; total chlorine = 1.22 mg/L. GAC = granular activated carbon.
[e] Recoveries corrected for native levels in the unfortified matrix.

TABLE 6. SINGLE LABORATORY PRECISION AND ACCURACY RESULTS FOR Cr(VI) IN DRINKING WATER MATRIXES USING CARBONATE/BICARBONATE ELUENT SYSTEM AND $NH_4OH/(NH_4)_2SO_4$ (LIQUID) PRESERVATIVE (n=7 unless noted)

	Native matrix, µg/L	Mean % Recovery[e]	% Relative Standard Deviation	Mean % Recovery[e]	% Relative Standard Deviation
Fortification:	-	**0.060 µg/L**		**1.0 µg/L**	
Well water treated only by chlorination [a]	None detected	103	16	93.5	0.46
Fortification:	-	**0.050 µg/L**		**1.0 µg/L**	
Finished groundwater [b]	0.031	76.3	35	97.5	1.2
Finished surface water [c]	0.053 (n=3)	92.7	9.4	97.5	1.1
Finished surface water with GAC filtration [d]	0.033	98.6	4.4	96.1	1.6

[a] Well water parameters: pH = 7.94; total hardness = 252 mg/L as $CaCO_3$; free chlorine = 0.03 mg/L; total chlorine = 0.64 mg/L.

[b] Ground water parameters: pH = 7.66; total hardness = 322 mg/L as $CaCO_3$; free chlorine = 0.84 mg/L; total chlorine = 0.84 mg/L.

[c] Surface water parameters: TOC = 3.1 mg/L C; pH = 6.77; total hardness = 120 mg/L as $CaCO_3$; free chlorine = 1.2 mg/L; total chlorine = 1.52 mg/L.

[d] Surface water parameters: total hardness = 96 mg/L as $CaCO_3$; free chlorine = 1.12 mg/L; total chlorine = 1.22 mg/L. GAC = granular activated carbon.

[e] Recoveries corrected for native levels in the unfortified matrix.

TABLE 7. SAMPLE HOLDING TIME DATA FOR Cr(VI) IN CHLORINATED SURFACE WATER[a] PRESERVED AND STORED ACCORDING TO METHOD SECTION 8 (n = 2 for each experimental condition)

Experimental Condition	Fortification, µg/L	Day 0		Day 1		Day 2		Day 7		Day 14		Day 21	
		Mean Cr(VI) µg/L	RPD	Result. %	RPD	Result, %	RPD	Result, %	RPD	Result, %	RPD	Result, %	RPD
$NH_4OH/(NH_4)_2SO_4$ (liquid) preservative, 6 °C [b]	Native	0.059	1.5	103	1.2	98.5	2.6	106	2.9	110	5.3	113	4.7
$CO_3^{-2}/HCO_3^-/(NH_4)_2SO_4$ (solid) preservative, 6 °C [b]	Native	0.055	6.5	97.8	0.0	99.8	3.3	99.2	0.18	101	3.4	101	1.3
$NH_4OH/(NH_4)_2SO_4$ (liquid) preservative, 6 °C [b]	1.0 Cr(VI)	1.04	0.33	100	1.8	100	0.46	104	1.4	102	0.12	102	1.1
$CO_3^{-2}/HCO_3^-/(NH_4)_2SO_4$ (solid) preservative, 6 °C [b]	1.0 Cr(VI)	1.03	1.2	100	1.0	100	0.70	103	1.5	100	2.1	102	0.24
$NH_4OH/(NH_4)_2SO_4$ (liquid) preservative, 6 °C [c]	1.0 Cr(III)	0.072	3.2	0.43	7.7	0.67	4.8	1.6	6.0	2.7	8.2	3.2	5.0
$CO_3^{-2}/HCO_3^-/(NH_4)_2SO_4$ (solid) preservative, 6 °C [c]	1.0 Cr(III)	0.068	0.74	0.45	5.1	0.24	2.1	0.60	5.1	0.73	6.6	0.93	10
$NH_4OH/(NH_4)_2SO_4$ (liquid) preservative, 6 °C (fortified w/additional 3 mg/L Cl_2) [c]	1.0 Cr(III)	0.077	4.7	-0.025	4.5	-0.16	8.6	2.4	7.5	3.4	4.2	4.7	0.88
$CO_3^{-2}/HCO_3^-/(NH_4)_2SO_4$ (solid) preservative, 6 °C (fortified w/additional 3 mg/L Cl_2) [c]	1.0 Cr(III)	0.064	7.8	-0.53	10	-0.76	2.3	0.17	15	-0.12	3.5	0.53	0.57
$NH_4OH/(NH_4)_2SO_4$ (liquid) preservative, ambient storage [b]	Native	0.060	1.7	100	8.7	100	6.7	110	3.4	117	15	118	2.0
$CO_3^{-2}/HCO_3^-/(NH_4)_2SO_4$ (solid) preservative, ambient storage [b]	Native	0.056	2.5	99.0	4.2	94.9	3.6	98.7	3.6	105	4.1	101	2.3

