MINISTRY OF ENVIRONMENT
LABORATORY SERVICES BRANCH

METHOD TITLE: **The Determination of Hexavalent Chromium in Waters by Ion Exchange Chromatography-Inductively Coupled Plasma Mass Spectrometry (IC-ICP-MS)**

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SECTION: **SPECTROSCOPY AND PHYSICAL CHEMISTRY SECTION**

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APPLICABLE REGULATIONS/GUIDELINES: NONE

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AUTHORIZATION DATE: _____JUNE 17, 2013_____

This method is deemed fit for purpose as of the date shown in the header of this cover page by the data provided in section 1.6 (Analytical Performance Summary).

*** The approval of this document is valid for two years at which time it will be subject to review to determine if any updates or modifications are warranted.***

NOTE: Equivalent suppliers to those stated in the method are acceptable. Reference to a particular brand does not constitute an endorsement by the Ontario Ministry of the Environment

The Determination of Hexavalent Chromium in Waters by Ion Exchange Chromatography-Inductively Coupled Plasma Mass Spectrometry (IC-ICP-MS)

1 SUMMARY

Hexavalent chromium Cr(VI) is a known toxic metal in the environment and a known carcinogen to humans, even at relatively low doses (Ref. 1.7.1). Chromium may occur in the environment either from natural or anthropogenic sources, and can exist in various chemical forms, most commonly as trivalent Cr(III) and hexavalent Cr(VI). The distribution of Cr between Cr(III) and Cr(VI) is strongly controlled by Eh-pH of the system. Typically, Cr(III) is dominant in highly oxygenated and low pH environment, whereas Cr(VI) becomes dominant in high pH environment. In aqueous environment, Cr(III) and Cr(VI) can also exist in various ionic species, such as Cr^{3+}, $CrOH^{2+}$, $Cr(OH)^{2+}$, $HCrO_4^-$, and CrO_4^{2-}, depending on the activity of electrons (Eh) and the activity of hydrogen ions (pH). In most treated drinking water, Cr(VI) is expected to be dominate due to the presence of strong oxidants such as chlorine (Cl) and the elimination of dissolved organic carbon after treatment (Ref. 1.7.1).

Because of the human heath risks of Cr(VI), Cr in drinking water is regulated by various jurisdictions. The World Health Organization's (WHO) Guidelines for Drinking Water Quality states "…because the heath effects are determined largely by the oxidation state, different guideline values for Cr(III) and Cr(VI) should be derived. However, current analytical methods and the variable speciation of Cr in water favor a guideline value for total Cr". The WHO and Canadian Federal drinking water guidelines for total Cr is 50 µg/L. The Ontario Drinking Water Quality Standards (Ontario Reg. 169/03 under the Ontario Safe Drinking Water Act) for total Cr is also 50 µg/L. :The United States Environmental Protection Agency (USEPA) and California Office of Environmental Health Hazard Assessment (OEHHA) however, have recently proposed a guideline specific for Cr(VI) with a Maximum Contaminant Level (MCL) of 0.02 µg/L. In Canada, federal/provincial/territorial environmental agencies are planning to reassess current Canadian drinking water guidelines and may consider a separate Cr(VI) drinking water standard.

This method is developed in anticipation of a possible Cr(VI) specific drinking water standard which will require a much lower detection limit than existing methods at the Laboratory Service Branch (LaSB) of the Ontario Ministry of the Environment (MOE).

1.1 Principle of Method

This method utilizes a hyphenated technique, i.e. ion exchange chromatography (IC) coupled to an inductively couple plasma mass spectrometry (ICP-MS) to determine Cr(VI) in treated drinking water, surface water and ground water. Samples are collected and preserved at a pH > 9 condition, and then injected directly into an anion exchange column. Cr(VI) is separated from other possible Cr species and other metals by the anion exchange functioning group inside the column. The column eluent is introduced directly into the sample introduction

interface and the ionization source of the ICP-MS. Chromium chromatographic peak is identified and quantified by the mass spectrometry with external calibration.

1.1.1 Relationship to Other Methods

This method is developed and validated "in-house". The method is complimentary to LaSB HEXCR-E3056 "The Determination of Hexavalent Chromium in Waters, Landfill leachates and Effluents by Colourimetry".

1.2 Parameters Measured

Hexavalent chromium Cr(VI) is measured using this method. The LaSB LIMS product codes are:

Department: 6410 – Analysis and Reporting

Product Code: CHROM3510

Element	Parameter	CAS Number
Cr(VI) as CrO_4^{2-}	Hexavalent Chromium	13907-45-4

1.3 Sample Matrices

Treated drinking water preserved in pH > 9 can be analyzed for Cr(VI) using this method. Surface and ground water may be analyzed for Cr(VI) using this method, provided that it has been established that sample is highly oxygenated, free of dissolved organic carbon, and preserved in pH > 9. Surface and ground water that are anoxic and high in dissolved organic carbon may contain significant amount of Cr(III). When such surface and ground water samples are analyzed using this method, the Cr(VI) result may be biased high.

Matrix Code: WD – Drinking Water
WS – Surface Water
WG – Ground Water

Refer to 1.5.3 for further details for WS and WG matrices.

1.4 Sample Requirements

1.4.1 Sample Preservatives

Sample must be preserved to achieve pH > 9 with ultra pure concentrated NH_4OH (see Appendix A for Certificate of Analysis). The amount of NH_4OH required will depend on the original pH of the water. For a typical

treated drinking water with a pH between 5 and 8, 1% v/v of NH_4OH/sample will be sufficient.

NOTE: NH_4OH is toxic to the upper respiratory tract, skin, and eyes. Ensure that all handling of this material is performed inside a fume hood and observe all the applicable safe laboratory practices. Refer to the MSDS for further information.

1.4.2 Sample Collection

Sample is collected in a 15 mL amber high density polyethylene (HDPE) bottle with a plastic cap.

For tap water, turn on the tap and allow the system to flush for approximately 5 minutes. Fill sample bottle with the tap water slowly to approximately 10 to 12 mL. Add 1 to 2 drops of the ultra pure concentrated NH_4OH preservative from a drop battle. Mix thoroughly and check that pH is > 9 using a pH-indicator strip.

For surface and ground waters, fill sample bottle with the tap water slowly to approximately 10 to 12 mL. Add 1 to 2 drops of the ultra pure concentrated NH_4OH preservative from a drop battle. Mix thoroughly and check that pH is > 9 using a pH-indicator strip.

1.4.3 Sample shipping and Storage

It was demonstrated at the initial method development stage that treated drinking water sample can be stored in a fridge at 8 °C or below for up to 30 days (see Appendix C), without the risk of Cr(VI) being converted into other species, provided that sample pH is adjusted to > 9 (refer to method validation documents).
Samples are stored at < 8 °C for up to 30 days, provided that the sample containers are sealed properly and stored in an acid fume free environment. However, it is recommended that samples be analyzed as soon as possible upon receipt.

1.4.4 Contingencies

If samples are not, preserved and shipped as prescribed in Section 1.4.1, analysis will be carried out and the results will be reported with a LaSB LIMS remark code “UNP” (unreliable: sample not preserved properly).
If samples are collected other than containers specified in section 1.4.2, the analysis will be carried out and the results will be qualified with LIMS remark code “UIC” (Unreliable, Improper Container).

1.5 Shortcomings

1.5.1 Interferences

Chromium has four naturally occurring isotopes, i.e. ^{50}Cr, ^{52}Cr, ^{53}Cr and ^{54}Cr with a relative abundance of 4.35%, 83.79%, 9.50% and 2.37%, respectively. ^{52}Cr and ^{53}Cr are measured in this method. There are some polyatomic species that will potentially interfere with ^{52}Cr and ^{53}Cr measurements. The most common ones include $^{12}C^{40}Ar$, $^{36}Ar^{16}O$, $^{14}N^{38}Ar$, $^{35}Cl^{17}O$, $^{37}Cl^{16}O$, $^{13}C^{40}Ar$, $^{35}Cl^{18}O$ and $^{36}Ar^{16}O^{1}H$.

Various techniques employed in this method can minimize or eliminate these polyatomic interferences. First, the collision / reaction interface of the Bruker 820 ICP-MS with H_2 as a reaction gas in the skimmer cone significantly reduces any Ar-based polyatomic interference (refer to SOP, SPEC-ICP-MS.001, "Standard Operating Procedure for Varian (Bruker) 820MS Routine Operation & optimization". Secondly, the ion exchange chromatography described in this method can separate other ions in the sample matrix (e.g. C and Cl) from Cr due to differences in retention time in the chromatography separation [see Appendix C for a typical chromatogram of Cr(VI)].

Accordingly, the remaining significant polyatomic interference is $^{14}N^{38}Ar$. Since N comes mainly from the mobile phases (NH_4NO_3 and NH_4OH, see Section 4) used in the chromatographic separation, this results in an elevated baseline in the chromatogram with the Cr(VI) peak superimposed over the baseline (see Appendix C).

1.5.2 Biases

When the method is followed properly, there should be no bias in the results of Cr(VI) measurement.

1.5.3 Limitations

This method analyzes Cr(VI) in an anion form CrO_4^{2-}, and is very sensitive to the Eh-pH of the sample. When the samples are collected and preserved as prescribed in 1.4, the method integrity is not compromised. However, if the sample is anoxic and highly acidic (e.g. ground water or mine waste), the sample collection / preservation prescribed in 1.4 may not be adequate to maintain all Cr(VI) in CrO_4^{2-} form, and the method performance may be negatively impacted.

1.6 Analytical Performance Summary (July 2012-Jan. 2013)

The method performance is measured using internal QC's, unspiked treated tap water, spiked treated tap water, and a CRM. The method has participated in proficiency testing study (PT) provided by external jurisdiction. All performance data are summarized below.

Table 1.6.1 Cr(VI) Data for deionized water blanks (July 2012-Jan. 2013)

Sample	N	Average (ppb)	std
DI H_2O Blank-E3510	52	0.0035	0.0032

Note: The data represent an average of within and between-run for Millipore deionized water (DI H_2O), integrated over the expected Cr(VI) retention time, and quantified as equivalent concentration.

Table 1.6.2 Cr(VI) Data for QC standard (July 2012-Jan. 2013)

Sample	N	Average (ppb)	std	RSD
QC-E3510	15	0.1989	0.025	12.4%

Note: QC standard is prepared in DI H_2O using a second source Cr(VI) standard independent of the calibration standards (see Section 5 for details).

Table 1.6.3 Cr(VI) Data for Tap Water from Room E212 (July 2012-Jan. 2013)

Sample	N	Average (ppb)	std	RSD
Tap Water unspiked-E3510	45	0.1424	0.023	16.3%

Note: This is tap water collected from Room E212 in the LaSB lab and the pH is adjusted to > 9 using ultra pure concentrated NH_4OH. It is used as a matrix equivalent QC for continuous monitoring of method performance for real matrix samples.

Table 1.6.4 Cr(VI) Data for Spiked Tap Water from Room E212 (July 2012-Jan. 2013)

Sample	N	Average (ppb)	std	RSD	Spike Recovery
Tap Water Spiked-E3510	51	0.3358	0.021	6.2%	96.7%

Note: This is the same tap water as above, but spiked with 0.2 µg/L Cr(VI) using a second source Cr(VI) standard independent of the calibration standards (see Section 5 for details).

Table 1.6.5 Cr(VI) Data for ERA UCMR3-E3510 (July 2012-Jan. 2013)

Sample	N	Average (ppb)	std	RSD	Accuracy
ERA UCMR3-E3510	16	0.3929	0.028	7.2%	98.5%

Note: This is a certified reference material (CRM) supplied by Environmental Resources Associates (ERA) and was designed specifically for the US EPA 3rd unregulated contaminant monitoring rule (UCMR3). The certified value is 0.399 µg/L with an uncertainty of 3.5% and the accepted range of 0.319 – 0.479 µg/L.

Table 1.6.6 Estimated MDL

Analyte	MDL (ppb)
Cr^{6+}	0.049

Note: The MDL is estimated using the standard deviation of the spiked tap water data listed in Table 1.6.4 and a student *t* value of 2.369, following the LSBSOP.026.

1.7 Bibliography

Note: Current versions of Branch and Section SOPs and Forms are posted and available on LaSB desktop.

1.7.1 Dana R. Lindsay et al., 2012, Oxidation of Cr(III) to Cr(VI) during chlorination of drinking water. Journal of Environmental Monitoring, 14:1789-1797.

1.7.2 Varian 820 ICP-MS Customer Training Manual

1.7.3 Section SOP SPEC-ICP-MS.001 "Standard Procedure for Varian 820MS Routine Operations & Optimization"

1.7.4 ProStar 210/410 HPLC Operation Manuals

1.7.5 Galaxie Manuals (electronic) on the Control PC "Start\All Programs\Galaxie\Galaxie Manuals"

1.7.6 Ministry of Environment, 2009. Practices for the Collection and Handling of Drinking Water Samples, Version 2.0. Laboratory Services Branch, Etobicoke, Ontario

1.7.7 Ministry of the Environment, Laboratory Services Branch. Procedures Manual, LSBSOP.026, The Determination of W, T, and MDL

1.7.8 Ministry of the Environment, Laboratory Services Branch. Procedures Manual, LSBSOP.031, Drinking Water Exceedance Reporting Protocol

1.7.9 Ministry of the Environment, Laboratory Services Branch. Procedures Manual, LSBSOP.039 "Laboratory Services Branch Procedures for Processing and Reporting Drinking-Water Samples."

