

**QuikChem METHOD 10-510-13-1-B**

**DETERMINATION OF DISSOLVED HEXAVALENT  
CHROMIUM IN DRINKING WATER BY ION  
CHROMATOGRAPHY**

**QC8500 ONLY**

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Applications Group

**Revision Date:**

**28 January 2011**

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QuikChem Method 10-510-13-1-B  
**Dissolved Hexavalent Chromium (VI) in  
Drinking Waters**

0.05 to 10 µg Cr/L

– Principle –

This is an ion chromatographic method with post-column derivatization. Cr (VI) as  $\text{CrO}_4^{2-}$  is separated on the anion-exchange separator column, derivatized with diphenylcarbazide, and then the colored complex is detected at 530 nm. The method provides results which are equivalent to those of USEPA method 218.6<sup>1</sup>.

For reference, where this method is approved for use in compliance monitoring programs (e.g. Clean Water Act (NPDES) or Safe Drinking Water Act (SDWA), consult both the appropriate sections of the Code of Federal Regulations (40CFR136 Table 1B for NPDES and 40CFR141 and 141.23 for Drinking Water) and the latest Federal Register announcements.

– Special Apparatus –

1. Lachat Instrument QC8500 IC Ion Chromatograph and FIA System.
2. Sample tubes are needed for 60 Position Samplers (Lachat Part No. 21042).
3. PVC pump tubes must be used for this method.
4. 2-cm Detector Assembly [Lachat Part No. 58025 (Assembly includes 2 cm flow cell, Lachat Part No. 58062)].

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## QUIKCHEM METHOD 10-510-13-1-B

# DETERMINATION OF DISSOLVED HEXAVALENT CHROMIUM IN DRINKING WATER BY ION CHROMATOGRAPHY

### 1. SCOPE AND APPLICATION

- 1.1 This method provides procedures for determination of dissolved chromium (as  $\text{CrO}_4^{2-}$ , CASRN 11104-59-9) in drinking water.
- 1.2 The range tested was 0.05 to 10  $\mu\text{g Cr/L}$ . The method detection limit (MDL, defined in Section 3) is 0.019  $\mu\text{g Cr/L}$  in reagent water. The method throughput is 9 injections per hour.
- 1.3 Samples containing high levels of anionic species such as sulfate and chloride may overload the column. Samples containing high levels of organics or sulfides cause rapid reduction of soluble Cr (VI) to Cr (III). Samples must be stored at 4°C and analyzed within 24 h of collection.
- 1.4 This method should be used by analysts experienced in the use of ion chromatography and the interpretation of ion chromatograms.
- 1.5 Users of the method data should state the data-quality objectives prior to analysis. Users of the method must demonstrate the ability to generate acceptable results with this method, using the procedure described in Section 9.0.

### 2. SUMMARY OF METHOD

- 2.1 This is an ion chromatographic method with post-column derivatization. An aqueous sample is filtered through a 0.45  $\mu\text{m}$  filter and the filtrate is adjusted to a pH of 9 to 9.5 with a buffer solution. A measured volume of the sample (3 mL) is introduced into the ion chromatograph. A guard column removes organics from the sample before Cr (VI) as  $\text{CrO}_4^{2-}$  is separated on the anion-exchange separator column. Post-column derivatization of the Cr (VI) with diphenyl carbazide is followed by detection of the colored complex at 530 nm. The method provides results which are equivalent to those of USEPA method 218.6<sup>1</sup>, Standard Method 3500-Cr<sup>2</sup>.

### 3. DEFINITIONS

- 3.1 CALIBRATION STANDARD (CAL) -- A solution prepared from the primary standard solution or stock standard solution and the internal standards and surrogate analytes. The CAL solutions are used to calibrate the instrument response with respect to analyte concentration.
- 3.2 DISSOLVED ANALYTE: The concentration of analyte in an aqueous sample that will pass through a 0.45  $\mu\text{m}$  membrane filter assembly prior to adjustment of pH.
- 3.3 INSTRUMENT PERFORMANCE CHECK SOLUTION (IPC) -- A solution of one or more method analytes, surrogates, internal standards, or other test substances used to evaluate the performance of the instrument system with respect to a defined set of criteria.

- 3.4 LABORATORY DUPLICATES (LD1 and LD2): two aliquots of the same sample, taken in the laboratory and analyzed separately with identical procedures. Analyses of LD1 and LD2 indicate precision associated with laboratory procedures, but not with sample collection, preservation or storage procedures.
- 3.5 LABORATORY FORTIFIED BLANK (LFB) -- An aliquot of reagent water or other blank matrices to which known quantities of the method analytes are added in the laboratory. The LFB is analyzed exactly like a sample, and its purpose is to determine whether the methodology is in control, and whether the laboratory is capable of making accurate and precise measurements.
- 3.6 LABORATORY FORTIFIED SAMPLE MATRIX (LFM) -- An aliquot of an environmental sample to which known quantities of the method analytes are added in the laboratory. The LFM is analyzed exactly like sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the LFM corrected for background concentrations.
- 3.7 LABORATORY REAGENT BLANK (LRB) -- An aliquot of reagent water or other blank matrices that are treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, internal standards, and surrogates that are used with other samples. The LRB is used to determine if method analytes or other interferences are present in the laboratory environment, the reagents, or the apparatus.
- 3.8 LINEAR CALIBRATION RANGE (LCR) -- The concentration range over which the instrument response is linear. FIELD DUPLICATES (FD) -- Two separate samples collected at the same time and place under identical circumstances and treated exactly the same throughout field and laboratory procedures. Analyses of field duplicates indicate the precision associated with sample collection, preservation and storage, as well as with laboratory procedures.
- 3.9 METHOD DETECTION LIMIT (MDL) -- The minimum concentration of an analyte that can be identified, measured and reported with 99% confidence that the analyte concentration is greater than zero
- 3.10 QUALITY CONTROL SAMPLE (QCS) -- A solution of method analytes of known concentrations that is used to fortify an aliquot of LRB or sample matrix. The QCS is obtained from a source external to the laboratory and different from the source of calibration standards. It is used to check laboratory performance with externally prepared test materials.
- 3.11 PERFORMANCE EVALUATION SAMPLE (PE) -- A solution of method analytes distributed by the Quality Assurance Research Division (QARD), Environmental Monitoring Systems Laboratory (EMSL-Cincinnati), U.S. Environmental Protection Agency, Cincinnati, Ohio, to multiple laboratories for analysis. A volume of the solution is added to a known volume of reagent water and analyzed with procedures used for samples. Results of analyses are used by QARD to determine statistically the accuracy and precision that can be expected when a method is performed by a competent analyst. Analyte true values are unknown to the analyst.
- 3.12 STOCK STANDARD SOLUTION (SSS) -- A concentrated solution containing one or more method analytes prepared in the laboratory using assayed reference materials or purchased from a reputable commercial source.

## 4. INTERFERENCES

- 4.1 Trace amounts of Cr are sometimes found in reagent grade salts. Since a concentrated buffer solution is used in this method to adjust the pH of samples, reagent blanks should be analyzed to assess Cr (VI) contamination. Contamination can also come from improperly cleaned glassware, caustic or acidic reagents, and contact with stainless steel or pigmented materials.
- 4.2 Oxidation of Cr (III) to Cr (VI) can occur in an alkaline medium in the presence of oxidants such as Fe (III) and oxidized Mn or as a result of the aeration that occurs in most extraction procedures. Reduction of Cr (VI) to Cr (III) can occur in the presence of reducing species in an acidic medium. At a pH of 6.5 or greater, however,  $\text{HCrO}_4^-$  is converted to  $\text{CrO}_4^{2-}$  which is less reactive than the  $\text{HCrO}_4^-$ .
- 4.3 Samples of high ionic strength (e.g. high  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$ ) may overload the column. The symptom is abnormal peak shapes, and poor recoveries. (Samples up to 2 mS conductivity were tested with this method).

## 5. SAFETY

- 5.1 The toxicity or carcinogenicity of each reagent used in this method has not been fully established. Each chemical should be regarded as a potential health hazard and exposure should be as low as reasonably achievable. Cautions are included for known extremely hazardous materials.
- 5.2 Each laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of Material Safety Data sheets (MSDS) should be made available to all personnel involved in the chemical analysis. The preparation of a formal safety plan is also advisable.
- 5.3 The following chemicals have the potential to be highly toxic or hazardous, for detailed explanations consult the MSDS.
  - 5.3.1 Hexavalent chromium is toxic and a suspected carcinogen and should be handled with appropriate precautions<sup>3,4</sup>. Extreme care should be exercised when weighing the salt for preparation of the stock standard.
  - 5.3.2 Sulfuric acid
  - 5.3.3 Methanol
  - 5.3.4 Diphenylcarbazide

## 6. EQUIPMENT AND SUPPLIES

- 6.1 Balance -- analytical, capable of accurately weighing to the nearest 0.0001 g.
- 6.2 Glassware -- Class A volumetric flasks and pipettes as required. **Note:** Chromic acid must not be used to clean glassware for this method.
- 6.3 Ion Chromatograph -- Analytical system complete with ion chromatograph and all required accessories including analytical columns and detectors.
  - 6.3.1 Anion guard column: AN2-HCG (Lachat part no. 58211) A protector of the separator column. If omitted from the system the retention times will be shorter. Usually packed with a substrate the same as that in the separator column.

