



Chromium (III) and Chromium (VI) Speciation in Water by IC-ICP-MS (Ion Chromatography- Inductively Coupled Plasma Mass Spectrometry)

UOP Method 1031-19

Scope

This method is intended for the separation and quantification of trivalent and hexavalent chromium ions in complex water systems including: refinery wastewater, power industry wastewater Flue Gas Desulphurization (FGD) wastewater, and contaminated groundwater at parts per billion (ppb) levels using IC-ICP-MS (Ion chromatograph (IC) coupled to an Inductively Coupled Plasma Mass Spectrometer (ICP-MS) system). Samples are run with minimal sample preparation and do not require digestion. The chromium species Cr(III) and Cr(VI) can be detected at 0.1 ppb and quantitated at < 1 ppb. The linearity range for the method is from 1 ppb to 50 ppb. Quantitation of the total chromium value is suggested prior to analysis by this method to avoid overloading the column. Higher concentrations can be determined by volume dilution.

References

ASTM Specification D1193, "Reagent Water," www.astm.org

ASTM Method D1687, "Chromium in Water," www.astm.org

iCAP Q Operating Manual, ThermoFisher Scientific, Revision B - 1288090, June 2012

UOP Method 999, "Precision Statements in UOP Methods," www.astm.org

Outline of Procedure

A 25 µl sample is injected into the IC where the chromium species are separated using a mobile phase consisting of a 300 mM nitric acid. The chromium (III) and chromium (VI) species are eluted from the IC and then aspirated into the ICP-MS where species are quantified based on retention times, using the calibration curves.

Apparatus

References to catalog numbers and suppliers are included as a convenience to the method user. Other suppliers may be used.

Column, ThermoFisher Scientific, AG7 Dionex IonPac™ 2x50 mm, Cat. No. NC0214199

IT IS THE USER'S RESPONSIBILITY TO ESTABLISH APPROPRIATE PRECAUTIONARY PRACTICES AND TO DETERMINE THE APPLICABILITY OF REGULATORY LIMITATIONS PRIOR TO USE. EFFECTIVE HEALTH AND SAFETY PRACTICES ARE TO BE FOLLOWED WHEN UTILIZING THIS PROCEDURE. FAILURE TO UTILIZE THIS PROCEDURE IN THE MANNER PRESCRIBED HEREIN CAN BE HAZARDOUS. SAFETY DATA SHEETS (SDS) OR EXPERIMENTAL SAFETY DATA SHEETS (ESDS) FOR ALL OF THE MATERIALS USED IN THIS PROCEDURE SHOULD BE REVIEWED FOR SELECTION OF THE APPROPRIATE PERSONAL PROTECTION EQUIPMENT (PPE).
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Flasks, volumetric, glass, Class A, 10-mL, 50-mL, and 2-L VWR, Cat. Nos. 89001-916, 89001-934, and 89001-926 respectively

Ion Chromatography System, ThermoFisher Scientific Model Dionex™ ICS-5000⁺ Hybrid HPIC or equivalent. System including: ICS-5000⁺ DP Dual Pumps, Dionex™, AS-AP Auto-sampler Trays, ICS-5000⁺ DC Dector/Chromatography Compartment

ICP-MS, iCAP Q, ThermoFisher Scientific

Pipet, automatic, 100-1000-μL, VWR, Cat. No. 89079-974; calibrated and/or certified according to manufacturer's recommendations

Pipet, automatic, 1–10-mL, Rainin Classic Pipette PR-10ML, Rainin, Item No. 17008655 calibrated and/or certified according to manufacturer's recommendations

Regulator, argon, two-stage, high purity, delivery pressure range 30-700 kPa (4-100 psi), Matheson Tri-Gas, Model 3122A-580

Regulator, helium, duel stage high purity stainless steal, delivery pressure range 0-345 kPa (0-50 psi), Matheson Tri-Gas, Model 3813A-580

Water purification system, 18 MΩ, ASTM D1193 Type I reagent grade water, unless otherwise specified Barnstead™ GenPure™ ThermoFisher Scientific Cat. No. 10-451-212)

Reagents and Materials

References to catalogue numbers and suppliers are included as a convenience to the method user. Other suppliers may be used (see note 1). Unless otherwise specified, references to water mean 18 MΩ water.

Argon, 99.995% minimum purity

Auto sampler vials, 2 mL polypropylene, ThemoFisher Scientific, Cat. No. 10-800-167

Auto Sampler Caps, Pre slit, ThermoFisher Scientific, Cat. No. 03-376-482

Chromium +3 Single Inorganic Speciation Standard, 1,000 μg/mL, SPEX Industries, Inc., Cat. No. SPEC-CR3

Chromium +6 Single Inorganic Speciation Standard, 1,000 μg/mL, SPEX Industries, Inc., Cat. No. SPEC-CR6

Chromium (III) stock solution, 10 μg/mL. To prepare 50 mL, pipet 0.5 mL of the 1000- μg/mL chromium (III) standard solution into a 50 mL volumetric flask. Fill to the mark with 2% nitric acid. Cap and invert several times to mix. This solution should stay stable for one month.