1.7.10 Ministry of the Environment, Laboratory Services Branch. SPECSOP01 "Procedures for Training and Proficiency Testing within the Spectroscopy Section & Physical Chemistry Section"

1.7.11 Ministry of the Environment, Laboratory Services Branch. LSBSOP.007 "Sample Reception and Routing Procedures"

1.7.12 SPC Section SOPs: CSMMSOP1a to CSMMSOP6, CSMMSTDSYS.001

1.7.13 United States Environmental Protection Agency, Method 218.7 "Determination of hexavalent chromium in drinking water by ion chromatography with post-column derivatization and UV-Visible spectroscopic detection"

1.7.14 LaSB SPC Section SOP SPEC-ICP-MS-003 "Standard operating procedure for data reporting using ONLINE LIMS"

1.7.15 List of forms and logbooks used (Current version of forms are posted and available on LaSB desktop.)

NON CONFORMANCE FORM - FRM_1925

Varian 820 ICP-MS Instrument Log Book Serial No: IP0903M009

Varian 820 ICP-MS Instrument Service/performance Reports binder (IP0903M009)

Varian 820 ICP-MS Instrument Log Book Serial No: EL06013871

Varian 820 ICP-MS Instrument Service/performance binder (EL06013871)

Millipore Log Book (Serial No: F5AN28094)

Millipore Log Book (Serial No: F5AN99734A)

Millipore Log Book (Serial No: F5AN28094B)

Balance Log Book-Adam Balance Model AEA-250G Serial No: AE164121657

Balance Log Book-Adam Balance Model AEA-250G Serial No: AE164113258

Balance Log Book-Satorius Balance Model CPA2202S Serial No: 2655310

Balance Log Book-Ohaus Balance Model AP250D Serial No: 09675

Balance Log Book-Mettler Balance Model AE163 Serial No: F55873

Log Book – Record of labware pre-cleaning

Certificates of Analysis binder for standards used in E3510

FRM_LSB_054 “Customer Software Validation Summary Approval Form Laboratory Service Branch”

Primary & Intermediate N.I.S.T. Spectrometric Standard Solution binder 3

Expired/Exhausted Spectroscopy Standards Binder 4

Expired/Exhausted Spectroscopy Standards Binder 5

Expired/Exhausted Spectroscopy Standards Binder 6

Discarded Sample Binder

Stock Standard Logbook

Sample Login Binder HEXCR-E3510

NOTE: Verification of acid dispensers and pipettes (Eppendorfs and VWR) are recorded in ONLINE LIMS.

1.8 History of Changes/Revisions

1.8.1 June, 2013 – Version 1.0

New method documented with initial development and validation summary data.

1.9 Safety

Ultraviolet Radiation

The plasma **must never** be viewed with naked eyes. The Varian 820 ICP-MS provides safety interlocks that shut off the plasma when the torch compartment is open. Do not attempt to defeat these interlocks. During operation, the plasma must be viewed only through the protective tinted window located in the torch compartment.

WARNING: Failure to wear safety glasses of a type prescribed for use with ultraviolet sources or to use the built-in viewing glass while observing the lit plasma may cause permanent blindness or permanent impairment of eyesight.

High Voltage

The Radio Frequency (RF) generator provides up to 1.5 kW RF power to the plasma. The resulting plasma may cause extensive burns. Under no circumstances should you attempt any physical adjustment of the plasma torch when the plasma is on, other than through operation software controls. The instrument has an extensive set of interlocks to ensure the safety of operator. The RF generator also has numerous safety features which turn off the high-voltage power should the plasma be extinguished or a high reflected power occurs.

WARNING: The equipment contains high-voltages, which may be lethal. Observe all cautions in this method and those posted on the equipment. No instrument operator must attempt to access or adjust high voltages.

Radio Frequency Radiation

Exposure of personnel to Radio Frequency (RF) Radiation should be minimized. Personnel should not be permitted in the vicinity of open energized RF generating circuits, RF transmission systems (cables, connectors, etc.), or energized antennae. It is generally accepted that exposure

to "high levels" of RF radiation can result in severe bodily harm including blindness.

NOTE: Cardiac pacemakers may be affected.

Toxic Chemicals

It is essential that the toxic effects of compounds being analyzed are understood, and that adequate ventilation is provided. If the ventilation system is not working, do NOT operate the plasma torch.

WARNING: Some of the products of combustion of the plasma torch can be highly toxic. Operation of the equipment without a torch exhaust vent may constitute a serious health hazard.

NOTE: Ozone is hazardous and always produced when the ICP is in operation.

High pressure and flammable gases

Argon gas is used in this method and a suffocation hazard exists.

Hydrogen gas is used in this method and a flammable hazard exists.

High pressure gas cylinders can be dangerous if mishandled. Move gas cylinders with an approved handcart after ensuring that the valve caps are secured. Locate gas cylinders away from heat or ignition sources. Cylinders have a high pressure-relief device which releases the contents of the cylinder if the temperature exceeds 520 °C (1250 °F). Arrange gas hoses where they will not be damaged or stepped on or where things will not drop on them. Always wear approved safety footwear when moving empty or full cylinders.

Personal protective equipments: labcoat, safety glasses and gloves

Concentrated acids are moderately toxic and extremely irritating to skin and mucus membranes. Use these reagents in a fume hood and if skin contact occurs flush with large quantities of water. Some type of eye protection must always be worn when working with these reagents. Basic safety precautions must be taken such as the use of rubber or plastic gloves when cleaning lab wares. Good housekeeping practices should be observed at all times.

2 SAMPLE PREPARATION

2.1 Labware

2.1.1 pH strip 0 to 14 range.

2.1.2 4 mL LDPE drop bottle

2.2 Reagents

2.2.1 Ultra pure concentrated NH_4OH (Anachemia Science or equivalent. See Appendix A for minimum specification requirements)

2.3 Procedure

Upon receipt of samples in the lab, check sample pH using a pH testing strip by transferring a small volume of sample to prevent cross contamination.

If the pH is > 9, sample is ready for IC-ICP-MS analysis, and no further sample preparation is required.

If pH is < 9, a LIMS remark code “SIP” (sample improperly preserved) will be issued to the customer to qualify the results. The sample, however, can still be analysed, provided that the sample container is intact. Adjust the pH to > 9 by adding 1 – 2 drops of ultra pure concentrated NH_4OH and allow the sample to sit in the walk-in fridge (located in E237 and labeled as “Alkaline preserved samples”) at < 8 °C for 24 hours before analysis.

3 ANALYTICAL PROCESSING

3.1 This method does not require any further sample processing.

3.2 Reagents

3.2.1 Reagent grade HNO_3 (see Appendix B for minimum specification requirements).

3.2.2 Pure Water that has been further deionized (DI H_2O) by Millipore (Milli-Q water).
Note: The resistivity of deionized water is maintained at 18.0 megaohms per centimetre or greater. Cartridges on the water systems will be changed as soon as the resistivity drops below 18.0.

NOTE: Throughout this document, DI H_2O is always referred to the water as defined in 3.2.2

3.3 Lab wares

3.3.1 Thomson 0.45 μm PTFE filter vials or equivalent

3.3.2 Pipettes, adjustable volumes

3.3.3 Disposable gloves

3.3.4 Pre-cleaned 15 mL Corning tube with cap

NOTE: Cleaning procedure for labwares
- remove cap
- place tubes and caps into 10% HNO_3 (made from reagent grade) acid bath
- allow tubes and caps to soak inside acid bath for at least 24 hours
- transfer tubes and caps into a DI H_2O bath
- allow tubes and caps to soak in DI H_2O bath for at least 24 hours
- remove tubes and caps, rinse with DI H_2O at least three times
- remove water as much as possible, place them inside a Class 10 vertical lamina flow metal free bench and let them dry
- log the date and initials on the labware pre-cleaning log book

NOTE: It is absolutely critical to pre-clean and dry labwares in a clean flow bench, in order to minimize contamination.

3.4 Procedure

3.4.1 Label a Thomson shell vial according the sequence number

3.4.2 Use an adjustable volume pipette and pipette 0.5 mL sample solution into the vial

3.4.3 Insert the filter top into the vial and place them on the vial pressor (the pressor holds 5 vials each time) and press the filter top into place.

3.4.4 Load vials on to the Varian ProStar 410 autosampler in sequence

3.5 Run Sequence

A typical run sequence must include two DI H2O blanks, a set of calibration standards, a set of QC standard, 20 samples, a sample duplicate, a second set of QC standards, a second set of calibration standards, another 20 samples, a sample duplicate, QC standards, two DI H_2O blanks, calibration standards, and so on (see section 6.1).

4 DETECTION SYSTEM

4.1 Safety

Refer to Section 1.9, SPEC-ICP-MS.001 and Varian ProStar 210/410 Operation Manuals for safety in operation of all equipment and in handling of all chemicals listed in this section.

ONLY PROFICIENT ANALYSTS CAN OPERATE THE INSTRUMENTS USED IN THIS METHOD.

4.2 Labwares

NOTE: The determination of trace level Cr(VI) requires a consideration of potential sources of contamination. A clean laboratory work area designated for trace element sample handling must be used. All reusable labware (glass, quartz, polyethylene, Teflon etc.) must be cleaned prior to use. (see Reference 1.7.12).

NOTE: Nalgene volumetric flasks are used for the preparation of calibration and QC standards. These volumetric flasks are available only in Class B. The volume of each volumetric flask is checked upon initial receipt of the volumetric, and once a year following this time. Each volumetric flask is independently labeled, and the verification data is stored under S:\ICPMS\ICP-MS Nalgene Volumetric Flasks.

4.2.1 Thomson 0.5 mL syringerless filter vials

4.2.2 50 mL Nalgene volumetric flasks

4.2.3 Adjustable volume pipettes (Eppendorf or equivalent)

4.2.4 Disposable gloves

4.2.5 Disposable plastic transfer pipettes, 3 mL (a precise volume is not necessary)

4.2.6 2 L Teflon bottles (these are re-used from Optima grade acid containers after being cleaned following the procedure in Ref. 1.7.12)

4.2.7 Acid dispensers, variable volumes Fortuna Optifix or equivalent

4.2.8 125 mL high density polyethylene (HDPE) bottles (Nalgene or equivalent)

4.3 Equipments

4.3.1 Bruker (formerly Varian) 820MS ICP-MS with a CRI skimmer cone and a standard sampler cone

4.3.2 Kodiak re-circulating water chiller

4.3.3 Varian ProStar 210 inert dual pump HPLC and autosampler or equivalent

4.3.4 Hamilton PRP-X100 anion exchange column with guard column or equivalent

4.3.5 Instrument control PC with ICP-MS control software and a chromatographic data acquisition system

4.3.6 A Microzone class 10 metal-free vertical laminate flow bench or equivalent

4.4 Reagents

4.4.1 DI H_2O

4.4.2 Ultra pure 20% NH_4OH (VWR or equivalent, see Appendix A for the minimum specifications). It must be stored in a fume hood or vented storage cabinet.

4.4.3 Ultra pure concentrated HNO_3, Optima grade or equivalent (see Appendix B for the specifications). It must be stored in a fume hood or vented storage cabinet.

4.4.4 Primary Cr(VI) calibration standard, 1 µg/mL in H_2O, High Purity or equivalent. This standard must be capped and re-sealed with para-film, and stored in the designated fridge in E212 at < 8°C.

Note: This standard must be from the different source or lot # than the QC Primary Cr(VI) standard.

4.4.5 Primary Cr(VI) QC standard, 1 µg/mL in H_2O, Inorganic Venture or equivalent. This standard must be capped and re-sealed with para-film, and stored in the designated fridge in E212 at < 8°C.

Secondary Cr(VI) standards diluted from the primary standards listed in 4.4.4 and 4.4.5, 100 µg/L in DI H_2O.

Preparation of the secondary Cr(VI) standards:

- fill half of a 100 mL flask with DI H_2O
- pipette 10 mL primary Cr(VI) standard into the flask
- fill up to the line with DI H_2O
- cap and mix the solution thoroughly
- transfer it completely to a 125 mL HPDE bottle and label it accordingly

The secondary standards must be stored in the designated fridge in E212 at <8°C, and have the same expiry date as the primary standards used for the preparation.

4.4.6 1 µg/L Cr(VI) in DI H2O solution for checking instrument signal to noise ratio (see Section 4.5.2)

Preparation of 1 µg/L Cr(VI) solution (the precise concentration is not necessary)

- pipette 0.5 mL of the secondary Cr(VI) standard from 4.4.6 into a 50 ml Corning tube
- fill up to 50 mL mark with DI H_2O
- cap and mix the solution thoroughly

4.4.7 IC mobile phase A, 100 mmol/L NH_4NO_3, pH ≥ 9

NOTE: The precise concentration of the mobile phase is not critical. An approximate concentration of 100 mmol/L is sufficient.

Preparation of mobile phase A:

- fill a 2 L Teflon bottle with ~1 L DI H_2O
- dispense 12.5 mL Optima grade HNO_3 (16 N) into the bottle
- add 39.2 mL ultra pure NH_4OH (20% v/v) using an adjustable pipette
- fill up to 2 L line with DI H_2O
- cap and mix the solution thoroughly
- check prepared solution to ensure pH > 9 with a pH strip.
  Note: If the pH is not >9 then re-prepare the mobile phase

4.4.8 HPLC mobile phase B, DI H_2O, pH ≥ 9

Preparation of mobile phase B:

- fill a 2 L Teflon bottle with ~1 L DI H_2O
- pipette 5 x 3 mL (a precise volume is not necessary) plastic disposable transfer pipettes ultra pure NH_4OH
- fill up to 2 L line with DI H_2O
- cap and mix the solution thoroughly check pH > 9 with a pH strip
  Note: If the pH is not >9 then re-prepare the mobile phase

NOTE: Handling of NH_4OH and HNO_3 must be carried out inside a fume hood.

4.5 Instrument Setup Procedure

NOTE: Refer to relevant instrument manuals and SOP's listed in Section 1.7 for further details.

4.5.1 Switch the three-way valve mounted on the side of the ProStar HPLC to by-pass position so the solution can be introduced from peristaltic pump.