- 6.3.2 Anion profiling column: AN2-HC (Lachat part no. 58212) This column produces the separation shown in Figure 1. An optional column may be used if comparable resolution of peaks is obtained, and the requirements of Section 9.2 can be met.
- 6.3.3 Sample tubes are needed for 60 Position Samplers (Lachat Part No. 21042)
- 6.3.4 PVC pump tubes must be used for this method.
- 6.3.5 2-cm Detector Assembly [Lachat Part No. 58025 (Assembly includes 2 cm flow cell, Lachat Part No. 58062)]
- 6.4 Helium gas for degassing reagents.
- 6.5 0.45 µm membrane filters

## **7. REAGENTS AND STANDARDS**

- 7.1 **Sample bottles:** High density polypropylene of sufficient volume to allow replicate analyses.
- 7.2 **Reagent water:** Use deionized water, with resistance of at least 18.0 megohm-cm and with particles no larger than 0.20 µm, for preparing reagents.
- 7.3 **Eluent solution**

**By Volume:** In a 1 L volumetric flask containing approximately **600 mL DI water**, dissolve **7.385 g ammonium sulfate** (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> (CASRN 7783-20-2), and add **1.5 mL ammonium hydroxide** (NH<sub>4</sub>OH) (CASRN 1336-21-6). Dilute to mark with **DI water** and invert to mix. Degas the eluent by helium sparging (one minute for each liter) or by sonication. This reagent is stable for 1 to 2 days.
- 7.4 **Post-column Derivatization Reagent**

**By Volume:** Cautiously add **28 mL concentrated sulfuric acid** (H<sub>2</sub>SO<sub>4</sub>) to about **500 mL DI water** in a 1 L volumetric flask. Swirl to mix. In a separate container, dissolve **0.5 g 1,5-diphenylcarbazide** (CASRN 140-22-7) in **100 mL HPLC grade Methanol**. Add the methanol solution to the flask. Dilute with water to **1 L** and invert to mix. Degas with helium. This reagent is stable for four to five days.
- 7.5 **Buffer Solution**

**By Volume:** Dissolve **3.3 g ammonium sulfate** (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, in **75 mL DI water** and add **6.5 mL concentrated ammonium hydroxide** (NH<sub>4</sub>OH). Dilute to **100 mL** with **DI water**. This buffer is used to adjust the pH of the standards and samples 9.0 – 9.5.
- 7.6 **15% Methanol**

**By Volume:** To a **500 mL volumetric flask** add **75 mL methanol (MeOH)** to **300 mL DI water**. Dilute to mark with **DI water** and invert to mix.
- 7.7 **Stock Standard 1: 1000 mg/L (1 mg/mL):** Stock standards may be purchased as certified solutions or prepared from ACS reagent grade materials (dried at 105°C for 30 min) as listed below.

**By Volume:** In a 1 L volumetric flask containing approximately **600 mL DI water**, dissolve **3.735 g potassium chromate** (K<sub>2</sub>CrO<sub>4</sub>). Dilute to the mark with **DI water** and invert to mix.

**By Weight:** To a tared **1 L** container, add **3.7 ± 0.1g potassium chromate** (K<sub>2</sub>CrO<sub>4</sub>). Note the exact weight and divide it by **3.735**. Multiply the ratio by **1000** to find out the

exact final weight needed. Make up to that weight with **DI water**. Stir until the material is dissolved.

**7.8 Intermediate Stock Standard 2: 10 mg Cr/L**

**By Volume:** In a **1 L** volumetric flask containing approximately **600 mL DI water**, add **10 mL of Stock Standard 1**. Dilute to the mark with **DI water** and invert to mix.

**By Weight:** In a tared **1 L** container add about **10 g Standard 1**. Note the exact weight and divide it by **10**. Multiply the ratio by **1000** to find out the exact final weight needed. Add **DI water** to obtain that final weight. Invert to mix.

**7.9 Working Stock Standard 3: 50 µg Cr/L**

**By Volume:** In a **500 mL** volumetric flask containing approximately **300 mL DI water**, add **2.5 mL of Intermediate Stock Standard 2**. Add **5 mLs of the buffer** (reagent 7.5) (1 mL/100 mL of standard or sample). Dilute to the mark with **DI water** and invert to mix.

**By Weight:** In a tared **500 mL** container add about **2.5 g Intermediate Stock Standard 2**. Add **5 mLs of the buffer** (reagent 3) (1 mL/100 mL of standard or sample). Note the exact weight and divide it by **5**. Multiply the ratio by **500** to find out the exact final weight needed. Add **DI water** to obtain that final weight. Invert to mix.

**7.10 Set of seven working standards**

Std	Stock Standard 3	Final Sol'n.	Concentration (µg/L)
	- mL or g -	- mL or g -	CrO <sub>4</sub> <sup>2-</sup>
A	50	250	10.0
B	25	250	5.0
C	5	250	1.0
D	2.5	250	0.5
E	1.0	250	0.2
	<b>Std A</b>		
F	2.5	250	0.1
G	1.25	250	0.05
H	---	250	0.0

*Note: The buffer reagent should be added to the standards in the same proportion that it will be added to the samples. The method was developed by using 2.5 mL of reagent 3 to 250 mLs of the standards and samples without interference due to sulfate (1 mL buffer /100 mL of standard or sample). The pH is adjusted to 9.3 – 9.7. See Section 8.*

**8. SAMPLE COLLECTION, PRESERVATION AND STORAGE**

8.1 For reference, where this method is approved for use in compliance monitoring programs (e.g. Clean Water Act (NPDES) or Safe Drinking Water Act (SDWA) consult both the appropriate sections of the Code of Federal Regulations (40CFR136 Table 1B for NPDES and 40CFR141 and 141.23 for Drinking Water) and the latest Federal Register announcements

8.2. Prior to sample collection, consideration should be given to the type of data required so that appropriate preservation and pretreatment steps can be taken. Filtration and pH adjustment should be performed at the time of sample collection or as soon as thereafter as practically possible.

- 8.3 Adjust the pH of the sample to 9.3-9.7 by adding 1 mL of the buffer (**Reagent 7.5**) to 100 mLs of sample, periodically checking the pH with the pH meter. The same amount of buffer should be added to both the samples and the standards. The method was tested by adding 1.0% (v/v) of **Reagent 7.5** to the samples which did not result in interference due to sulfate.
- 8.4. Samples must be filtered immediately (within 15 minutes of collection) through a 0.45µm filter to prevent inter-conversion of chromium species. Use a portion of the sample to rinse the syringe filtration unit and filter and then collect the required volume of filtrate.
- 8.6. EPA Method 218.6 for drinking water specifies a 24-hour holding time.
- 8.5 Store the samples at 4°C. Bring to ambient temperature prior to analysis. Drinking water samples must be analyzed within 24 hours of collection.

## **9. QUALITY CONTROL (USEPA GUIDELINE)**

- 9.1 Each laboratory using this method is required to operate a formal quality control (QC) program. The minimum requirements of this program consist of an initial demonstration of laboratory capability, and the periodic analysis of laboratory reagent blanks, fortified blanks and other laboratory solutions as a continuing check on performance. The laboratory is required to maintain performance records that define the quality of the data that are generated.
- 9.2 INITIAL DEMONSTRATION OF PERFORMANCE
  - 9.2.1 The initial demonstration of performance is used to characterize instrument performance (determination of LCRs and analysis of QCS) and laboratory performance (determination of MDLs) prior to performing analyses by this method.
  - 9.2.2 Linear Calibration Range (LCR) -- The LCR must be determined initially and verified every six months or whenever a significant change in instrument response is observed or expected. The initial demonstration of linearity must use sufficient standards to ensure that the resulting curve is linear. The verification of linearity must use a minimum of a blank and three standards. If any verification data exceeds the initial values by +/- 10%, the calibration curve is nonlinear, and sufficient standards must be used to clearly define the nonlinear portion.
  - 9.2.3 Quality Control Sample (QCS) -- When beginning the use of this method, on a quarterly basis or as required to meet data-quality needs, verify the calibration standards and acceptable instrument performance with the preparation and analyses of a QCS. If the determined concentrations are not within +/-10% of the stated values, performance of the determinative step of the method is unacceptable. The source of the problem must be identified and corrected before either proceeding with the initial determination of MDLs or continuing with on-going analyses.
  - 9.2.4 Method Detection Limit (MDL) -- MDLs must be established for all analytes, using reagent water (blank) fortified at a concentration of two to three times the estimated instrument detection limit. To determine MDL values, take seven replicate aliquots of the fortified reagent water and process through the entire analytical method<sup>3</sup>. Perform all calculations defined in the method and report the concentration values in the appropriate units. Calculate the MDL as follows:

$$\text{MDL} = (t) \times (S)$$

Where, t = Student's t value for a 99% confidence level and a standard deviation estimate with n-1 degrees of freedom [t = 3.14 for seven replicates, t= 2.528 for twenty one replicates].