[a] Surface water parameters: TOC = 3.1 mg/L C; pH = 6.77; total hardness = 120 mg/L as $CaCO_3$; free chlorine = 1.2 mg/L; total chlorine = 1.52 mg/L.

[b] Result expressed as the percent recovery of Cr(VI) relative to the mean concentration at Day 0, e.g. at Day 1: (Mean [Cr(VI)] / Mean [Cr(VI)] Day 0) * 100.

[c] Result expressed as the percent conversion of Cr(III) to Cr(VI) using the mean concentrations at Day 0 as the baseline, e.g. at Day 1: (Mean [Cr(VI)] - Mean [Cr(VI)] Day 0) / 1.0 µg/L Cr(III) * 100.

TABLE 8. INITIAL DEMONSTRATION OF CAPABILITY (IDC) QUALITY CONTROL REQUIREMENTS

Method Reference	Requirement	Specification and Frequency	Acceptance Criteria
Section 9.2.1	Demonstration of low system background	Analyze an LRB after the high calibration standard during the IDC calibration.	Cr(VI) concentration is <1/3 of the MRL.
Section 9.2.2	Demonstration of precision	Analyze seven replicate Laboratory Fortified Blanks (LFBs) fortified near the midrange of the calibration curve.	Percent relative standard deviation must be ≤15%.
Section 9.2.3	Demonstration of accuracy	Calculate average recovery for replicates used in Section 9.2.2.	Mean recovery within ±15% of the true value.
Section 9.2.4	MRL confirmation	Fortify and analyze seven replicate LFBs at the chosen MRL concentration. Confirm that the Upper Prediction Interval of Results (PIR) and Lower PIR (Sect. 9.2.4.2) meet the recovery criteria.	Upper PIR ≤ 150% Lower PIR ≥ 50%
Section 9.2.5	Quality Control Sample (QCS)	Analyze mid-level QCS.	Cr(VI) must be within ±15% of the true value.

TABLE 9. ONGOING QUALITY CONTROL REQUIREMENTS

Method Reference	Requirement	Specification and Frequency	Acceptance Criteria
Section 10.2	Initial calibration	Use the external standard calibration technique to generate a linear or quadratic calibration curve. Use at least six standard concentrations. Validate the calibration curve as described in Section 10.2.3.	When each calibration standard is calculated as an unknown using the regression equations, the lowest level standard should be within ±50% of the true value. All other points should be within ±15% of the true value.
Section 9.3.1	Laboratory Reagent Blank (LRB)	Analyze one LRB with each Analysis Batch.	Demonstrate that Cr(VI) is below ⅓ the Minimum Reporting Level (MRL), and that other sources of interference do not prevent identification and quantitation.
Section 10.3	Continuing Calibration Check (CCC)	Verify initial calibration by analyzing a low-level CCC at the beginning of each Analysis Batch. Subsequent CCCs are required after every 10 field samples and after the last field sample in a batch.	The lowest level CCC must be within ±50% of the true value. All other points must be within ±15% of the true value. Results for field samples that are not bracketed by acceptable CCCs are invalid.
Section 9.3.4	Laboratory Fortified Sample Matrix (LFSM)	Analyze one LFSM per Analysis Batch. Fortify the LFSM with Cr(VI) at a concentration greater than the native concentrations. Calculate LFSM recovery.	For LFSMs fortified at concentrations ≤2 x MRL, the result must be within ±50% of the true value. At concentrations greater than the 2 x MRL, the result must be within ±15% of the true value.
Section 9.3.5	Laboratory Fortified Sample Matrix Duplicate (LFSMD) or Laboratory Duplicate (LD)	Analyze at least one LFSMD or LD with each Analysis Batch.	For LFSMDs or LDs, relative percent differences must be ≤15%. (≤50% if concentration ≤2 x MRL.)
Section 9.3.6	Quality Control Sample (QCS)	Analyze mid-level QCS with each new calibration curve.	Cr(VI) must be ±15% of the true value.