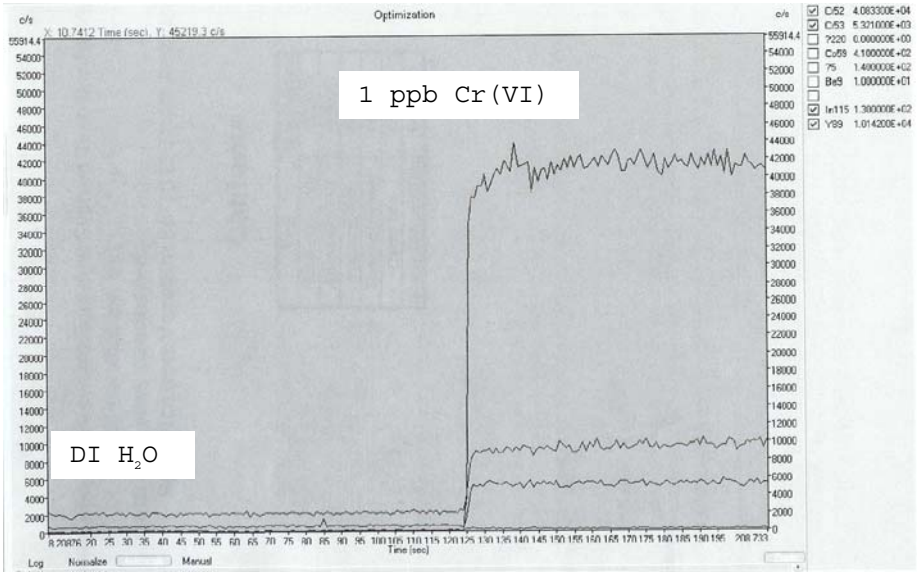
4.5.2 Start the plasma on 820MS ICP-MS and optimize the instrument according to SOP SPEC-ICP-MS.001. Print the "Daily Performance Check" results and keep a copy in the "Varian 820 ICP-MS Performance Test Reports Binder (SN: IP0903M009).

NOTE: The SOP outlines routine optimization. For this method, besides the routine optimization criteria, it is important to check the signal to noise ratio at mass 52.

When the instrument is optimized, with 1 µg/L Cr(VI) solution (see 4.4.7) and DI H_2O introduced via peristaltic pump, the signal/noise ratio (1 µg/L / DI H_2O) at mass 52 must be between 5 and 10. If not, re-optimize the instrument as outlined in the SOP SPEC-ICP-MS.001.

Print the tuning window which shows 1 µg/L Cr(VI) solution and DI H_2O signals, and attach it to the daily performance report.

Typical signal / noise ratio



4.5.3 Create worksheet in Quantum ICP-MS software

- Create a new worksheet from a template "Cr Speciation-E3510.msws". The template contains all information for ICP-MS operation
- Copy the optimized ICP-MS parameters to the newly created worksheet.

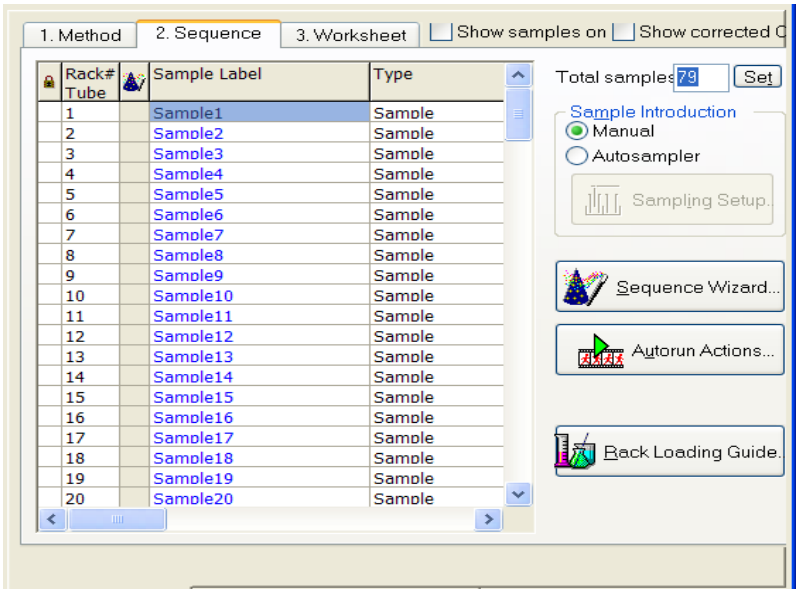
A typical set of ICP-MS parameters is shown below:

Parameter	Value
Flow Parameters (L/min)	
Plasma Flow	18.0
Auxiliary Flow	2.10
Sheath Gas	0.20
Nebulizer Flow	0.94
Torch Alignment (mm)	
Sampling Depth	5.5
Other	
RF Power (kW)	1.40
Pump Rate (rpm)	20
Stabilization delay (s)	0
Ion Optics (volts)	
First Extraction Lens	-1
Second Extraction Lens	-130
Third Extraction Lens	-236
Corner Lens	-230
Mirror Lens Left	46
Mirror Lens Right	26
Mirror Lens Bottom	26
Entrance Lens	-2
Fringe Bias	-1.5
Entrance Plate	-26
Pole bias	0.0
CRI (mL/min)	
Skimmer Gas Source	H2
Sampler Gas Source	OFF
Skimmer Flow	30
Sampler Flow	0

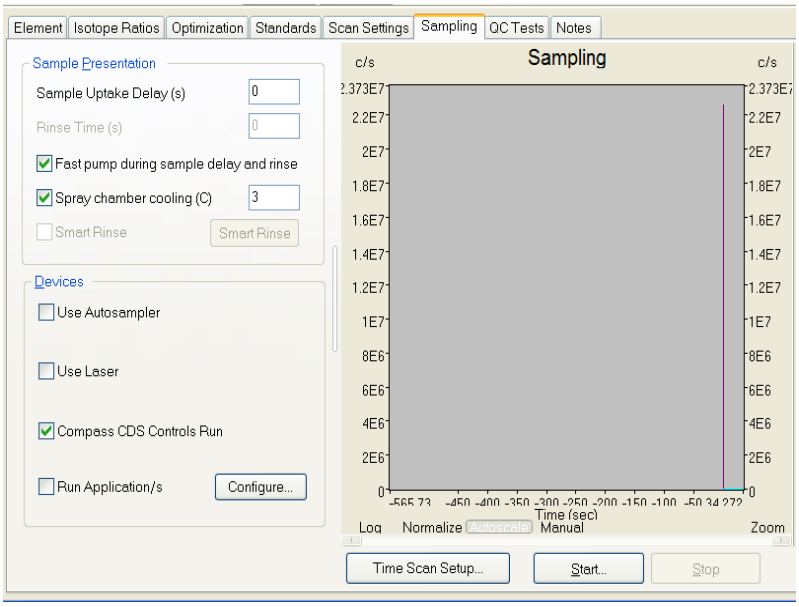
NOTE: After copying all the parameters from the daily optimization worksheet "System Setup Normal Sensitivity.msws", make sure that these parameters are set as following:

"Pump Rate (rpm)": 20
"Stablization delay(s)": 0
"Skimmer Gas Source": H2
"Skimmer Flow": 30

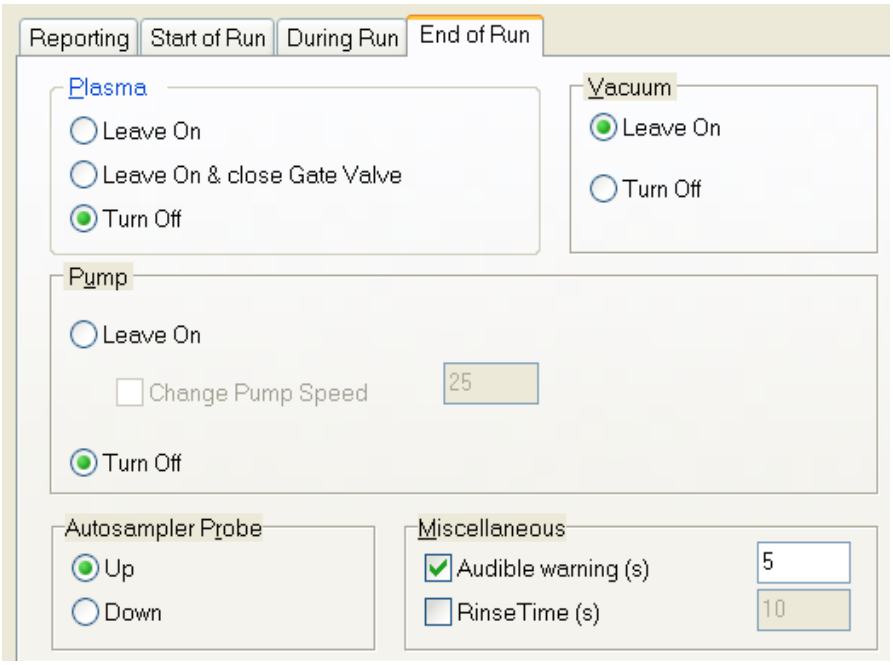
- Set the "total samples" in accordance with the total number of analysis in the chromatographic run sequence in the Galaxie (See 4.5.5).



- Ensure that "Compass CDS Controls Run" is selected under "Sampling"



- Select the "End of Run" in "Autorun Actions" is set correctly.

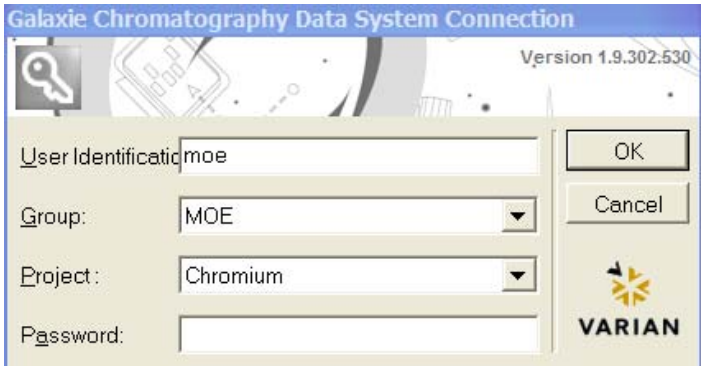


- Save the worksheet as "Cr6-WGXXXXXX-dd-mm-yy.msws".

4.5.4 Switch the three-way valve to the HPLC position, so that the eluent from the ProStar HPLC is introduced into the ICP-MS.

4.5.5 Open "Galaxie" and ensure that the communication between ICP-MS software "Quantum" and chromatographic software "Galaxie" is established correctly (Refer to SOP SPEC-ICP-MS.001 "Varian 820MS Routine Operation & Optimization" for further details).

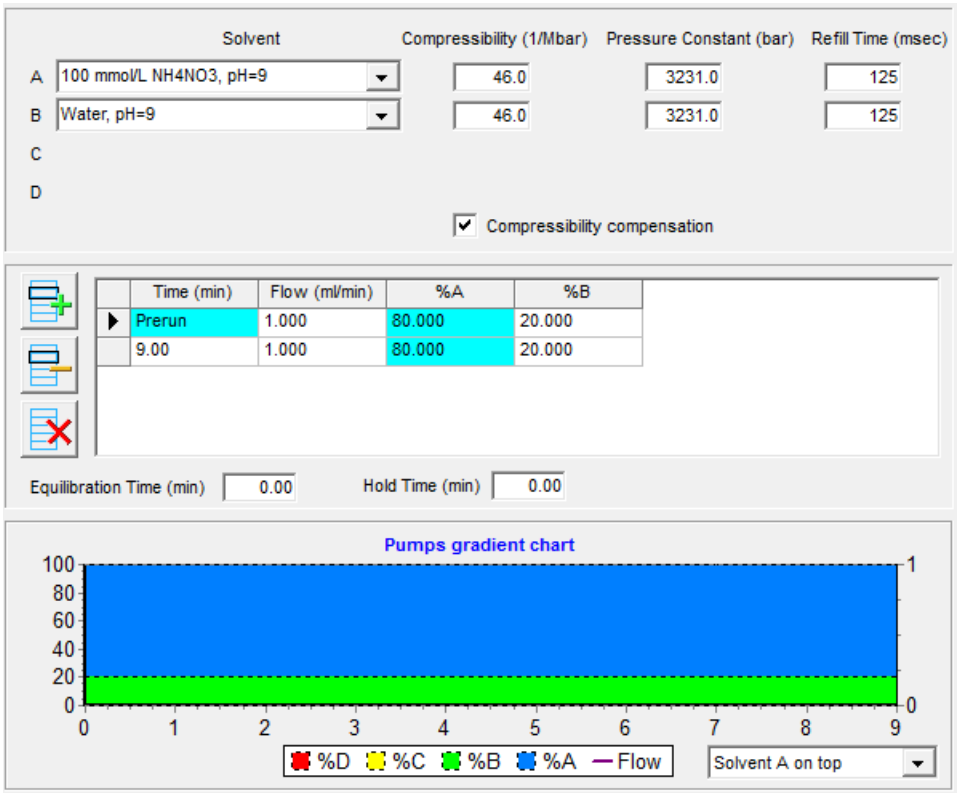
4.5.6 For this method, the "User Identification" is "MOE", the "Group" is "MOE", and the "Project" is "Chromium", no password in the log in window is required, as shown below, however entry to lab is restricted by combination locked doors.



4.5.7 Follow SOP SPEC-ICP-MS.001 "Varian 820MS Routine Operation & Optimization" to create a run sequence in Galaxie and to establish the communication between ICP-MS software "Quantum" and chromatography software "Galaxie".

4.5.8 The "Galaxie method" used is named "Cr Speciation E3510.METH" and can be found under "C:\Galaxie\Data\Chromium". The chromatography conditions and a typical sequence is shown below.