S = standard deviation of the replicate analyses.

MDLs are to be determined every six months, when a new operator begins work, or whenever there is a significant change in the background or instrument response.

### 9.3 ASSESSING LABORATORY PERFORMANCE

- 9.3.1 Laboratory Reagent Blank (LRB) -- The laboratory must analyze at least one LRB with each batch of samples. Data produced are used to assess contamination from the laboratory environment. Values that exceed the MDL indicate laboratory or reagent contamination should be suspected and corrective actions must be taken before continuing the analysis.
- 9.3.2 Laboratory Fortified Blank (LFB) -- The laboratory must analyze at least one LFB with each batch of samples. Calculate accuracy as percent recovery (Section 9.4.2). If the recovery of any analyte falls outside the required control limits of 90-110%, that analyte is judged out of control, and the source of the problem should be identified and resolved before continuing analyses.
- 9.3.3 The laboratory must use LFB analyses data to assess laboratory performance against the required control limits of 90-110%. When sufficient internal performance data become available (usually a minimum of 20-30 analyses), optional control limits can be developed from the percent mean recovery ( $\bar{X}$ ) and the standard deviation (S) of the mean recovery. These data can be used to establish the upper and lower control limits as follows:

$$\text{UPPER CONTROL LIMIT} = \bar{X} + 3S$$

$$\text{LOWER CONTROL LIMIT} = \bar{X} - 3S$$

The optional control limits must be equal to or better than the required control limits of 90-110%. After each five to ten new recovery measurements, new control limits can be calculated using only the most recent 20-30 data points. Also, the standard deviation (S) data should be used to establish an on-going precision statement for the level of concentrations included in the LFB. These data must be kept on file and be available for review.

- 9.3.4 Instrument's Performance Check Solution (IPC) -- For all determinations the laboratory must analyze the IPC (a mid-range check standard) and a calibration blank immediately following daily calibration, after every tenth sample (or more frequently, if required) and at the end of the sample run. Analysis of the IPC solution and calibration blank immediately following calibration must verify that

the instrument is within +/-10% of calibration. Subsequent analyses of the IPC solution must verify the calibration is still within +/-10%. If the calibration cannot be verified within the specified limits, reanalyze the IPC solution. If the second analysis of the IPC solution confirms calibration to be outside the limits, sample analysis must be discontinued, the cause determined and/or in the case of drift the instrument recalibrated. All samples following the last acceptable IPC solution must be reanalyzed. The analysis data of the calibration blank and IPC solution must be kept on file with sample analyses data.

#### 9.4 ASSESSING ANALYTE RECOVERY AND DATA QUALITY

- 9.4.1 Laboratory Fortified Sample Matrix (LFM) -- The laboratory must add a known amount of analyte to a minimum of 10% of routine samples. In each case the LFM aliquot must be a duplicate of the aliquot used for sample analysis. The analyte concentration must be high enough to be detected above the original sample and should not be less than four times the MDL. The added analyte concentration should be the same as that used in the laboratory fortified blank.
- 9.4.2 Calculate the percent recovery for each analyte, corrected for concentrations measured in the unfortified sample, and compare these values to the designated LFM recovery range 90-110%. Percent recovery may be calculated using the following equation:

$$R = \frac{C_s - C}{s} \times 100$$

Where,            R            = percent recovery  
                      C<sub>s</sub>            = fortified sample concentration.  
                      C                = sample background concentration.  
                      s                = concentration equivalent of analyte added to sample.

- 9.4.3 Until sufficient data becomes available (usually a minimum of 20 to 30 analysis), assess laboratory performance against recovery limits of 80 to 120%. When sufficient internal performance data becomes available develop control limits from percent mean recovery and the standard deviation of the mean recovery.
- 9.4.4 If the recovery of any analyte falls outside the designated LFM recovery range and the laboratory performance for that analyte is shown to be in control (Section 9.3), the recovery problem encountered with the LFM is judged to be either matrix or solution related, not system related.
- 9.4.5 Where reference materials are available, they should be analyzed to provide additional performance data. The analysis of reference samples is a valuable tool for demonstrating the ability to perform the method acceptably.
- 9.4.6 In recognition of the rapid advances occurring in chromatography, the analyst is permitted certain options, such as the use of different columns and/or eluents, to improve the separations or lower the cost of measurements. Each time such modifications to the method are made, the analyst is required to repeat the procedure in Section 9.2.

- 9.4.7 It is recommended that the laboratory adopt additional quality assurance practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and nature of the samples. Field duplicates may be analyzed to monitor the precision of the sampling techniques. When doubt exists over the identification of peak in the chromatogram, confirmatory techniques such as sample dilution and fortification, must be used. Whenever possible, the laboratory should perform analysis of quality control check samples and participate in relevant evaluation of samples studied.
- 9.4.8 At least quarterly, replicates of LFBs should be analyzed to determine the precision of the laboratory measurements. Add these results to the on-going control charts to document data quality.

## **10. CALIBRATION AND STANDARDIZATION**

- 10.1 For each analyte of interest, calibration standards are prepared at a minimum of three concentration levels. The preparation of calibration standards as given in Section 7 is a guideline. The calibration standards employed must bracket the concentration of the analytes of interest. After calibration, a blank should be run for validation.
- 10.2 Suggested sample loop size is 3.0 mL for the range of 0.05 to 10 µg Cr/L. This is obtained by connecting a 2.0 mL loop and a 1.0 mL loop with a PEEK union (Lachat Part No. 28125). A 3.00 mL loop volume is sufficient for samples containing 0.05 to 10.0 µg/L.
- 10.3 Before using this method to analyze samples, there must be data available documenting initial demonstration of performance. The required data and procedure is described in section 9.2. This data must be generated using the same instrument operating conditions and calibration routine to be used during sample analysis. The documented data must be kept on file and be available for review by the data user.
- 10.4 Prepare a standard curve by plotting instrument response against concentration values. A calibration curve may be fitted to the calibration solution concentration/response data using the computer. Acceptance or control limits should be established using the difference between the measured value of the calibration solution and the "true value" concentration.
- 10.5 After the calibration has established, it must be verified by the analysis of a suitable quality control sample (QCS). If measurements exceed +/-10% of the established QCS value, the analysis should be terminated and the instrument recalibrated. The new calibration must be verified before continuing analysis. Periodic reanalysis of the QCS is recommended as a continuing calibration check.
- 10.6 Nonlinear response can result when the analytical column capacity is exceeded (overloading). The responses for the sample when diluted 1:1, and when not diluted, should be compared. If the determined results are the same, accounting for dilution, then the samples having this total ionic concentration need not be diluted.

## **11. PROCEDURE**

### **11.1 SAMPLE PRETREATMENT**

- 11.1.1 Filtered, pH adjusted samples at 4°C should be brought to ambient temperature prior to analysis (see Section 8).

## 11.2 CALIBRATION PROCEDURE

- 11.2.1 Prepare reagents and standards as described in Section 7.
- 11.2.2 Set up the IC manifold as shown in Section 17.1 or 17.2. Inspect the manifold carefully for proper connections.
- 11.2.3 Input data system parameters as in Section 17.3.
- 11.2.4 Place the eluent inlet tubing in the eluent container and prime the pump.
- 11.2.5 With the columns out of the system, pump eluent until all air is removed from the tubings.
- 11.2.8 Place samples and/or standards in the autosampler. Set up the method with appropriate standards and samples in the Run Worksheet.
- 11.2.9 Calibrate the instrument by injecting a minimum of three standards. The calibration range should bracket the anticipated concentration range of samples. The data system will then associate the concentrations with the instrument responses for each standard. The R - squared value for the curve should be 0.999 or greater.
- 11.2.10 **System shut-down:** At the end of day's work, place the inlet tubing for both pumps in deionized water and flush the system. If the eluent-delivery and post-column reagent pumps will be idle for longer than three days, first remove the columns and close them with end caps. Long term storage of the eluent pump is in isopropanol.