Chromium (VI) stock solution, 10 μg/mL. To prepare 50 mL, pipet 0.5 mL of the 1000- μg/mL chromium (VI) standard solution into a 50 mL volumetric flask. Fill to the mark with water. Cap and invert several times to mix. This solution should stay stable for one month.

Chromium (III) and (VI) intermediate solution, 500 ppb. To prepare 10 mL, pipet 0.5 mL each of the chromium (III) and chromium (VI) stock solutions into a 10 mL volumetric flask. Fill to the mark with water. Cap and invert several times to mix. This solution should stay stable for one week.

Eluent Bottles, Dionex EO, 2 L, plastic with cap, Thermo Fisher Scientific, Cat. No. NC9881156

Helium, 99.995% minimum purity

Nitric acid, concentrated, Ultrex II Ultrapure reagent, 500 mL, J.T. Baker, Cat. No. 6901-05

Nitric acid, 2%. Pipet 1 mL of concentrated nitric acid into a 50-mL volumetric flask containing ~40 mL of deionized water; fill to mark with deionized water. Cap and invert several times to mix.

Nitric acid, 400 mM. To prepare 2 L, pipet 51.0 mL of concentrated nitric acid into a 2-L volumetric flask containing ~1.5 L of deionized water; fill to mark with deionized water. Cap and invert several times to mix; transfer to properly labeled eluent bottle.

Pipet, low density polyethylene, VWR, Cat. No. 16001-174

Pipet tips, 10-mL, Rainin, Item No. 17001122

Pipet tips, 100-1250- μ L, VWR, Cat. No. 53508-922

Syringes, 2 mL Luer-Lock, ThermoFisher Scientific, Cat. No. 03-377-27

Syringe Filters, Acrodisc Premium, 25 mm, 0.45 μ m PTFE Membrane, HPLC Certified, PALL Life Sciences, Product ID 4219 (See *Notes*)

Transfer pipets, disposable polyethylene Fischer Scientific Cat. No. 13-711-9AM

Procedure

The analyst is expected to be familiar with general laboratory practices, the technique of IC-ICP-MS, and the equipment being used. Dispose of all used supplies and samples in an environmentally safe manner according to local regulations. See safety data sheet (SDS) for each material used.

Preparation of Standards

Three standards containing chromium (III) and chromium (VI) are prepared from an intermediate solution to generate a calibration curve. Water is used as a blank.

1. Fill 3 cleaned and rinsed 10 mL volumetric flasks with approximately 7.5 mL of water.
2. Pipet 200, 500, and 1000 μ L aliquots of 500 ppb chromium intermediate solution into each one of the 10 mL of the flasks from step 1.
3. Fill each of the flasks to the mark with water and mix well. The resulting solutions will be 10, 25 and 50 ppb, respectively in both chromium (III) and chromium (VI).
4. Fill a syringe with 10 ppb standard and attach syringe filter. Press the standard through the syringe filter discarding the first 0.5 mL, then rinsing the properly labeled autosampler vial three times with about 1.0 mL of standard. Fill the autosampler vial.
5. Repeat step 4 for blank, 25, and 50 ppb standards.

Preparation of Samples

Rinse an autosampler vial three times with water and discard. Purge the vial with dry air or nitrogen. Using a syringe and a syringe filter, filter the sample directly into the autosampler vial discarding the first 0.5 mL of filtrate. Cap the vial and add to the auto sampler tray (see *Notes*).

Preparation of IC-ICP-MS

Start the instruments and prepare per the manufacturer's recommendations according to the parameters listed in Tables 1 and 2. Wait a minimum of 30 minutes after the plasma is ignited for the instrument to stabilize. When recommended by manufacturer, run appropriate auto-tuning and performance report measurements to ensure optimal instrument performance.

Table 1

IC Parameters

IC Instrument:	Dionex™ ICS-5000+ System or equivalent
Column	AG7 Dionex IonPac™ guard, 2x50mm
Column Temperature	25.0 °C
Flow Rate	0.400 mL/min
Elution	Isocratic (75% mobile phase A, 25% mobile phase B)
Mobile Phase A	400 mM nitric acid
Mobile Phase B	Water
Sample injection volume	25µL
Run Time	360 s