The chromatogtaphy conditions are specified in the method "Cr Speciation E3510.METH". These conditions must not be changed, unless the method is re-validated.



A typical run sequence

Run #	Enabl	Method	Methc	RunName (pre	RunID	Description	Rur	No. c	Vial	Rac	Inj. Vc	Sample type	Calibration	Level
1	☑	Cr Speciation.METH	···	$AcqMethc ···	1	DI H2O Blank ···	13	1	1	1	200	Unknown		
2	☑	Cr Speciation.METH	···	$AcqMethc ···	2	Calib-Std-1 ···	13	1	2	1	200	Standard	Clear old points	1
3	☑	Cr Speciation.METH	···	$AcqMethc ···	3	Calib-Std-2 ···	13	1	3	1	200	Standard	Add	2
4	☑	Cr Speciation.METH	···	$AcqMethc ···	4	Calib-Std-3 ···	13	1	4	1	200	Standard	Add	3
5	☑	Cr Speciation.METH	···	$AcqMethc ···	5	Calib-Std-4 ···	13	1	5	1	200	Standard	Add	4
6	☑	Cr Speciation.METH	···	$AcqMethc ···	6	QC-E3510 ···	13	1	6	1	200	Unknown		
7	☑	Cr Speciation.METH	···	$AcqMethc ···	7	TapWaterUnspiked-E3510 ···	13	1	7	1	200	Unknown		
8	☑	Cr Speciation.METH	···	$AcqMethc ···	8	TapWaterSpiked-E3510 ···	13	1	8	1	200	Unknown		
9	☑	Cr Speciation.METH	···	$AcqMethc ···	9	ERA-CRM-E3510 ···	13	1	9	1	200	Unknown		
10	☑	Cr Speciation.METH	···	$AcqMethc ···	10	C000001 ···	13	1	10	1	200	Unknown		
11	☑	Cr Speciation.METH	···	$AcqMethc ···	11	C000002 ···	13	1	11	1	200	Unknown		
12	☑	Cr Speciation.METH	···	$AcqMethc ···	12	C000003 ···	13	1	12	1	200	Unknown		
13	☑	Cr Speciation.METH	···	$AcqMethc ···	13	C000004 ···	13	1	13	1	200	Unknown		
14	☑	Cr Speciation.METH	···	$AcqMethc ···	14	C000005 ···	13	1	14	1	200	Unknown		
15	☑	Cr Speciation.METH	···	$AcqMethc ···	15	C000006 ···	13	1	15	1	200	Unknown		
16	☑	Cr Speciation.METH	···	$AcqMethc ···	16	C000007 ···	13	1	16	1	200	Unknown		
17	☑	Cr Speciation.METH	···	$AcqMethc ···	17	C000008 ···	13	1	17	1	200	Unknown		
18	☑	Cr Speciation.METH	···	$AcqMethc ···	18	C000009 ···	13	1	18	1	200	Unknown		
19	☑	Cr Speciation.METH	···	$AcqMethc ···	19	C0000010 ···	13	1	19	1	200	Unknown		
20	☑	Cr Speciation.METH	···	$AcqMethc ···	20	C0000011 ···	13	1	20	1	200	Unknown		
21	☑	Cr Speciation.METH	···	$AcqMethc ···	21	C0000012 ···	13	1	21	1	200	Unknown		
22	☑	Cr Speciation.METH	···	$AcqMethc ···	22	C0000013 ···	13	1	22	1	200	Unknown		
23	☑	Cr Speciation.METH	···	$AcqMethc ···	23	C0000014 ···	13	1	23	1	200	Unknown		
24	☑	Cr Speciation.METH	···	$AcqMethc ···	24	C0000015 ···	13	1	24	1	200	Unknown		
25	☑	Cr Speciation.METH	···	$AcqMethc ···	25	C0000016 ···	13	1	25	1	200	Unknown		
26	☑	Cr Speciation.METH	···	$AcqMethc ···	26	C0000017 ···	13	1	26	1	200	Unknown		
27	☑	Cr Speciation.METH	···	$AcqMethc ···	27	C0000018 ···	13	1	27	1	200	Unknown		
28	☑	Cr Speciation.METH	···	$AcqMethc ···	28	C0000019 ···	13	1	28	1	200	Unknown		
29	☑	Cr Speciation.METH	···	$AcqMethc ···	29	C0000020 ···	13	1	29	1	200	Unknown		
30	☑	Cr Speciation.METH	···	$AcqMethc ···	30	DI H2O Blank ···	13	1	30	1	200	Unknown		
31	☑	Cr Speciation.METH	···	$AcqMethc ···	31	QC-E3510 ···	13	1	15	1	200	Unknown		
32	☑	Cr Speciation.METH	···	$AcqMethc ···	32	TapWaterUnspiked-E3510 ···	13	1	15	1	200	Unknown		
33	☑	Cr Speciation.METH	···	$AcqMethc ···	33	TapWaterUnspiked-E3510 ···	13	1	15	1	200	Unknown		
34	☑	Cr Speciation.METH	···	$AcqMethc ···	34	ERA-CRM-E3510 ···	13	1	15	1	200	Unknown		
35	☑	Cr Speciation.METH	···	$AcqMethc ···	35	Calib-Std-1 ···	13	1	31	1	200	Standard	Add	1
36	☑	Cr Speciation.METH	···	$AcqMethc ···	36	Calib-Std-2 ···	13	1	32	1	200	Standard	Add	2
37	☑	Cr Speciation.METH	···	$AcqMethc ···	37	Calib-Std-3 ···	13	1	33	1	200	Standard	Add	3
38	☑	Cr Speciation.METH	···	$AcqMethc ···	38	Calib-Std-4 ···	13	1	34	1	200	Standard	Add	4

NOTE: A sequence must include a set of the calibration standards, QC standards (DI H_2O blanks, QC-E3510, TapWaterUnspiked-E3510, TapWaterSpiked-E3510), CRM from ERA (ERA-CRM-E3510) for every 20 samples and one sample duplicate. Always bracket samples with standards (i.e. start with standards, sample 1 to 20, and then standards, and so on).

NOTE: Ensure that the number of the lines in both "Quantum" and "Galaxie" sequence agree with each other.

NOTE: The autosampler has a total of 84 positions. The analytical time for each vial is 9 minutes. A full autosampler load takes ~ 15 hours. However, one can continue replacing the completed sample vials during the run to have a longer run sequence when needed.

4.5.9 Once the analysis is complete, the raw data file, chromatographic data, and quantified results are stored and exported in the following locations:

Raw data file in C:\Galaxie\Data\Chromium\2013\Cr Speciation26_07_2012 1_59_13 PM1-1.DATA

Sequence file after run is complete: C:\Galaxie\Data\Chromium\2013\Cr Speciation-26-07-2012_27_07_2012 9_14_07 AM.SEQU*

* The file name is the same as the original sequence file with a time stamp when the last sample in the sequence was analyzed

Exported chromatographic data:

C:\Galaxie\Data\Chromium\Export\Cr52.XLS and Cr53.XLS

Quantified results: C:\Galaxie\Data\Chromium\Output\Cr Speciation.csv*

* This is the file that will be imported into ONLIMS for further processing

Calibration files: C:\Galaxie\Data\Cr52.CALB and Cr53.CALB

NOTE: Since "Cr Speciation.csv", Cr52.CALB and Cr53.CALB is overwritten each time a sequence is run or reprocessed, it must be archived once a sequence is complete by moving these files to an archive directly, e.g.

C:\Galaxie\Data\Chromium\Archived\2012\Calibrations\ WG-XXXXXX-dd-mm-yyyy-Cr52.CALB and WG-XXXXXX-dd-mm-yyyy-Cr53.CALB.

C:\Galaxie\Data\Chromium\Archived\2012\Quantified Results\WG-XXXXXX-dd-mm-yyyy-Cr Speciation.csv

5 CALIBRATION

5.1 Labware

5.1.1 Adjustable volume pipettes (Eppendorf or equivalent)

5.1.2 50 mL Nalgene flask

5.1.3 Thomson 0.5 mL syringerless filter vials

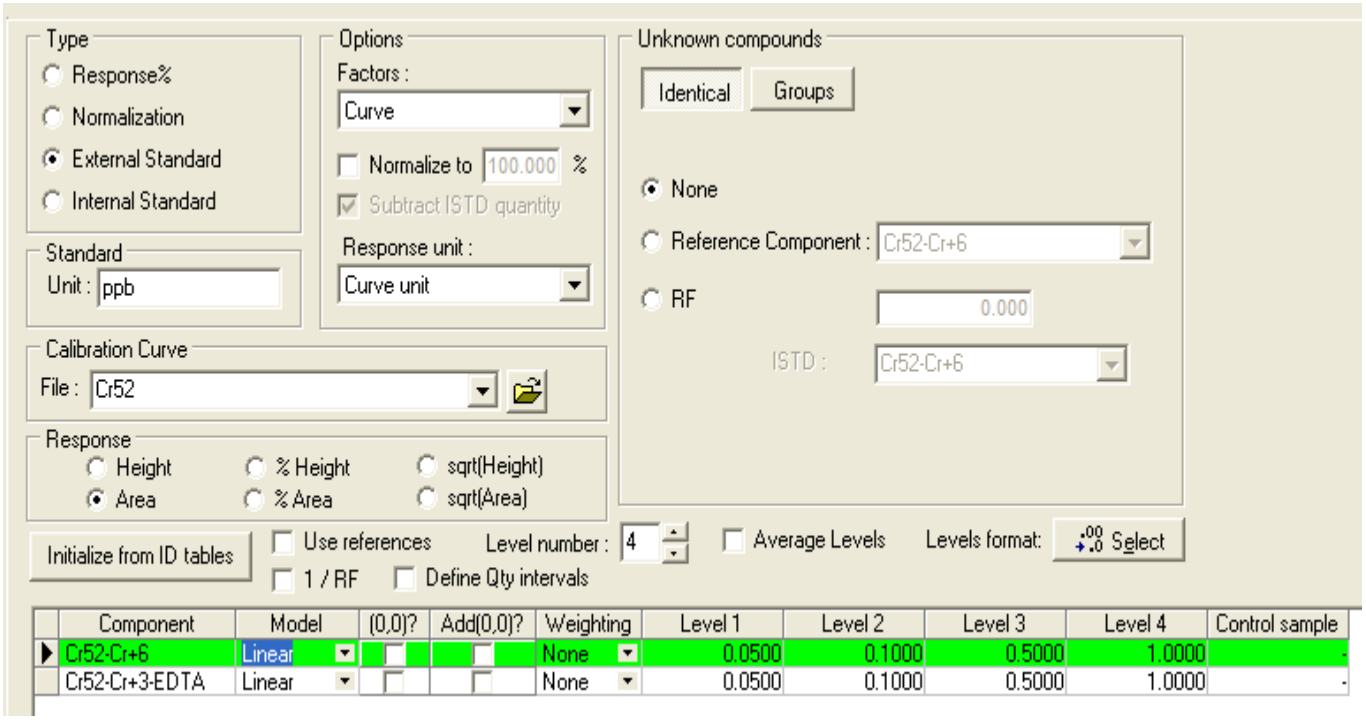
5.2 Reagents

5.2.1 DI H_2O

5.2.2 Secondary Cr(VI) standard 100 µg/L prepared in 4.4.6

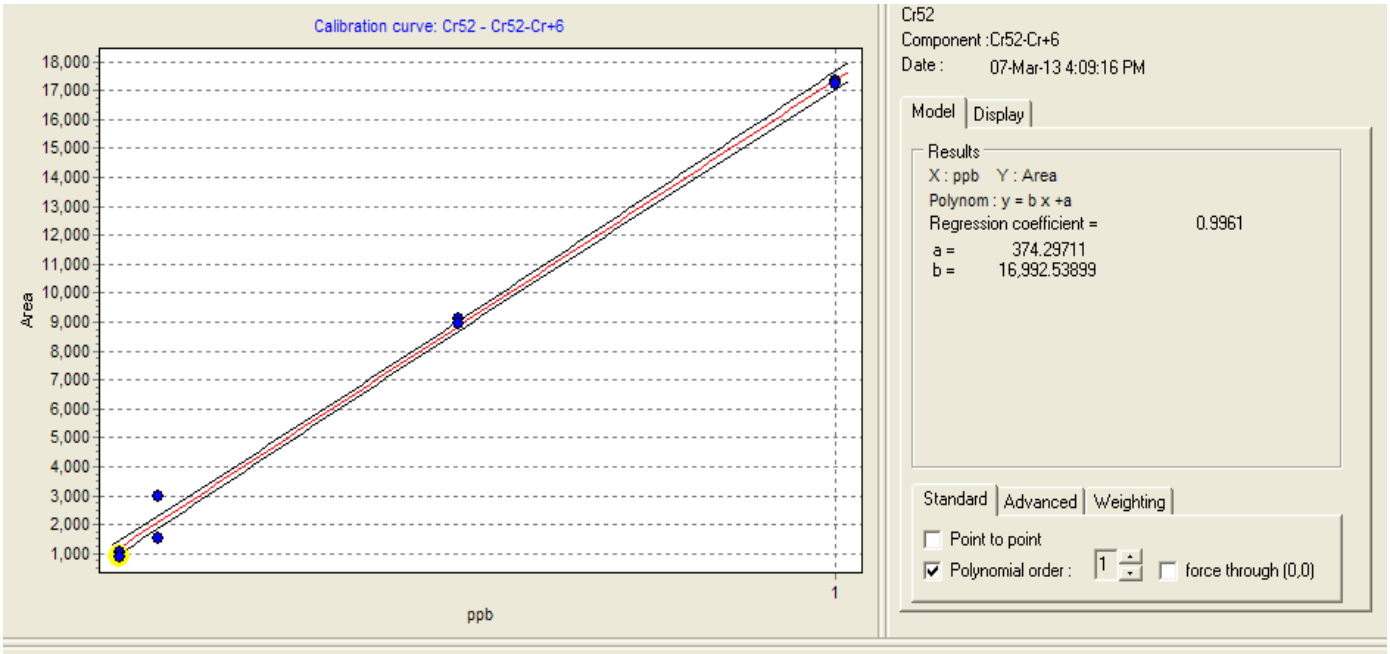
5.3 Procedures

There are four calibration standards in this method at 0.05, 0.1, 0.5, and 1 µg/L respectively (see 5.4 for preparation). This is specified in the calibration part of the "Galaxie method" "Cr Speciation.METH", as shown below



Other parts of calibration, such as model, "through zero" and "weighing", is also specified here.