## 11.3 SYSTEM NOTES

- 11.3.1. Inspect modules for proper connections.
- 11.3.2 Do not overtighten any of the PEEK fittings (Finger tight only).
- 11.3.3 If sample concentrations are greater than the high standard, dilute the sample with DI water.

## 12. DATA ANALYSIS AND CALCULATIONS

- 12.1 Calibration is done by injecting standards. The data system will then prepare a calibration curve by plotting the responses versus the standard concentrations. Analyte concentrations for unknown samples are calculated from the respective regression equations.
- 12.2 Report only those values that fall between the lowest and the highest calibration standards. Samples exceeding the highest standard should be diluted and reanalyzed.
- 12.3 Report results in  $\mu\text{g Cr/L}$ . Sample concentrations must be corrected for any Cr (VI) contamination found in LRB. The QC data obtained during sample analyses provide an indication of the quality of sample data and should be reported with sample results.

## 13. METHOD PERFORMANCE

- 13.1. The method support data are presented in Section 18.2. This data was generated according to a Lachat Work Instruction during development of the method.
- 13.2. Although Lachat Instruments, publishes method performance data, including MDL, precision, accuracy and carryover studies, we cannot guarantee that each laboratory will be capable of meeting such performance. Individual laboratory and instrument

conditions, as well as laboratory technique, play a major role in determining method performance. The support data serves as a guide of the potential method performance. Some labs may not be able to reach this level of performance for various reasons, while other labs may exceed it.

## **14. POLLUTION PREVENTION**

- 14.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operation. The EPA has established a preferred hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When wastes cannot be feasibly reduced at the source, the Agency recommends recycling as the next best option.
- 14.2 The quantity of chemicals purchased should be based on expected usage during its shelf life and disposal cost of unused material. Actual reagent preparation volumes should reflect anticipated usage and reagent stability.
- 14.3 For information about pollution prevention that may be applicable to laboratories and research institutions, consult "Less is Better: American Chemical Society's Department of Government Regulations and Science Policy", American Chemical Society, 115 16th Street N. W., Washington D. C. 20036, (202) 872-4477.

## **15. WASTE MANAGEMENT**

- 15.1 The Environmental Protection Agency (USEPA) requires that laboratory waste management practice be conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes should be characterized and disposed of in an acceptable manner. The agency urges laboratories to protect the air, water, and land by minimizing and controlling all releases from hoods, and bench operations, complying with the letter and spirit of any waster discharge permit and regulations, and by complying with all solid and hazardous waste regulations, particularly the hazardous waste identification rules and land disposal restrictions. For further information on waste management, consult the "Waste Management Manual for Laboratory Personnel", available from the American Chemical Society at the address listed in Section. 14.3.

## **16. REFERENCES**

1. Arar, E.J., Pfaff, J.D., Martin, T.D., U.S. Environmental Protection Agency, Methods for Chemical Analysis of Water and Wastes, EPA-600/4-79-020, Revised May 1994 (revision 3.3), Method 218.6
2. Standard Methods, For the Examination of Water and Waste Water, 18th edition supplement Revised 1994, Method 3500-Cr
3. "Proposed OSHA Safety and Health Standards, Laboratories". Occupational Safety and Health Administration, Federal Register, July 24, 1986.
4. "OSHA Safety and Health Standards, General Industry", (29 CFR 1910), Occupational Safety and Health Administration, OSHA 2206, revised January 1976.

## **17. MANIFOLD DIAGRAMS**

**APPARATUS:** An IC injection valve (6-port), a reagent and high pressure eluent pump and a colorimetric detector module with a 2-cm path length flow cell are required.

**Note:** Do not use the same set of columns for method 10-510-13-1-B and 10-510-00-1-F.  
The sulfate contained in the eluent may cause an interference.

## **18. PARAMETERS AND VALIDATION DATA**

### **18.1 SETTINGS, TIMINGS, AND PARAMETERS**

#### **Separation Conditions**

Eluent 55.9 mM (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, 23.1 mM NH<sub>4</sub>OH  
Post column reagent 2 mM diphenylcarbazide, 10% methanol (v/v), 0.5 M sulfuric acid  
Sample loop 3 mL  
Expected pressure 2500 ± 250 psi

#### **Pump Settings**

##### **Eluent Pump:**

Eluent flow rate 1.5 mL/min  
High pressure limit 4000 psi  
Low pressure limit 100 psi

**In Timing Properties make sure that Use Minutes for Channel and Analyte are selected.**

The timing values listed below are approximate and will need to be optimized using graphical events programming. In Analyte Properties use the FIA Detection Method, not IC.

Sample throughput: 9 samples/h, 6.5 min/sample  
Pump Speed: 35  
Cycle Period: 6.5 minutes

#### **Analyte Data:**

Concentration Units: µg Cr VI  
Chemistry Brackish  
Expected Inject to Peak Start 5.8 min  
Expected Peak Base Width 1.4 min  
Brackish Shutter Offset 0.19 min  
Brackish Shutter Width 0.31 min

#### **Calibration Data:**

Level	1	2	3	4	5	6	7	8	9
Concentration µg Cr VI	10.0	5.0	2.0	1.0	0.5	0.2	0.1	0.05	0.0

Calibration Fit Type: 1<sup>st</sup> Order Polynomial  
Weighting Method: 1/X  
Force through zero: No

#### **Sampler Timing:**

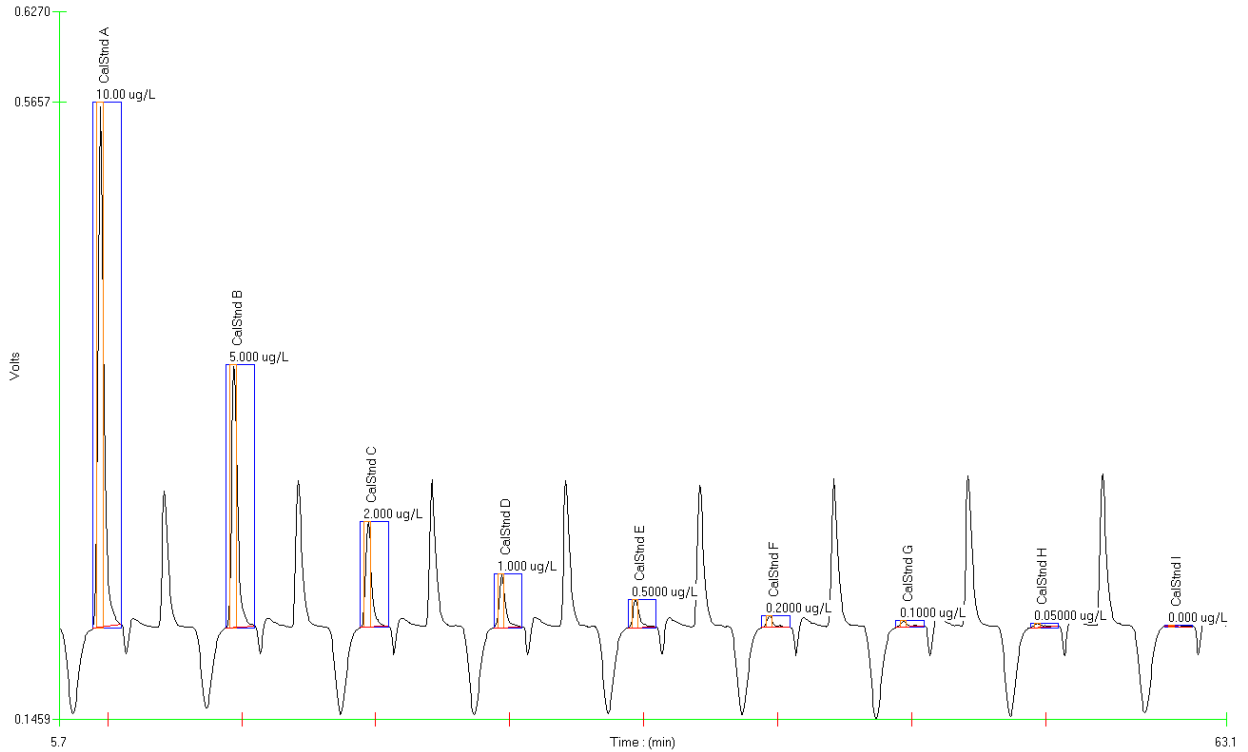
Min. Probe in Wash Period: 0.1 min  
Probe in Sample Period: 1.4 min