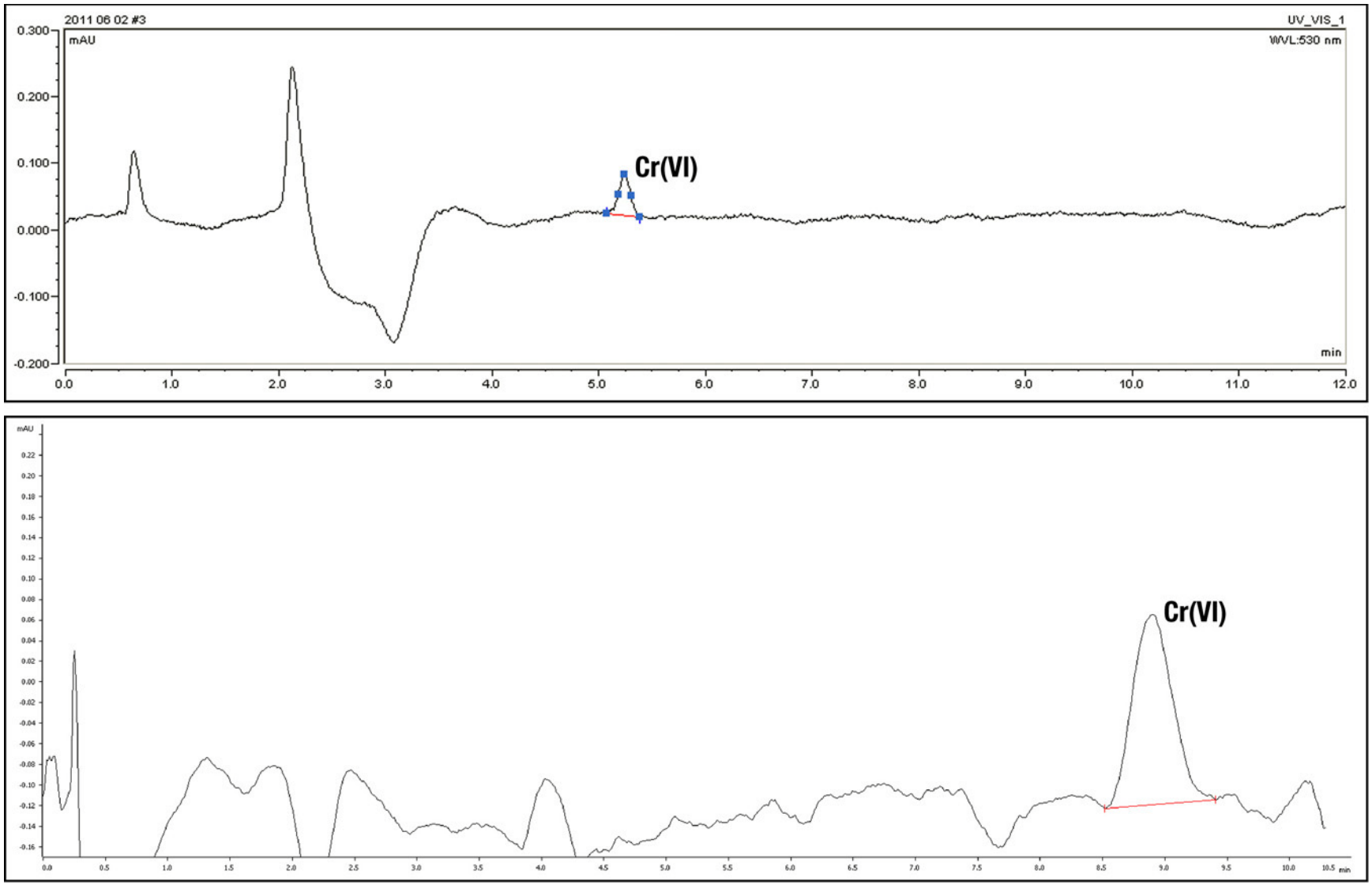

Figure 1. Calibration standards, $NH_4OH/(NH_4)_2SO_4$ (liquid) preservative: 0.020 µg/L analyzed using ammonium hydroxide/ammonium sulfate eluent system (top) and 0.050 µg/L analyzed using carbonate/bicarbonate eluent system (bottom).