A typical calibration curve is shown below. The regression coefficient must be > 0.995.



These calibration and QC standards must be made **daily** from the secondary standard listed in Section 4.4.

5.4 Preparation of Daily Calibration Standards.

CalStd-1 (0.05 µg/L)

- pipette 0.025 mL of the secondary Cr(VI) calibration standard (100 µg/L) into a 50 mL Nalgene flask
- fill up to 50 mL with DI H_2O
- cap and mix the solution thoroughly

CalStd-2 (0.1 µg/L)

- pipette 0.05 mL of the secondary Cr(VI) calibration standard (100 µg/L) into a 50 mL Nalgene flask
- fill up to 50 mL with DI H_2O
- cap and mix the solution thoroughly

CalStd-3 (0.5 µg/L)

- pipette 0.25 mL of the secondary Cr(VI) calibration standard (100 µg/L) into a 50 mL Nalgene flask
- fill up to 50 mL with DI H_2O
- cap and mix the solution thoroughly

CalStd-4 (1 μg/L)

- pipette 0.5 mL of the secondary Cr(VI) calibration standard (100 μg/L) into a 50 mL Nalgene flask
- fill up to 50 mL with DI H_2O
- cap and mix the solution thoroughly

5.2 Preparation of Daily Quality Control Standards

5.2.1 Lab QC-E3510 (0.2 μg/L)

- half fill a 50 mL Nalgene flask with DI H_2O
- pipette 0.1 mL of the secondary Cr(VI) QC standard (100 μg/L) into the flask
- fill up to 50 mL with DI H_2O
- cap and mix the solution thoroughly

5.2.2 TapWaterUnspiked-E3510

This is taken daily directly from a bottle labeled "Tap Water unspiked-E3510". Use a pre-cleaned Corning 15 mL tube and take directly from the spigot with a volume sufficient for an analytical session.

NOTE: The original water was taken from the tap in E212 after running for 30 minutes. The pH of the original water was 6 and was adjusted to > 9 with ultra-pure 20% NH_4OH.

NOTE: Never pipette directly from the inside of the bottle, and caution must be exercised to prevent contaminating the sample inside the bottle.

5.2.3 TapWaterSpiked-E3510 (spiked at 0.2 μg/L)

- use an adjustable Eppedorf pipette and pipette 9.98 mL of the above "TapWaterUnspiked-E3510" into a pre-cleaned 15 mL Corning tube
- pipette 0.02 mL of the secondary Cr(VI) QC standard (100 μg/L) into the tube
- cap and mix thoroughly

5.3 Daily use of the CRM from ERA

This CRM is taken directly from a concentrate that has been diluted as per the instructions given below; no further preparation is required. Care must be exercised to avoid any cross contamination to the primary solution. Pour a small aliquot (sufficient for one analytical session) into a pre-cleaned Corning tube for daily use.

NEVER PIPETTE DIRECTLY FROM THE DILUTED STOCK SOLUTION.

NOTE: The Primary Cr(VI) CRM from Environmental Resources Associates (ERA), ERA CAT# 149, is packaged in a 2 mL flame sealed amber ampoule containing approximately 1.5 mL of concentrate standard. The diluted standard contains 0.4 μg/L Cr(VI) (refer to the Certificate of Analysis).

Dilution of the primary CRM

- add 100 – 200 mL of DI H_2O to a clean 1000 mL volumetric flask.
- carefully snap the top off the UCMR-3 Hexavalent Chromium ampule.
- using a clean, dry, class A pipette, volumetrically pipette 0.5 mL of the concentrate into the 1000 mL volumetric flask.
- dilute the flask to the final volume of 1000 mL with DI H_2O.
- cap the flask and mix well.
- transfer the solution into a 2 L Teflon bottle (pre-cleaned from a re-used Optima acid container)
- store bottle in the designated fridge in E212 at <8°C and use up to expiry date stated on the C of A.

5.4 Reprocess the Data with a "Bracketing" Calibration

This method does not employ the internal standardization technique commonly used in ICP-MS analysis. Instead, it relies on bracketing samples between two consecutive calibration curves to correct for any instrumental drift over the sample analytical period. Such "Bracketing", however, can only be achieved after the data have already been acquired, i.e. in a re-processing. The reprocessing procedure is outlined here. Users are referred to the Galaxie Manuals for further details.

NOTE: When a sequence is complete, an exported .csv file is created automatically in

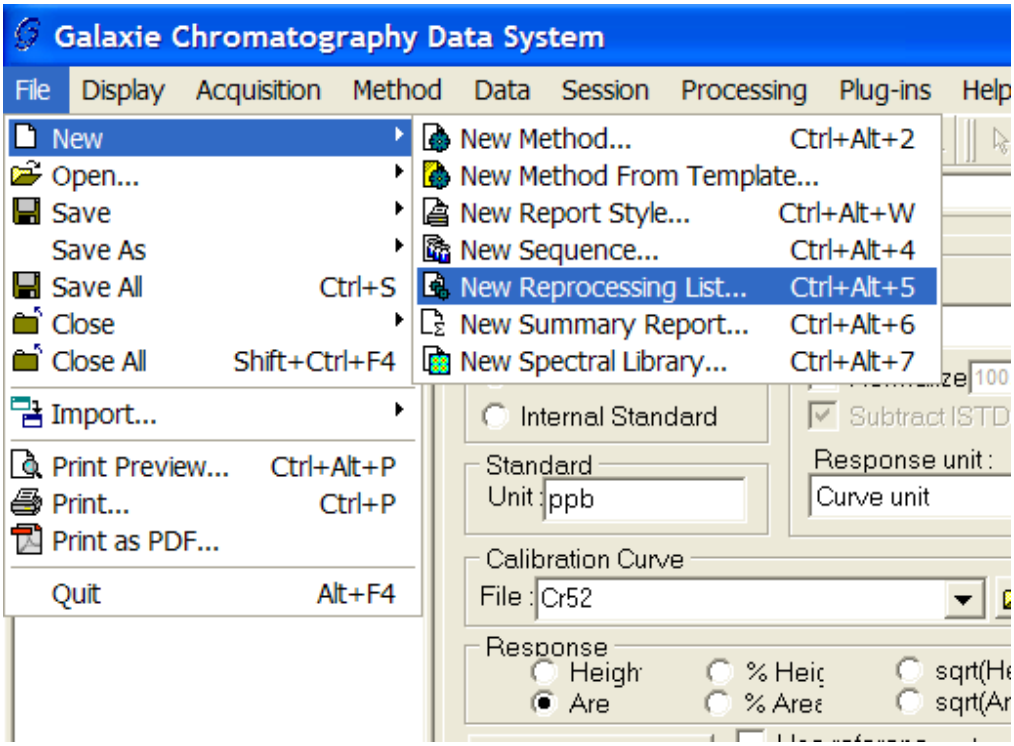
C:\Galaxie\Data\Chromium\Output\Cr Speciation.csv

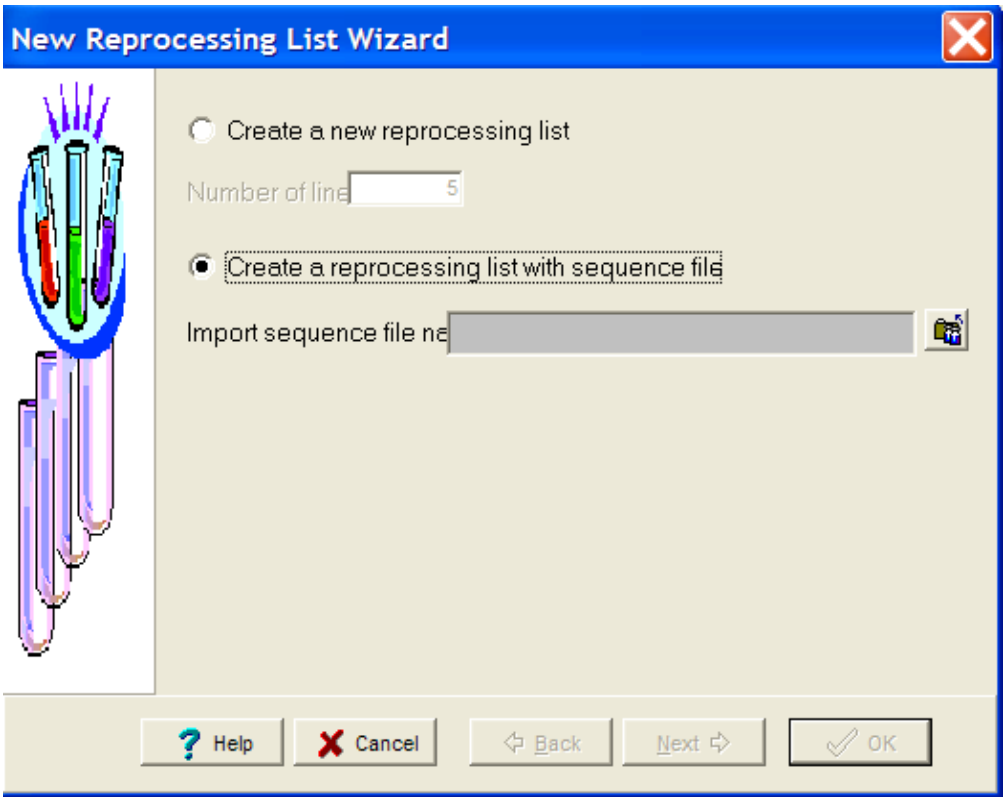
This is the quantified results with "non-bracketing" calibration. Since this file is created automatically each time a sequence is analyzed or re-processed, it must be renamed and moved to the achived directory with a file name "WGxxxxxx-dd-mm-yyyy-non-bracketing.csv":

C:\Galaxie\Data\Chromium\Archived\2012\Quantified Results\WG-XXXXXX-dd-mm-yyyy-non-bracketing.csv

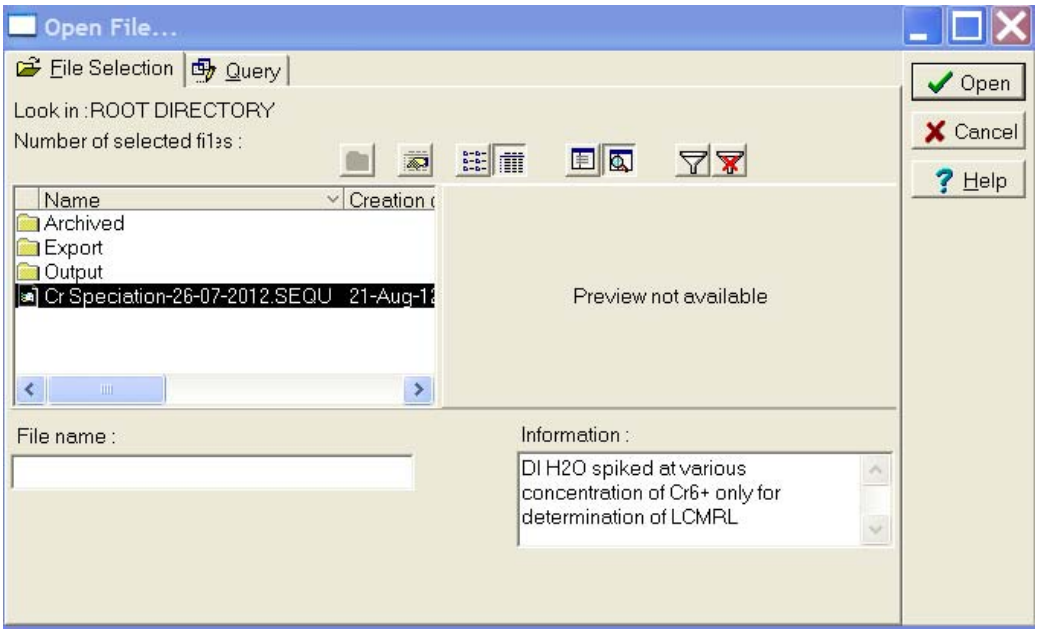
To reprocess the data in a sequence that has been completed,

- open a new reprocess list by "File/New/New Reprocessing List", Select "Create a reprocessing list with sequence file"