**Valve Timing:**

Load Period: 1.4 min  
Inject Period: 5.1 min  
Time to Valve: 0.05 min

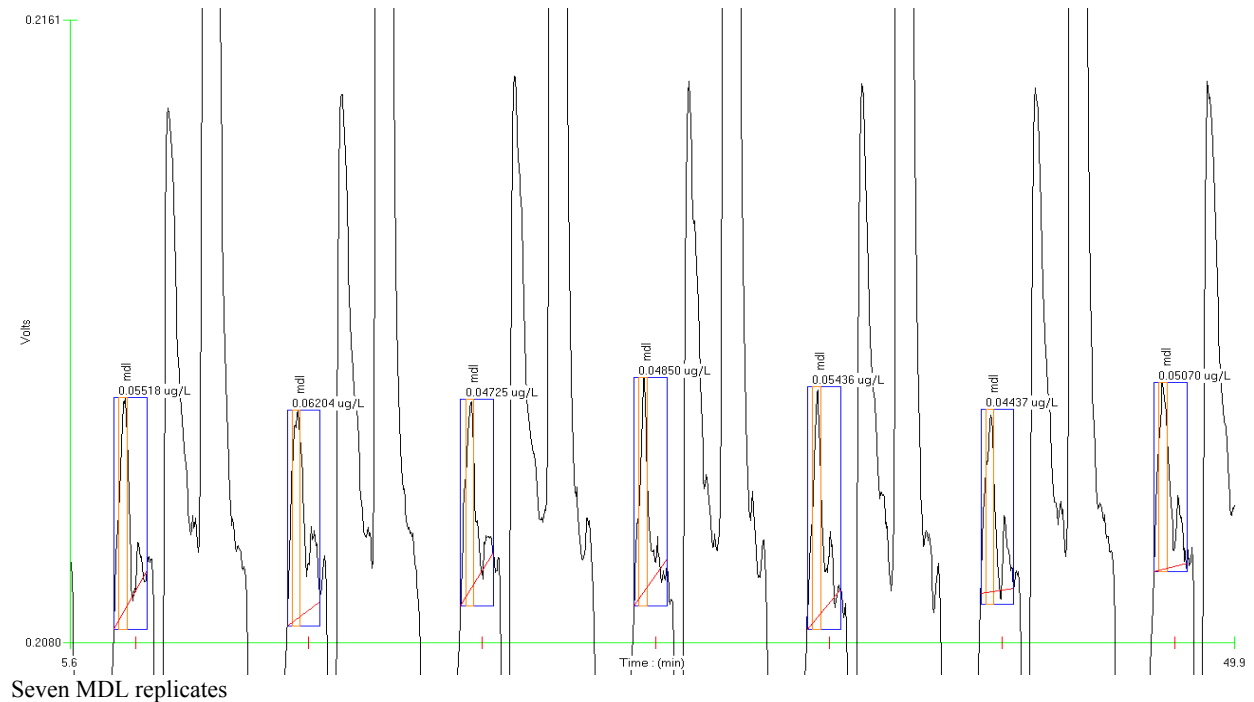
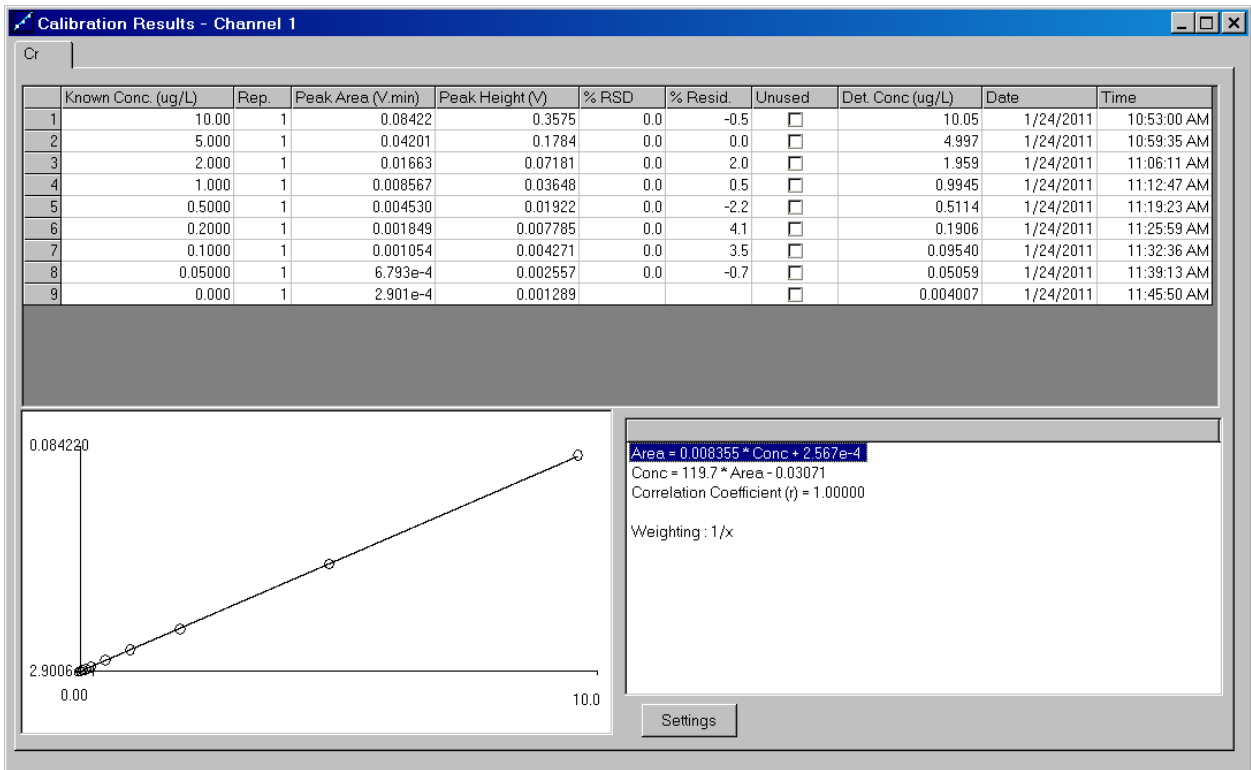
**18.2 METHOD SUPPORT DATA**