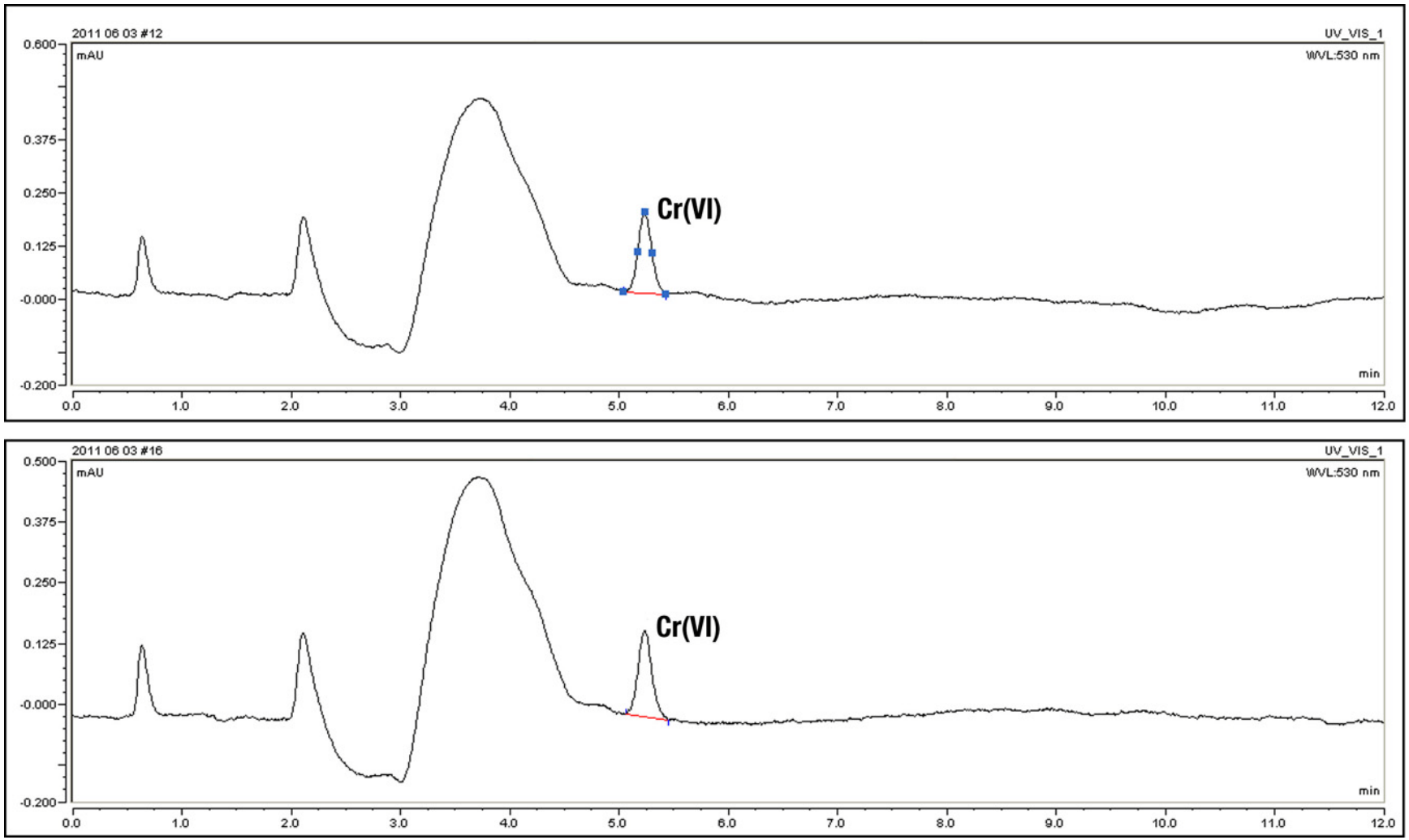

Figure 2. Field sample, tap water from surface water source analyzed using ammonium hydroxide/ammonium sulfate eluent system: $NH_4OH/(NH_4)_2SO_4$ (liquid) preservative (top) and $CO_3^{-2}/HCO_3^{-}/(NH_4)_2SO_4$ (solid) preservative (bottom); native concentration is ~0.060 µg/L.