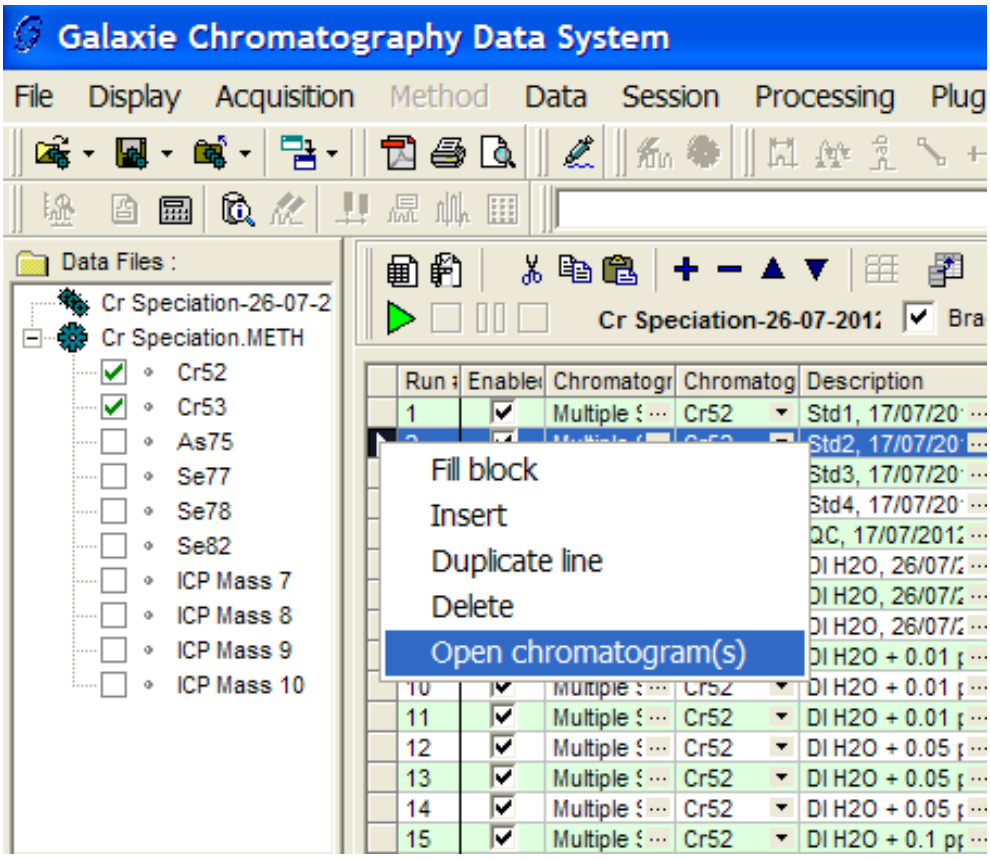


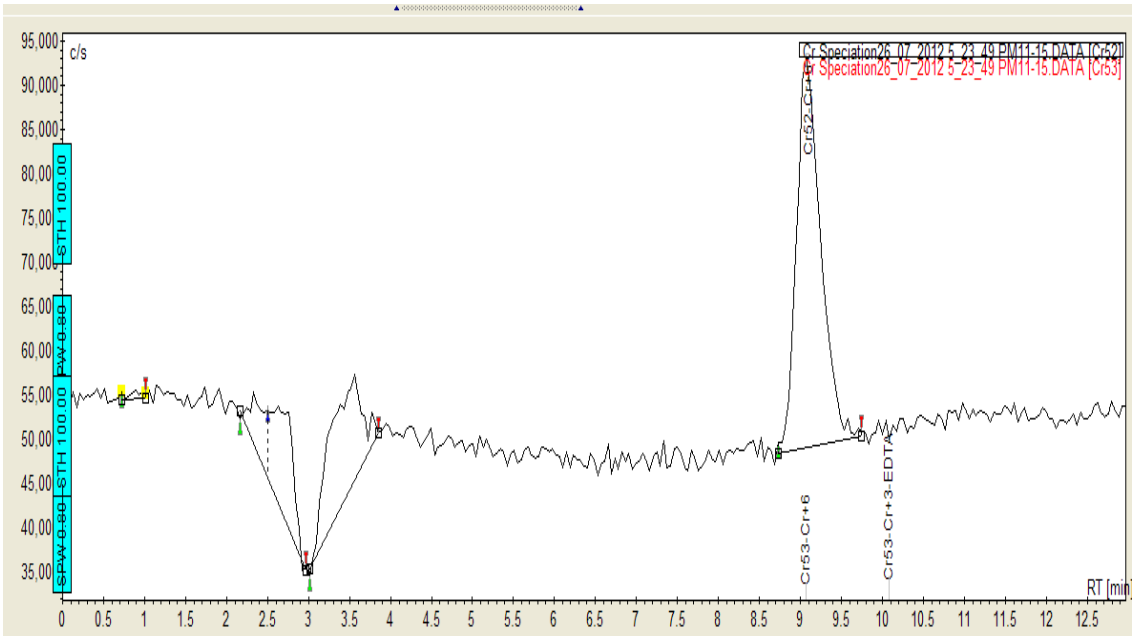


- select the finished sequence file and click on “Open”

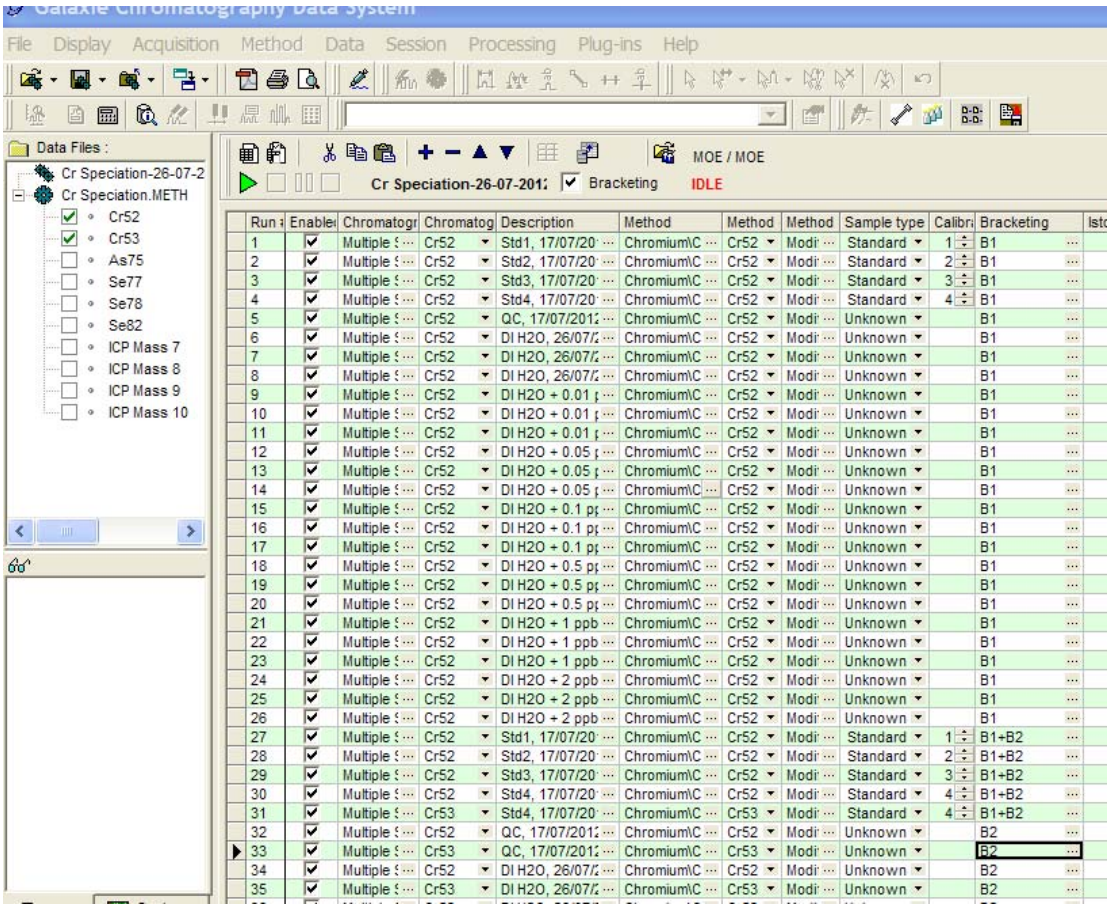


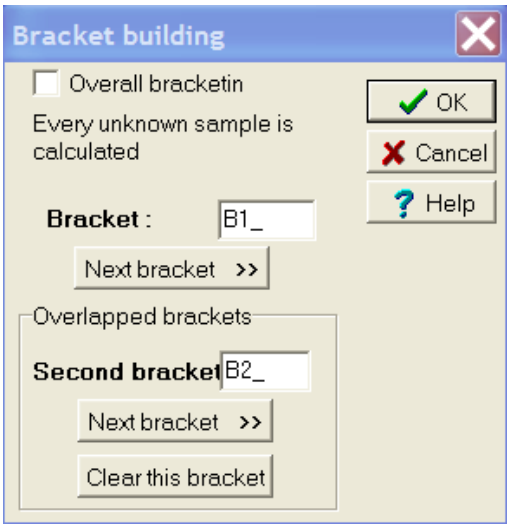
- check that Cr(VI) peak is identified correctly by opening the chromatogram and examine the peak and retention time (RT)





- select “Bracketing”

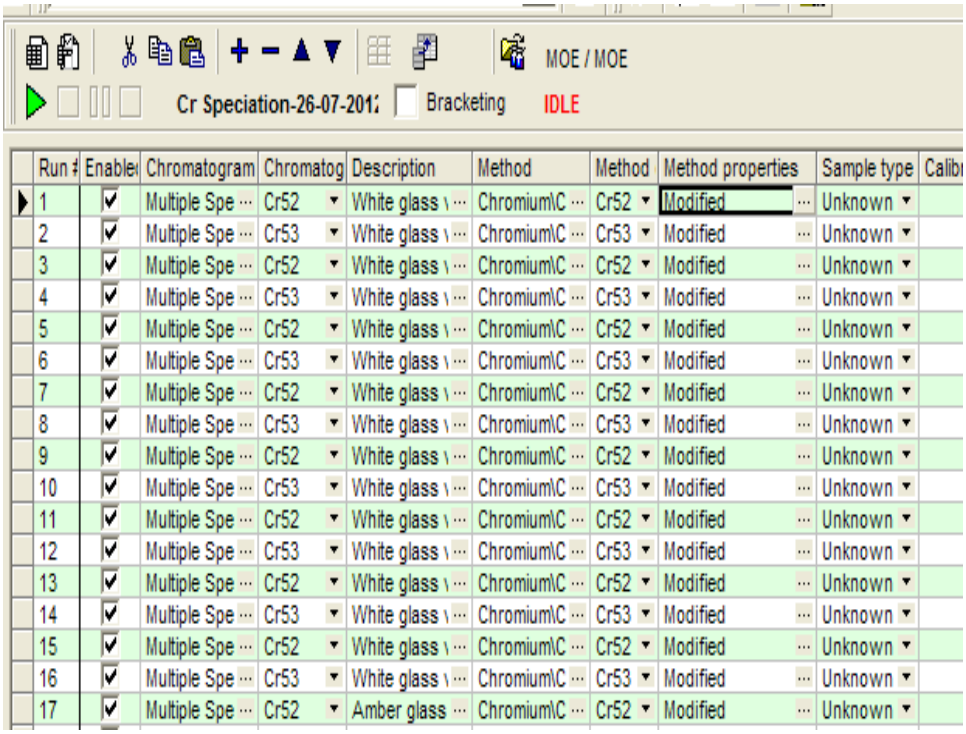




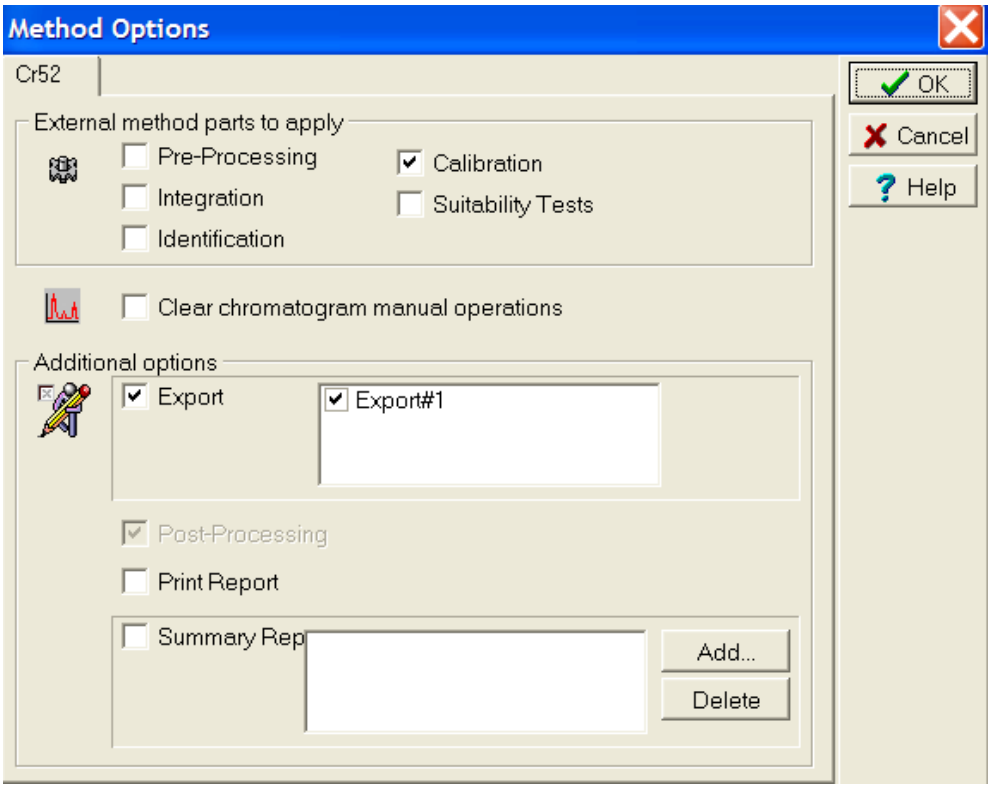
- Bracketing standards can be selected by clicking the drop-down button

- In this example, the first bracketing calibration is established using the first and second set of calibration standards, and the samples between the two sets of calibration standards will be quantified using the first bracketing calibration curve. The subsequent samples will be quantified in the same format.

- If any sample has been manually checked and re-integrated for misidentified peaks, and the manually integrated chromatogram has been saved, click on "Method Properties", and uncheck all except "Calibration", "Export", and Post Processing".