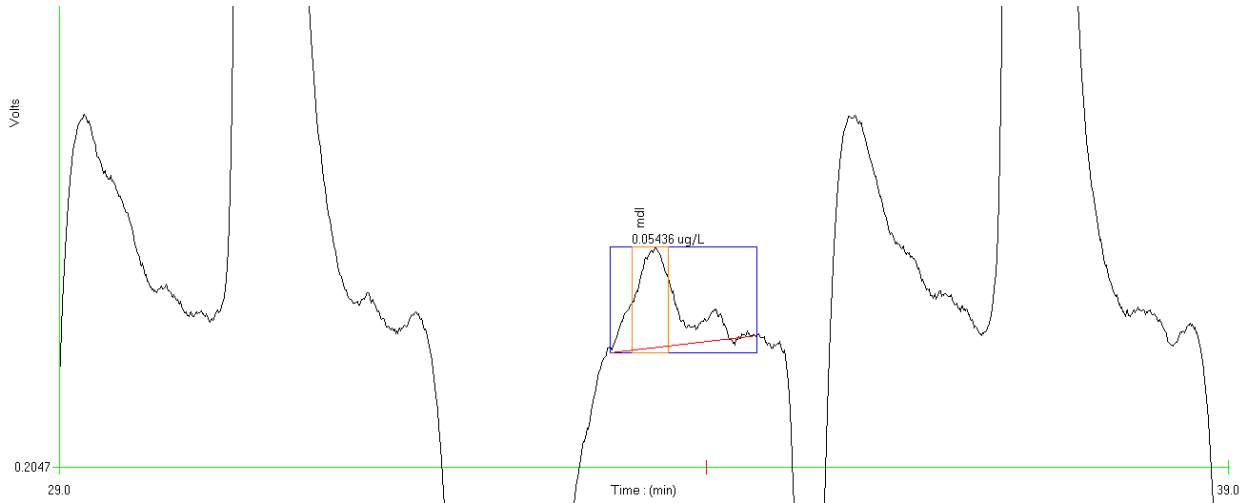
**Calibration Data for Cr VI**



File Name: 1-24 cal.omn  
Acq. Date: 24 January 2011

**Calibration Graph and Statistics**





One of the MDL replicates

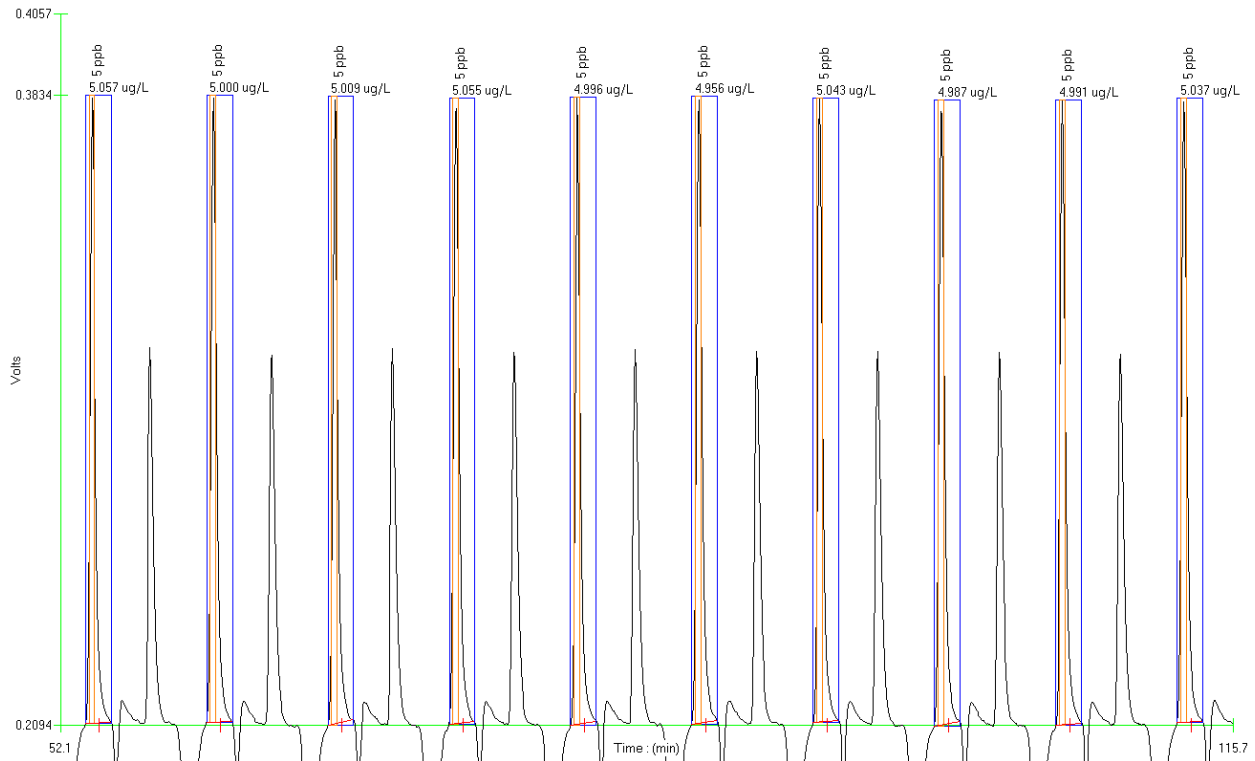
**Method Detection Limit for Chromium using 0.05 µg Cr/L standard**

**MDL = 0.019 µg Cr/L**

Standard Deviation (s) = 0.0059 µg Cr/L, Mean (x) = 0.518 µg Cr/L, Known value = 0.05 µg Cr/L

File Name: 1-24 mdl.omn

Acq. Date: 24 January 2011

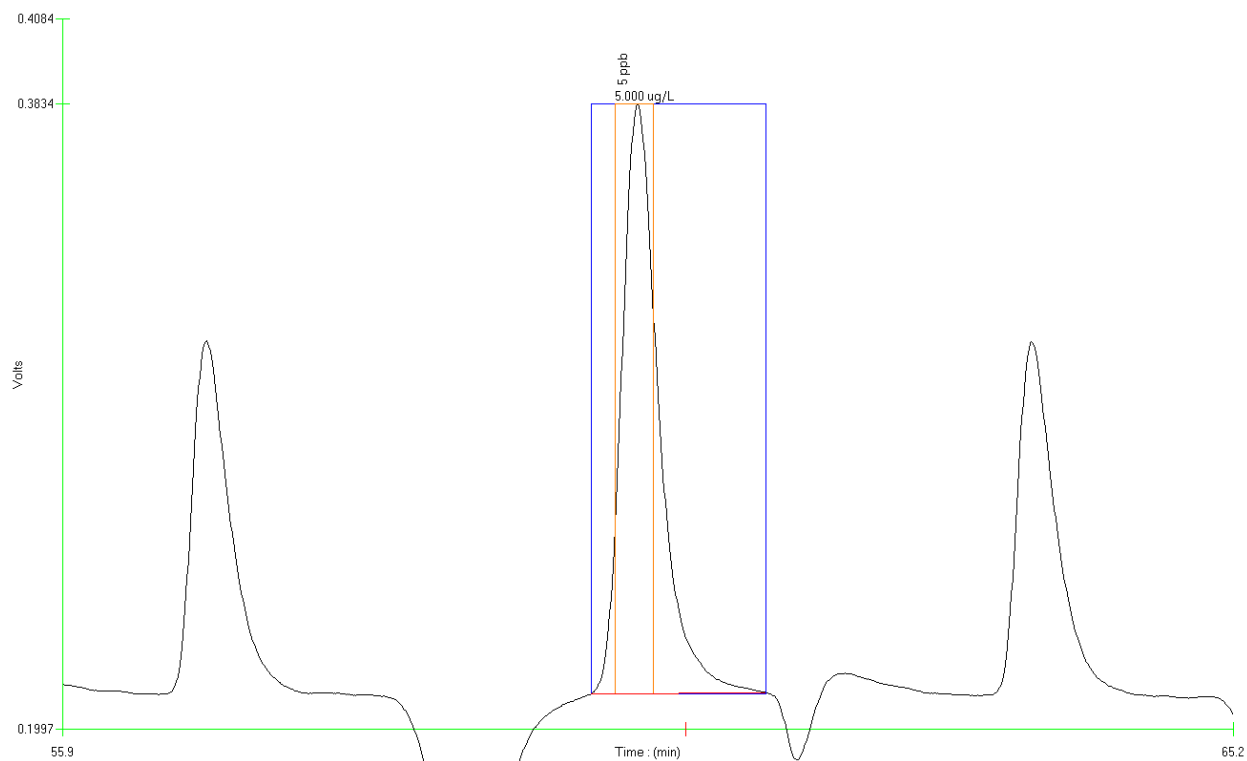


Ten 5.0 µg Cr/L replicates **% RSD = 0.66**

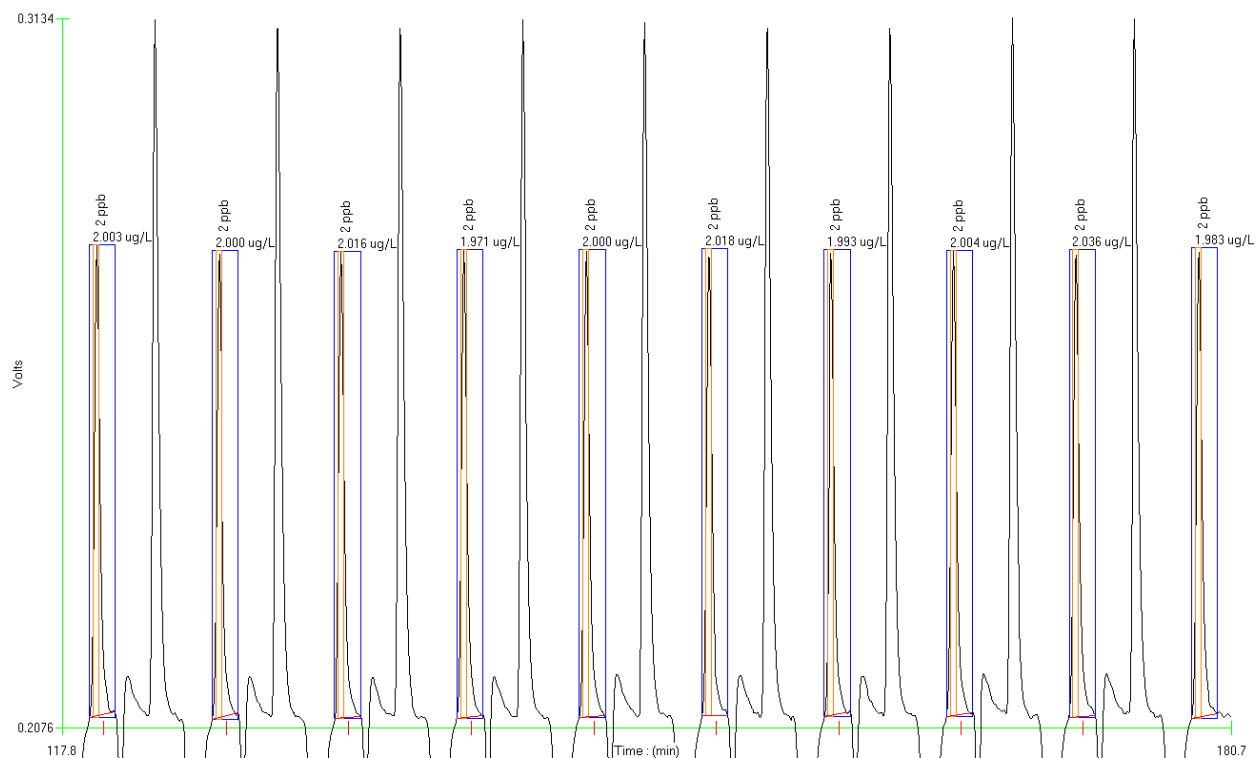
Standard Deviation (s) = 0.033 µg Cr/L, Mean (x) = 5.0 µg Cr/L, Known value = 5.0 µg Cr/L