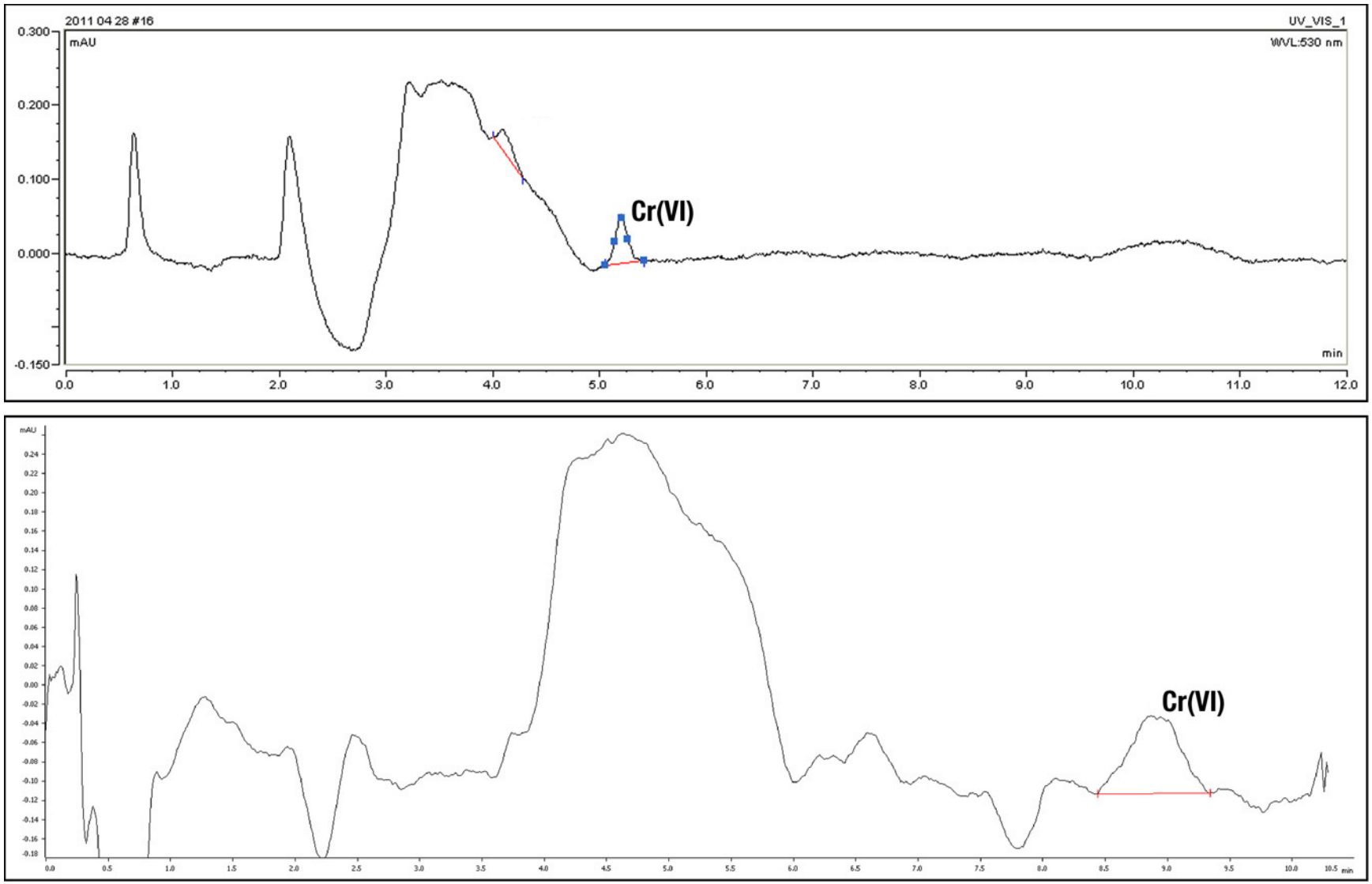

Figure 3. Field sample, tap water from a ground water source, $NH_4OH/(NH_4)_2SO_4$ (liquid) preservative: analyzed using ammonium hydroxide/ammonium sulfate eluent system (top) and using carbonate/bicarbonate eluent system (bottom); native concentration is ~0.020 µg/L.