Run #	Enable	Chromatogram	Chromatog	Description	Method	Method	Method properties	Sample type	Calib
1	☑	Multiple Spe	Cr52	White glass \	Chromium\C	Cr52	Modified	Unknown	
2	☑	Multiple Spe	Cr53	White glass \	Chromium\C	Cr53	Modified	Unknown	
3	☑	Multiple Spe	Cr52	White glass \	Chromium\C	Cr52	Modified	Unknown	
4	☑	Multiple Spe	Cr53	White glass \	Chromium\C	Cr53	Modified	Unknown	
5	☑	Multiple Spe	Cr52	White glass \	Chromium\C	Cr52	Modified	Unknown	
6	☑	Multiple Spe	Cr53	White glass \	Chromium\C	Cr53	Modified	Unknown	
7	☑	Multiple Spe	Cr52	White glass \	Chromium\C	Cr52	Modified	Unknown	
8	☑	Multiple Spe	Cr53	White glass \	Chromium\C	Cr53	Modified	Unknown	
9	☑	Multiple Spe	Cr52	White glass \	Chromium\C	Cr52	Modified	Unknown	
10	☑	Multiple Spe	Cr53	White glass \	Chromium\C	Cr53	Modified	Unknown	
11	☑	Multiple Spe	Cr52	White glass \	Chromium\C	Cr52	Modified	Unknown	
12	☑	Multiple Spe	Cr53	White glass \	Chromium\C	Cr53	Modified	Unknown	
13	☑	Multiple Spe	Cr52	White glass \	Chromium\C	Cr52	Modified	Unknown	
14	☑	Multiple Spe	Cr53	White glass \	Chromium\C	Cr53	Modified	Unknown	
15	☑	Multiple Spe	Cr52	White glass \	Chromium\C	Cr52	Modified	Unknown	
16	☑	Multiple Spe	Cr53	White glass \	Chromium\C	Cr53	Modified	Unknown	
17	☑	Multiple Spe	Cr52	Amber glass	Chromium\C	Cr52	Modified	Unknown	



In this way, all manually integrated chromatographic information is retained, except that sample is quantified using the bracketing calibrations.

- The results are automatically exported as a .csv file in C:\Galaxie\Data\Chromium\Output\Cr Speciation.csv

- Rename the file to "WGxxxxxx-dd-mm-yyyy-bracketing.csv

- Rename the calibration file to WGXXXXXX-dd-mm-yyyy-Cr52-bracketing.CALB

- Move both files to the archived directory

  C:\Galaxie\Data\Chromium\Archived\2012\Quantified Results\WG-XXXXXX-dd-mm-yyyy-non-bracketing.csv

  C:\Galaxie\Data\Chromium\Archived\2012\Quantified Results\WG-XXXXXX-dd-mm-yyyy-Cr52.CALB.

This is an example of "bracketing" calibration and can be found in the Galaxie Help in the chromatography data software.

Run Suffix	Run ID	Standard	Level	Bracketing
Run	1	Standard	1	B1
Run	2	Standard	2	B1
Run	3	Unknown		B1
Run	4	Unknown		B1
Run	5	Standard	1	B1+B2
Run	6	Standard	2	B1+B2
Run	7	Unknown		B2
Run	8	Unknown		B2
Run	9	Standard	1	B2
Run	10	Standard	2	B2

The processing of the chromatograms acquired in sequence with bracketing is made after the acquisition of the whole sequence.

In the previous example the 10 injections are performed, then the calibration curve of the first bracketing is created with the four standard chromatograms Run1, Run2, Run5 and Run6. Then the first two unknown chromatograms (Run3 and Run4) are processed with this calibration curve.

This calibration curve is then archived and deleted and a second calibration curve is created with the four standard chromatograms Run5, Run6, Run9 and Run10. The last two unknown chromatograms (Run7 and Run8) are processed with this calibration curve.

6 RUN PROCESSING AND QUALITY ASSURANCE

6.1 Run Format

Following is a typical run sequence. It is located under "Cr Speciation-E3510 Template.SEQU". There must be a set of calibration standards, QC standards and CRM for every 20 samples and one sample duplicate, and samples must always be bracketed with standards, in order to perform "bracketing calibration" as described in previous section.

Run #	Enabl	Method	Methc	RunName (pre	RunID	Description	Rur	No. c	Vial	Rac	Inj. Vc	Sample type	Calibration	Level
1	☑	Cr Speciation.METH	···	$AcqMethc ···	1	DI H2O Blank	···	13	1	1	1	200	Unknown		
2	☑	Cr Speciation.METH	···	$AcqMethc ···	2	Calib-Std-1	···	13	1	2	1	200	Standard	Clear old points	1
3	☑	Cr Speciation.METH	···	$AcqMethc ···	3	Calib-Std-2	···	13	1	3	1	200	Standard	Add	2
4	☑	Cr Speciation.METH	···	$AcqMethc ···	4	Calib-Std-3	···	13	1	4	1	200	Standard	Add	3
5	☑	Cr Speciation.METH	···	$AcqMethc ···	5	Calib-Std-4	···	13	1	5	1	200	Standard	Add	4
6	☑	Cr Speciation.METH	···	$AcqMethc ···	6	QC-E3510	···	13	1	6	1	200	Unknown		
7	☑	Cr Speciation.METH	···	$AcqMethc ···	7	TapWaterUnspiked-E3510	···	13	1	7	1	200	Unknown		
8	☑	Cr Speciation.METH	···	$AcqMethc ···	8	TapWaterSpiked-E3510	···	13	1	8	1	200	Unknown		
9	☑	Cr Speciation.METH	···	$AcqMethc ···	9	ERA-CRM-E3510	···	13	1	9	1	200	Unknown		
10	☑	Cr Speciation.METH	···	$AcqMethc ···	10	C000001	···	13	1	10	1	200	Unknown		
11	☑	Cr Speciation.METH	···	$AcqMethc ···	11	C000002	···	13	1	11	1	200	Unknown		
12	☑	Cr Speciation.METH	···	$AcqMethc ···	12	C000003	···	13	1	12	1	200	Unknown		
13	☑	Cr Speciation.METH	···	$AcqMethc ···	13	C000004	···	13	1	13	1	200	Unknown		
14	☑	Cr Speciation.METH	···	$AcqMethc ···	14	C000005	···	13	1	14	1	200	Unknown		
15	☑	Cr Speciation.METH	···	$AcqMethc ···	15	C000006	···	13	1	15	1	200	Unknown		
16	☑	Cr Speciation.METH	···	$AcqMethc ···	16	C000007	···	13	1	16	1	200	Unknown		
17	☑	Cr Speciation.METH	···	$AcqMethc ···	17	C000008	···	13	1	17	1	200	Unknown		
18	☑	Cr Speciation.METH	···	$AcqMethc ···	18	C000009	···	13	1	18	1	200	Unknown		
19	☑	Cr Speciation.METH	···	$AcqMethc ···	19	C0000010	···	13	1	19	1	200	Unknown		
20	☑	Cr Speciation.METH	···	$AcqMethc ···	20	C0000011	···	13	1	20	1	200	Unknown		
21	☑	Cr Speciation.METH	···	$AcqMethc ···	21	C0000012	···	13	1	21	1	200	Unknown		
22	☑	Cr Speciation.METH	···	$AcqMethc ···	22	C0000013	···	13	1	22	1	200	Unknown		
23	☑	Cr Speciation.METH	···	$AcqMethc ···	23	C0000014	···	13	1	23	1	200	Unknown		
24	☑	Cr Speciation.METH	···	$AcqMethc ···	24	C0000015	···	13	1	24	1	200	Unknown		
25	☑	Cr Speciation.METH	···	$AcqMethc ···	25	C0000016	···	13	1	25	1	200	Unknown		
26	☑	Cr Speciation.METH	···	$AcqMethc ···	26	C0000017	···	13	1	26	1	200	Unknown		
27	☑	Cr Speciation.METH	···	$AcqMethc ···	27	C0000018	···	13	1	27	1	200	Unknown		
28	☑	Cr Speciation.METH	···	$AcqMethc ···	28	C0000019	···	13	1	28	1	200	Unknown		
29	☑	Cr Speciation.METH	···	$AcqMethc ···	29	C0000020	···	13	1	29	1	200	Unknown		
30	☑	Cr Speciation.METH	···	$AcqMethc ···	30	DI H2O Blank	···	13	1	30	1	200	Unknown		
31	☑	Cr Speciation.METH	···	$AcqMethc ···	31	QC-E3510	···	13	1	15	1	200	Unknown		
32	☑	Cr Speciation.METH	···	$AcqMethc ···	32	TapWaterUnspiked-E3510	···	13	1	15	1	200	Unknown		
33	☑	Cr Speciation.METH	···	$AcqMethc ···	33	TapWaterUnspiked-E3510	···	13	1	15	1	200	Unknown		
34	☑	Cr Speciation.METH	···	$AcqMethc ···	34	ERA-CRM-E3510	···	13	1	15	1	200	Unknown		
35	☑	Cr Speciation.METH	···	$AcqMethc ···	35	Calib-Std-1	···	13	1	31	1	200	Standard	Add	1
36	☑	Cr Speciation.METH	···	$AcqMethc ···	36	Calib-Std-2	···	13	1	32	1	200	Standard	Add	2
37	☑	Cr Speciation.METH	···	$AcqMethc ···	37	Calib-Std-3	···	13	1	33	1	200	Standard	Add	3
38	☑	Cr Speciation.METH	···	$AcqMethc ···	38	Calib-Std-4	···	13	1	34	1	200	Standard	Add	4

6.2 Run Control and Quality Assurance

The quality assurance procedure involves evaluation of laboratory QC standards; these are DI H_2O Blank-E3510, QC-E3510, TapWaterUnspiked-E3510, TapWaterSpiked-E3510, ERA-CRM-E3510. These QC standards are prepared freshly at the beginning of each analytical session, as outlined in Section 5. The run control limits and data acceptance criteria are outlined below.

6.2.1 DI H_2O Blank-E3510

Within each analytical session, the results for DI H_2O blanks must be less than the the average blanks + 3 x standard deviations listed in Table 1.6.1. Otherwise, contamination from the DI H_2O or sample containers is suspected.

6.2.2 QC-E3510

Within each analytical session, the results for QC-E3510 must be within ±15% of the expected value (0.2 μg/L).

6.2.3 TapWaterUnspiked-E3510

Within each analytical session, the results for this QC standard must be within ± 20% of the long term average (currently 0.14 μg/L. see Table 1.6.3).

6.2.4 TapWaterSpiked-E3510

Within each analytical session, the spike recovery for the QC must be between 80 % and 120%. The spike recovery is calculated using the TapWaterUnspiked-E3510 and the TapWaterSpiked-E3510 analyzed immediately after.

6.2.5 ERA UCMR3-E3510

Within each analytical session, the results for the CRM must be within the certified accepted range of 0.319 – 0.479 μg/L.

NOTE: If any of the QC standards in sections 6.2.2 to 6.2.5 do not fall within the acceptance criteria listed, the samples within that run must be reanalyzed after recalibration of the instrument. Please see SOP SPEC-ICP-MS.001 (Varian 820 ICP-MS Routine Operation and Optimization) for a detailed description of instrument maintenance and performance.

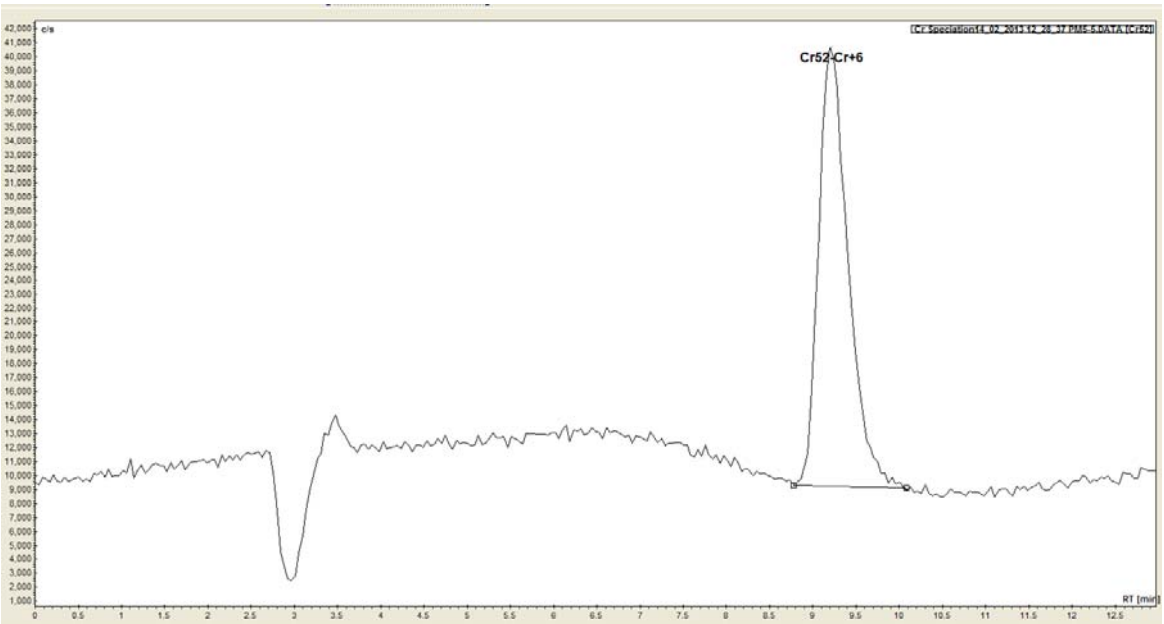
6.3 Calculations/Interpretations

The chromatography data acquisition software, Galaxie, calculates, quantifies and reports the final results in μg/L. There is no additional data calculation and interpretation required.