File Name: 1-24 support.omn

Acq. Date: 24 January 2011

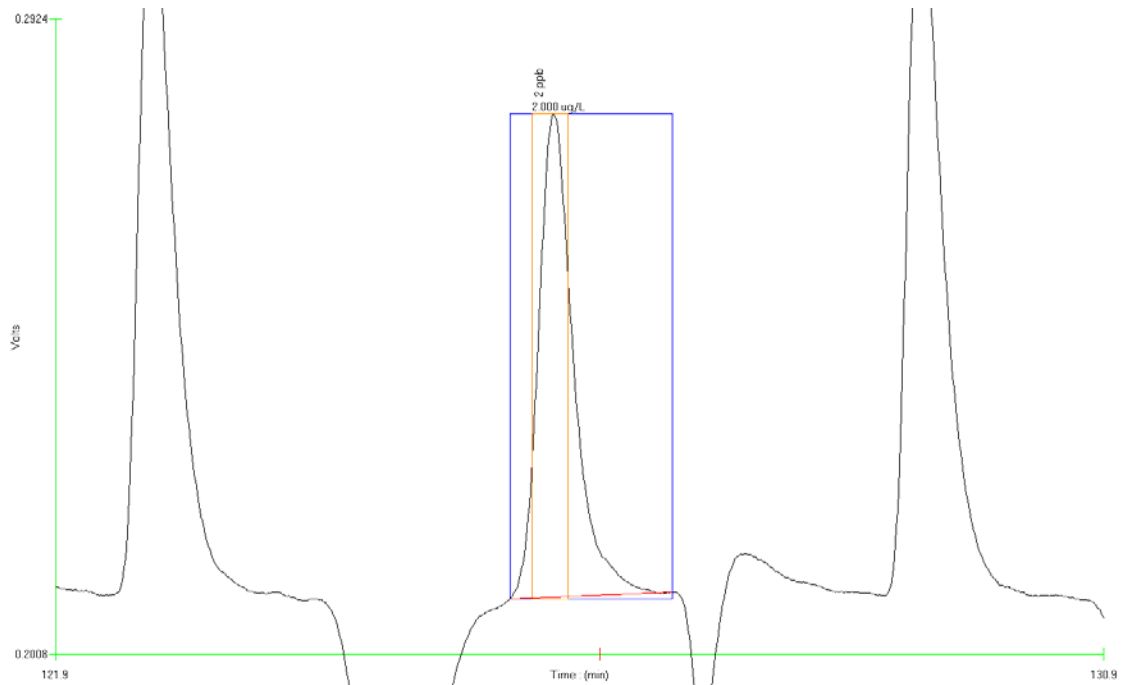


5.0 µg Cr/L replicate  
 Single replicate from Precision data for Nitrate using 5.0 µg Cr/L standard



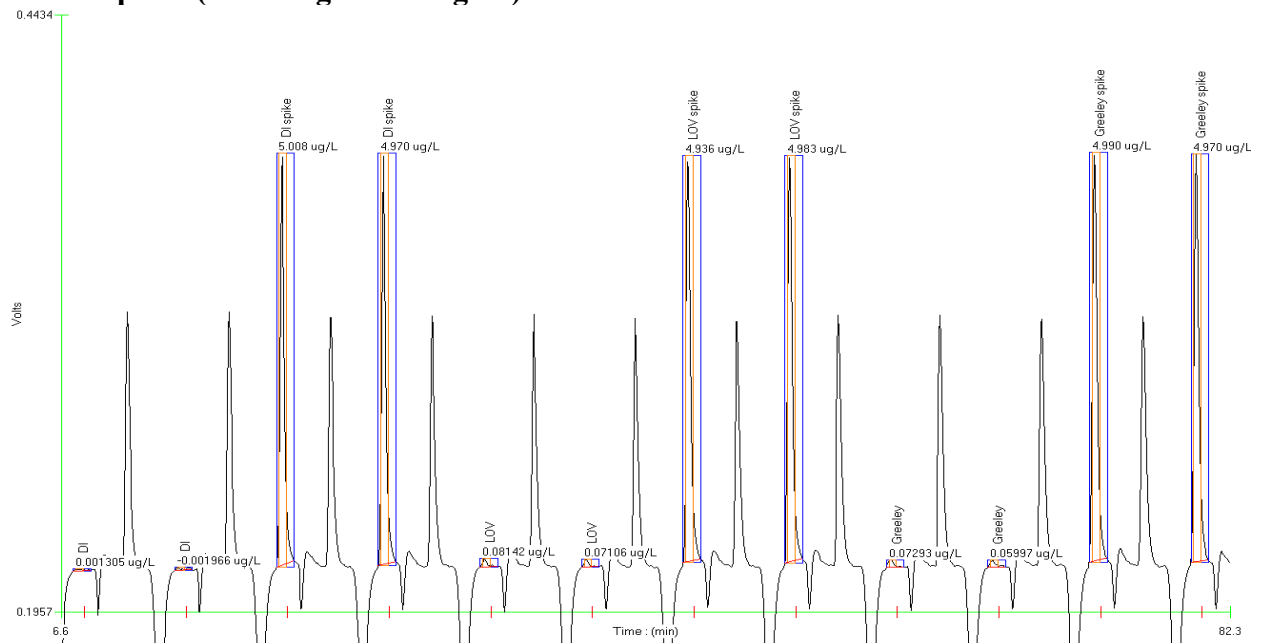
Ten 2.0 µg Cr/L replicates  
 Precision data for Nitrate using 2.0 µg Cr/L standard (ten replicates)  
**% RSD = 0.92**

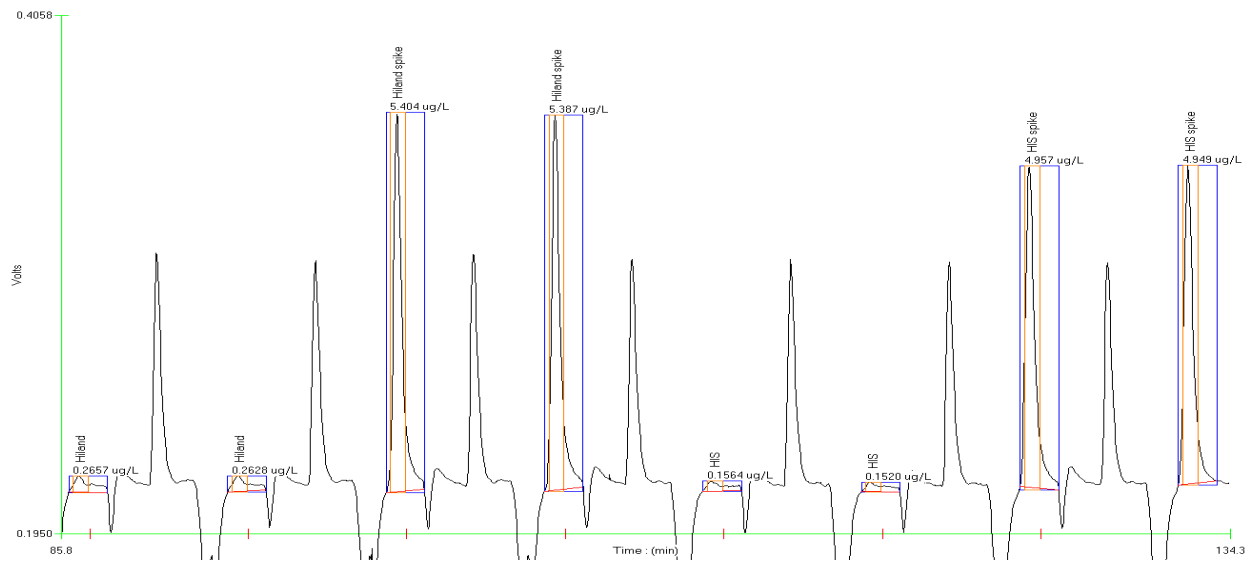
Standard Deviation (s) = 0.018 µg Cr/L, Mean (x) = 2.0 µg Cr/L, Known value = 2.0 µg Cr/L  
 File Name: 1-24 support.omn  
 Acq. Date: 24 January 2011