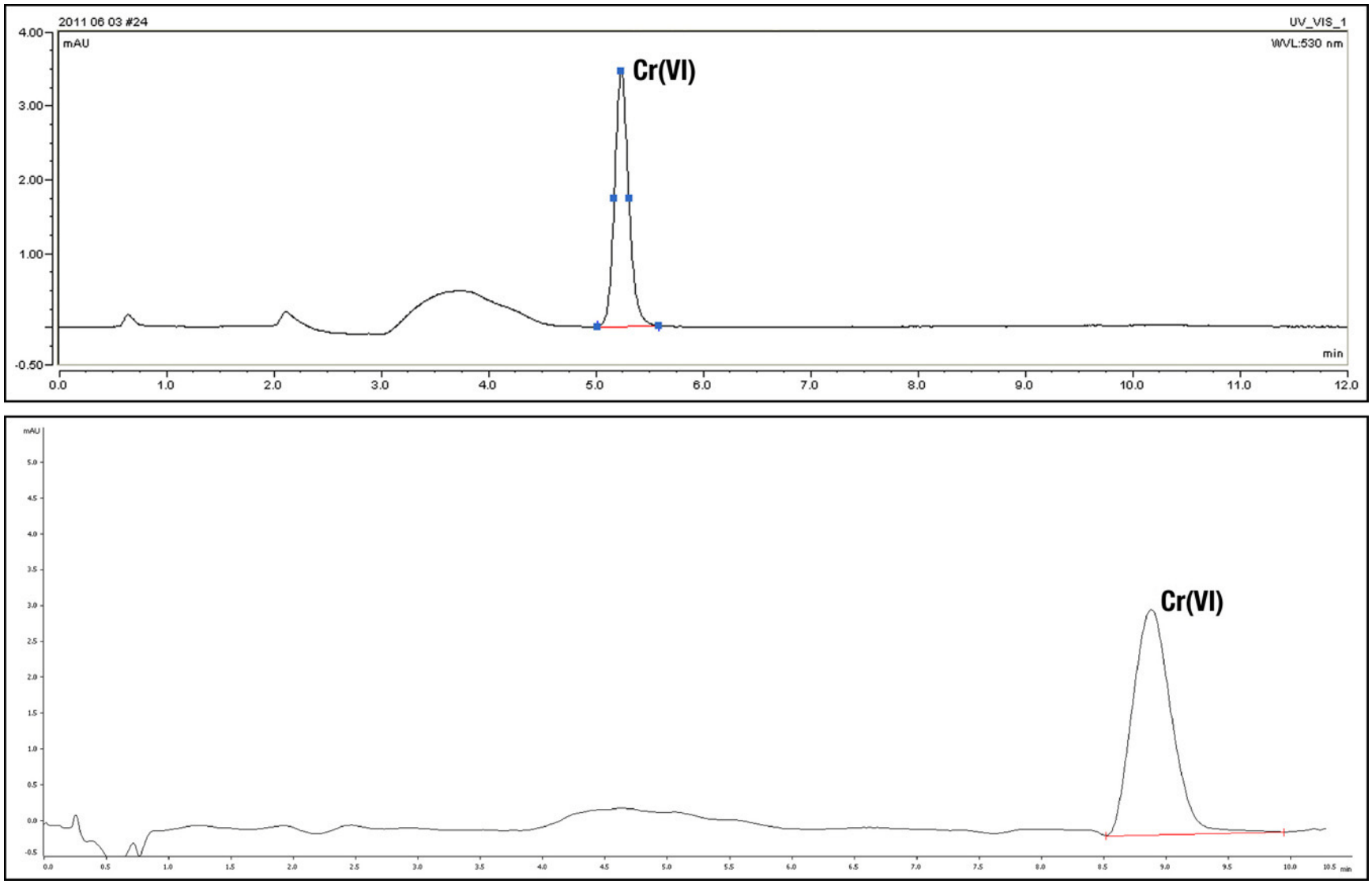

Figure 4. Field sample, tap water from a surface water source, $NH_4OH/(NH_4)_2SO_4$ (liquid) preservative: analyzed using ammonium hydroxide/ammonium sulfate eluent system (top) and using carbonate/bicarbonate eluent system (bottom); LFSM at 1.0 µg/L.