The chromatographic peak of Cr(VI) in each sample, however, needs to be checked by opening the chromatogram and verify the correct Cr(VI) peak by the retention time (RT). With the chromagraphy conditions shown in 4.5.8, the Cr(VI) retention time is 9.5 minutes.

Refer to refer to “Galaxie Manuals” for chromatogram reprocessing and recalculations.

Following is a typical chromatogram with Cr(VI) retention time



6.4 Reporting

The final results are exported automatically by Galaxie as "Cr Speciation.csv". This file is imported into ONLIMS database for QA/QC procedure, to review QC results, control charting and for final export / upload to elab and LaSB LIMS.

Refer to SOP SPEC-ICP-MS-003

LIMS USER MANUAL "Workgroups and Data Processing", August 10, 2005 (http://intra.moe.gov.on.ca/stdprodconsume/groups/lr/@moe/@essd/@lasb/documents/nativedocs/stdprod_069297.pdf) and elab Traning guide for further details about using these data reporting tools.

(http://intra.moe.gov.on.ca/Divisions/EnvironmentalSciencesStandards/OurBranches/LaboratoryServices/ToolsResources/STDU_055777.html)

The LIMS reported MDL is 0.05 µg/L. Results are reported to three significant figures with uncertainty (see the uncertainty document for details).

6.5 Proficiency Testing

Refer to SPECSOP.001 "Procedure for training and Proficiency Testing within the Spectroscopy & Physical Chemistry Section".

Appendix A:

Minimum Specifications for Environmental Grade Ammonium Hydroxide (concentrated) or equivalent.

Analyte	Maximum Specification	Actual Value (in ppb)
Aluminum (Al)	1 ppb	<0.5
Antimony (Sb)	0.5 ppb	<0.1
Arsenic (As)	1 ppb	<0.1
Barium (Ba)	0.1 ppb	<0.1
Beryllium (Be)	0.1 ppb	<0.1
Bismuth (Bi)	0.1 ppb	<0.1
Cadmium (Cd)	0.5 ppb	<0.1
Calcium (Ca)	1 ppb	<0.5
Cerium (Ce)	0.1 ppb	<0.1
Cesium (Cs)	0.1 ppb	<0.1
Chromium (Cr)	0.5 ppb	<0.1
Cobalt (Co)	0.5 ppb	<0.1
Copper (Cu)	0.5 ppb	<0.5
Dysprosium (Dy)	0.1 ppb	<0.1
Erbium (Er)	0.1 ppb	<0.1
Europium (Eu)	0.1 ppb	<0.1
Gadolinium (Gd)	0.1 ppb	<0.1
Gallium (Ga)	0.1 ppb	<0.1
Germanium (Ge)	0.1 ppb	<0.1
Gold (Au)	0.5 ppb	<0.1
Hafnium (Hi)	Information only	<0.5
Holmium (Ho)	0.1 ppb	<0.1
Indium (In)	0.1 ppb	<0.1
Iron (Fe)	1 ppb	<0.5
Lanthanum (La)	0.1 ppb	<0.1
Lead (Pb)	0.1 ppb	<0.1
Lithium (Li)	0.1 ppb	<0.1
Lutetium (Lu)	0.1 ppb	<0.1
Magnesium (Mg)	1 ppb	<0.2
Manganese (Mn)	0.5 ppb	<0.2
Mercury (Hg)	0.2 ppb	<0.2
Molybdenum (Mo)	0.5 ppb	<0.1
Neodymium (Nd)	0.1 ppb	<0.1
Nickel (Ni)	0.5 ppb	<0.2
Niobium (Nb)	0.1 ppb	<0.1
Palladium (Pd)	Information only	<1
Platinum (Pt)	Information only	<1
Potassium (K)	1 ppb	<0.2
Praseodymium (Pr)	0.1 ppb	<0.1
Rhenium (Re)	Information only	<1
Rhodium (Rh)	0.5 ppb	<0.1
Rubidium (Rb)	0.1 ppb	<0.1
Ruthenium (Ru)	Information only	<1
Samarium (Sm)	0.1 ppb	<0.1

Analyte	Maximum Specification	Actual Value (in ppb)
Scandium (Sc)	0.1 ppb	<0.1
Selenium (Se)	1 ppb	<0.1
Silver (Ag)	0.5 ppb	<0.1
Sodium (Na)	1 ppb	<1
Strontium (Sr)	0.1 ppb	<0.1
Tellurium (Te)	0.1 ppb	<0.1
Terbium (Tb)	0.1 ppb	<0.1
Thalium (Tl)	0.1 ppb	<0.1
Thorium (Th)	0.1 ppb	<0.1
Thulium (Tm)	0.1 ppb	<0.1
Tin (Sn)	0.5 ppb	<0.1
Titanium (Ti)	0.5 ppb	<0.1
Tungsten (W)	0.1 ppb	<0.1
Uranium (U)	0.1 ppb	<0.1
Vanadium (V)	0.5 ppb	<0.1
Ytterbium (Yb)	0.1 ppb	<0.1
Yttrium (Y)	0.1 ppb	<0.1
Zinc (Zn)	0.5 ppb	<0.5
Zirconium (Zr)	0.1 ppb	<0.1
Chloride	0.5 ppm	<0.5ppm
Phosphate	0.01ppm	<0.01
Sulfate	1 ppm	<1

NOTE: The actual value is dependent on the lot of the ammonium hydroxide purchased. It is the Minimum specification which is important to the method.

Appendix B: Minimum Specification of Optima Concentrated HNO_3 or equivalent.

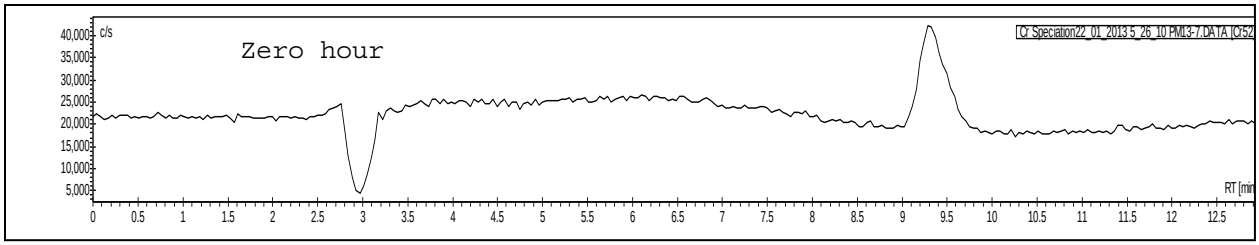
Result Name	Units	Specifications	Test Value (Typical)
Aluminum (Al)	ppt	<=20	<10
Antimony (Sb)	ppt	<=10	<5
Arsenic (As)	ppt	<=20	<10
Barium (Ba)	ppt	<=10	<1
Beryllium (Be)	ppt	<=10	<1
Bismuth (Bi)	ppt	<=10	<0.05
Boron (B)	ppt	<=10	<10
Cadmium (Cd)	ppt	<=10	<0.1
Calcium (Ca)	ppt	<=10	<10
Cerium (Ce)	ppt	<=10	<0.05
Cesium (Cs)	ppt	<=10	<0.05
Chromium (Cr)	ppt	<=10	<10
Cobalt (Co)	ppt	<=10	<1
Copper (Cu)	ppt	<=10	<1
Dysprosium (Dy)	ppt	<=1	<0.01
Erbium (Er)	ppt	<=1	<0.01
Europium (Eu)	ppt	<=1	<0.01
Gadolinium (Gd)	ppt	<=1	<0.01
Gallium (Ga)	ppt	<=10	<0.1
Germanium (Ge)	ppt	<=10	<0.1
Gold (Au)	ppt	<=20	<1
Hafnium (Hf)	ppt	<=10	<0.05
Holmium (Ho)	ppt	<=1	<0.01
Indium (In)	ppt	<=1	<0.1
Iron (Fe)	ppt	<=10	<10
Lanthanum (La)	ppt	<=1	<0.05
Lead (Pb)	ppt	<=10	<0.5
Lithium (Li)	ppt	<=10	<0.5
Lutetium (Lu)	ppt	<=1	<0.01
Magnesium (Mg)	ppt	<=10	<5
Manganese (Mn)	ppt	<=10	<1
Mercury (Hg)	ppt	<=50	<10
Molybdenum (Mo)	ppt	<=10	<1
Neodymium (Nd)	ppt	<=1	<0.05
Nickel (Ni)	ppt	<=20	<5
Niobium (Nb)	ppt	<=1	<1
Palladium (Pd)	ppt	<=20	<5
Platinum (Pt)	ppt	<=20	<1
Potassium (K)	ppt	<=10	<5
Praseodymium (Pr)	ppt	<=1	<0.05
Rhenium (Re)	ppt	<=10	<0.1
Rhodium (Rh)	ppt	<=10	<1
Rubidium (Rb)	ppt	<=10	<1
Ruthenium (Ru)	ppt	<=20	<1
Samarium (Sm)	ppt	<=1	<0.01
Scandium (Sc)	ppt	<=10	<1

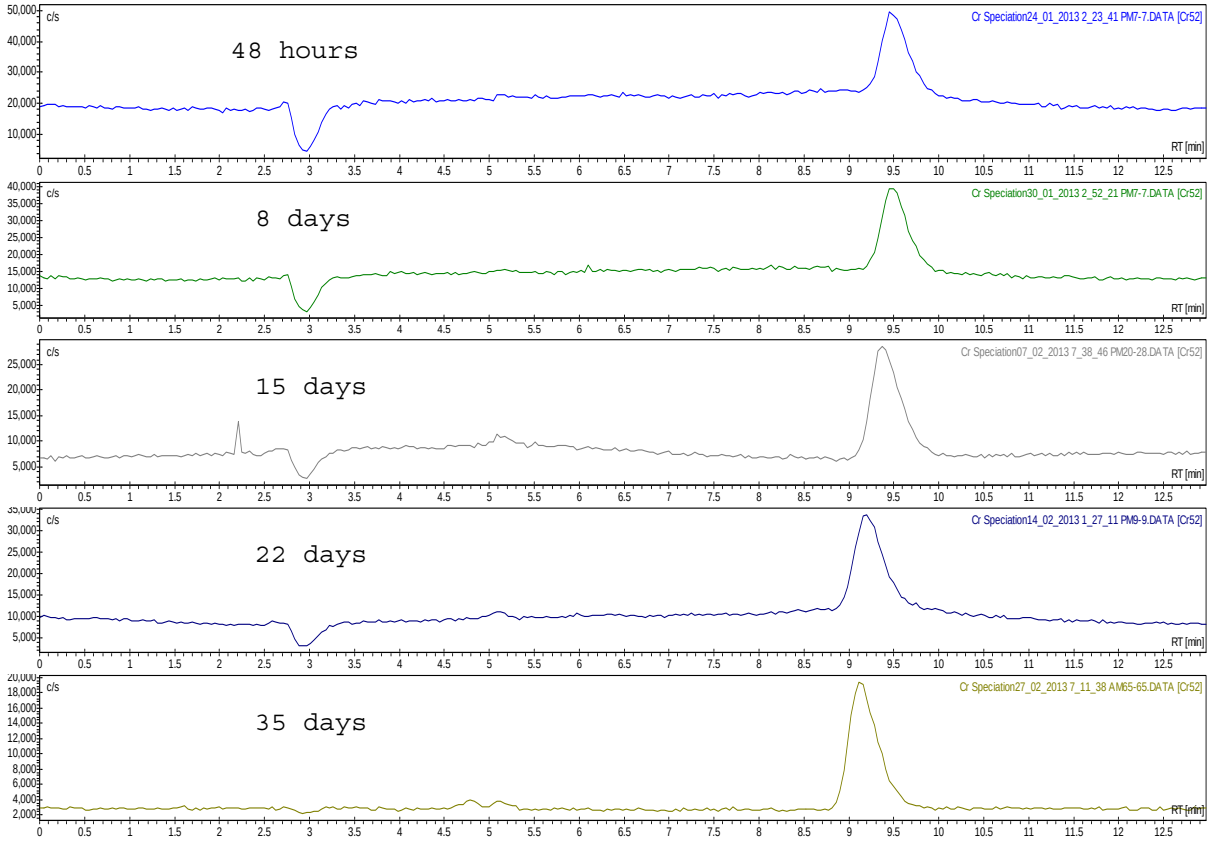
Result Name	Units	Specifications	Test Value (Typical)
Selenium (Se)	ppt	Information only	<5
Silver (Ag)	ppt	<=10	<0.5
Sodium (Na)	ppt	<=10	<5
Strontium (Sr)	ppt	<=10	<1
Tantalum (Ta)	ppt	Information only	<10
Tellurium (Te)	ppt	<=1	<0.5
Terbium (Tb)	ppt	<=1	<0.01
Thallium (Tl)	ppt	<=10	<0.05
Thorium (Th)	ppt	<=1	<0.05
Thulium (Tm)	ppt	<=1	<0.01
Tin (Sn)	ppt	<=20	<5
Titanium (Ti)	ppt	<=10	<5
Tungsten (W)	ppt	<=10	<1
Uranium (U)	ppt	<=1	<0.01
Vanadium (V)	ppt	<=10	<0.5
Ytterbium (Yb)	ppt	<=1	<0.01
Yttrium (Y)	ppt	<=1	<0.1
Zinc (Zn)	ppt	<=10	<1
Zirconium (Zr)	ppt	<=10	<0.5

NOTE: The typical test value is dependent on the lot of the acid purchased. It is the Minimum specifications which is important to the method.

Appendix C

Typical chromatograms of Cr(VI) using this method.





These chromatograms were obtained using the Tap Water Spiked-E3510. The days denote the time lap after the sample spiking. These results also demonstrate the Cr(VI) stability after 30 days. The baseline and retention time may change due to changes in mobile phases and instrument parts, the overall Cr (VI) peak position and quantified results remain the same.