One Precision 2.0 µg Cr/L replicate

### Water Spikes (Drinking and Reagent)

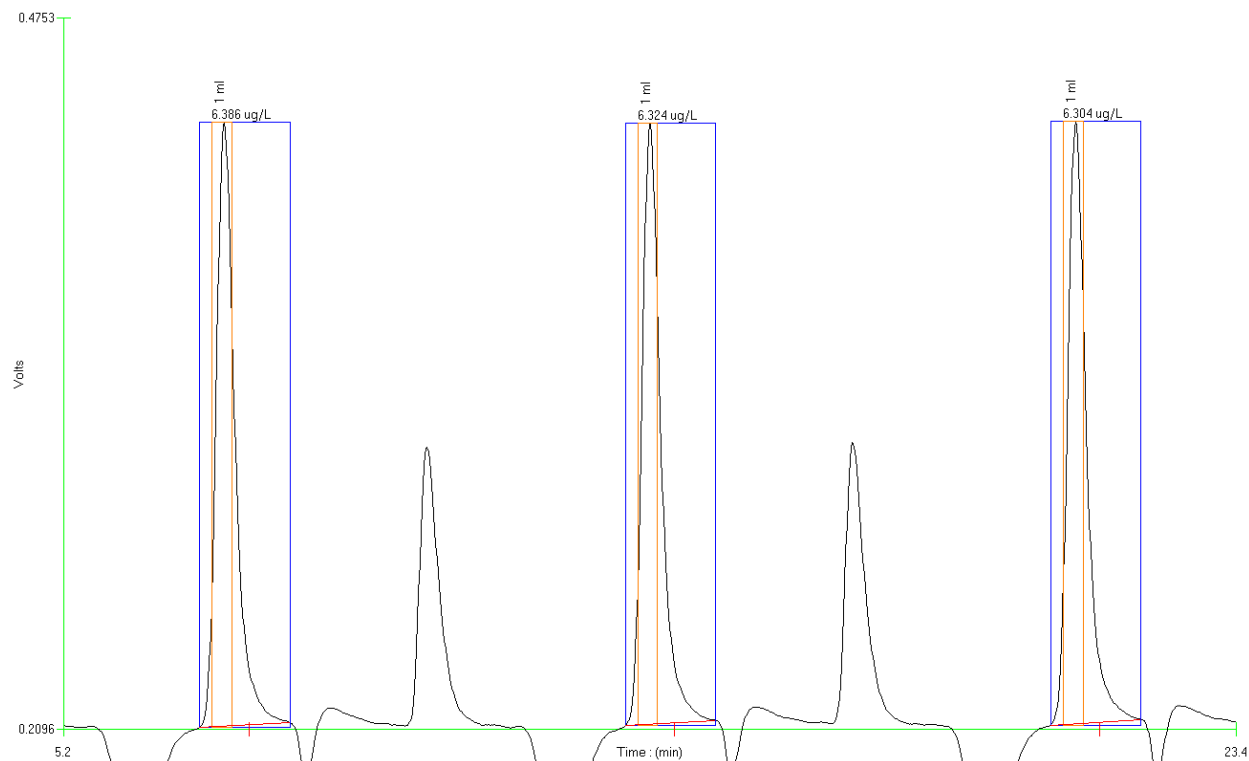




File Name: 1-25 spikes.omn  
 Acq. Date: 25 January 2011

Sample ID	Initial avg ( $\mu\text{g Cr/L}$ )	Spiked avg ( $\mu\text{g Cr/L}$ )	Spike Level ( $\mu\text{g Cr/L}$ )	Spike Recovery
DI Water	-0.00033	4.99	5.0	99.79
Tap 1	0.076	4.96	5.0	97.66
Tap 2	0.066	4.98	5.0	98.27
Tap 3	0.264	5.40	5.0	102.6
HIS*	0.15	4.95	5.0	95.98

\*High Ionic Strength sample: Conductivity is 2.0 mS/cm



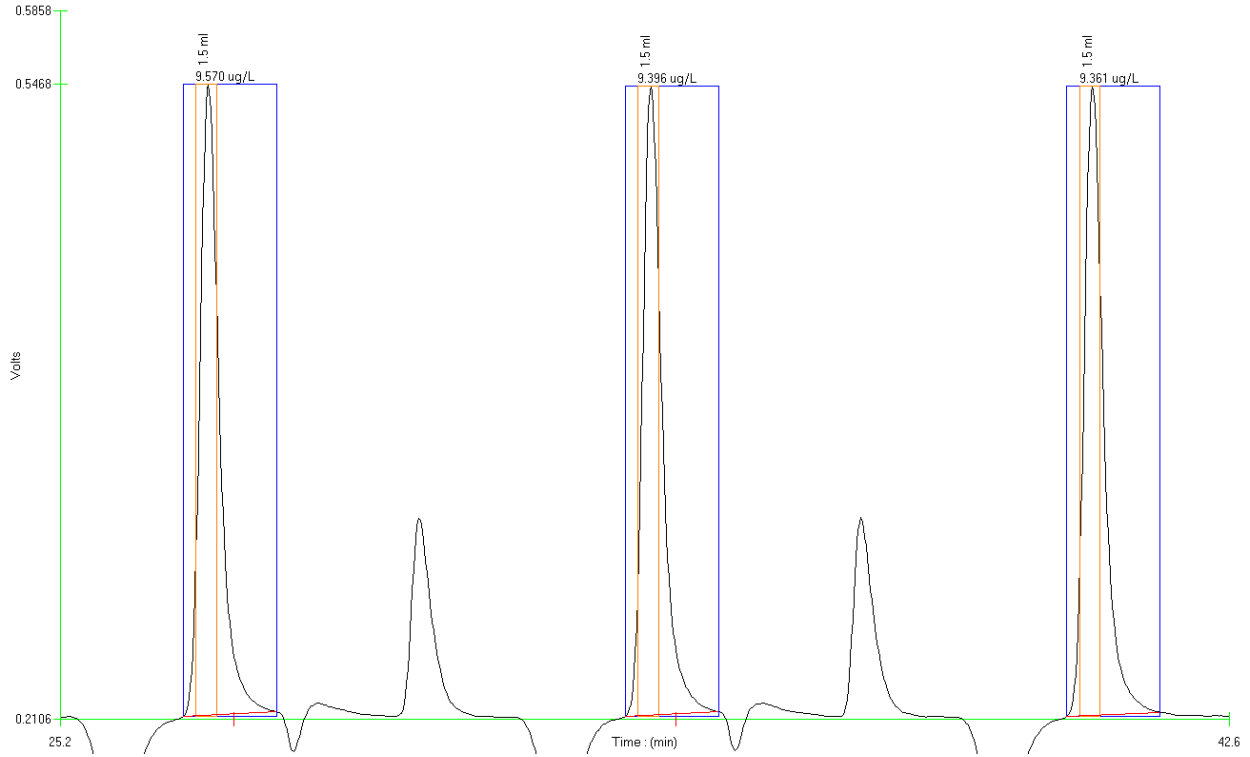
File Name: 1-25 era.omn  
 Acq. Date: 25 January 2011

ERA QC Standard WasteWatR Chromium VI, Catalog no.  
 984, Lot No. PO95505  
 ERA, Arvada, Colorado, US Phone: 303-431-8454  
 Mean Determined Concentration: **6.34 µg Cr/L**



**ENVIRONMENTAL  
 RESOURCE  
 ASSOCIATES**  
 The Industry Standard™

**Known Concentration:** 630 µg Cr/L  
 Interlaboratory Acceptance Range: 518 – 746 µg Cr/L  
**Diluted known standard 100 fold to produce 6.34 µg Cr/L**  
**100.6% Recovery**  
 Three Replicates were analyzed



File Name: 1-25 era.omn  
 Acq. Date: 25 January 2011

ERA QC Standard WasteWatR Chromium VI, Catalog no.  
 984, Lot No. PO95505  
 ERA, Arvada, Colorado, US Phone: 303-431-8454  
 Mean Determined Concentration: **9.44 µg Cr/L**



**ENVIRONMENTAL  
 RESOURCE  
 ASSOCIATES**  
 The Industry Standard™

**Known Concentration:** 630 µg Cr/L  
 Interlaboratory Acceptance Range: 518 – 746 µg Cr/L  
**Diluted known standard 66.6 fold to produce 9.44 µgCr/L**  
**99.92% Recovery**  
 Three Replicates were analyzed