Table 2

ICP-MS Parameters

ICP/MS Instrument:	Thermo Scientific iCAP Q
Measurement Mode	KED
Analytes	⁵² Cr, ⁵³ Cr (for monitoring)
RF Power	1550 W
Plasma Gas Flow	14 L/min
Nebulizer Gas Flow	1.08 L/min
Auxiliary gas Flow	0.80 L/min
QCell Helium Gas Flow	4.8 L/min
QCell KED	2 V
Injector	2 mm I.D., Quartz
Sampling and Skimmer Cone	Nickel
Nebulizer	PFA LC nebulizer with connector for IC
Sampling distance	5.00 mm
Acquisition Parameters:	
Resolution	Normal
Dwell time	0.1 s
Channels	1

IC-ICP-MS Determination of Chromium

The ICP-MS is calibrated with prepared standards using the auto sampler. Four calibration points are obtained by analyzing a blank with 18 MΩ DI water, 10-, 25-, and 50-ppb chromium standards. Recommended values for analysis including compounds and peak fitting parameters are shown in Table 3. The standards are checked periodically and the instrument is recalibrated after 5 samples are analyzed. See Figure 1 for example chromatogram. Consult iCAP operating manual for instructions on building calibration curve. After analysis is complete, dispose of remaining solutions in an environmentally safe manner according to applicable regulations.

Table 3

Compounds and peak fitting settings

Cr (III)	Retention Time	143 s
	Tolerance	10 s

Cr (VI)	Retention Time	50 s
	Tolerance	5 s
Smoothing number of points		20
Smoothing number of passes		7
Smoothing method		Moving mean
Peak detection integrator		ICIS
Baseline window		90 s
Area noise factor		6
Peak noise factor		3
Constrain peak width		Yes
Peak height percentage		1
Tailing factor		1

Calculations

All calculations and corrections are performed by Qtegra software. If any dilutions were required, be sure to enter pertinent values in the Qtegra software on the sample list. Enter the mass of the sample (in grams) and the final volume (in mL) on the sample list under the “Amount” and “Final Quantity” columns respectively.

Notes

Acrodisc Premium syringe filter was chosen because it was found to not remove either Cr³⁺ or Cr⁶⁺ from solution. Other syringe filters that were tested were found to remove Cr from solution. If using a different filter, test both species prior to analysis to make sure they are not removed during filtration.

If dilution is required based on total Cr analysis, prior to filtration, add appropriate amount of sample into a 10-mL volumetric flask onto a tared balance and record the sample mass. Fill to the line with water.

Precision

Precision statements were determined on the ThermoFisher Scientific ICS 5000⁺-iCAP Q IC-ICP-MS using UOP Method 999, “Precision Statements in UOP Methods.”

Repeatability and Site Precision

A nested design was carried out for chromium (III) and chromium (VI) (by spiking 15 and 35 ppb of each species) in water by two analysts in one laboratory, with each analyst performing analyses on two separate days, performing two analyses for each chromium species each day for a total of sixteen analyses. Using a stepwise analysis of variance procedure, the within-day estimated standard deviations (esd) were calculated at the concentration means listed in Table 4. Two analyses performed in one laboratory by the same analyst on the same day should not differ by more than the repeatability allowable differences shown in Table 4 with 95% confidence. Two analyses performed in one laboratory by different analysts on different days should not differ by more than the site precision allowable differences shown in Table 4 with 95% confidence.

The data shown in Table 4 is a short-term estimate of repeatability. When the test is run routinely in the field, a control standard and chart should be used to develop better estimates of the long-term repeatability.

Table 4 (15 and 35 ppb spike)
Repeatability and Site Precision, ng/g (mass-ppb)

<u>Sample</u>	<u>Component</u>	<u>Mean</u>	<u>Repeatability</u>		<u>Site Precision</u>	
			<u>Within-Day esd</u>	<u>Allowable difference</u>	<u>Within-Lab esd</u>	<u>Allowable difference</u>
A	Cr (III)	15.34	0.099	0.39	0.131	0.51
	Cr (VI)	15.48	0.083	0.33	0.305	1.85
B	Cr (III)	34.95	0.106	0.42	0.173	0.68
	Cr (VI)	36.48	0.298	1.17	0.307	1.38

Reproducibility

There is insufficient data to calculate the reproducibility of the test at this time.

Time for Analysis

The elapsed time for one analysis is approximately 1.5 hours. The labor requirement for analysis is 1 hours. In groups of up to five samples, the labor requirement is 1 hours for the first analysis and 0.25 hours for each additional analysis up to five analyses.

Suggested Suppliers

Matheson Tri-Gas, 150 Allen Rd. #302, Basking Ridge, NJ 07920, USA, 1-908-991-9200,
www.mathesontrigas.com

Rainin Instrument Co., Mack Road, Woburn, MA 01801, USA, 1-800-472-4646, www.rainin.com

SPEX CertiPrep, Inc., 203 Norcross Ave., Metuchen, NJ 08840, USA, 1-732-549-7144,
www.spexcsp.com

ThermoFisher Scientific, 3175 Staley Road, Grand Island, NY 14072, USA, 1-800-955-6288,
www.thermofisher.com

VWR International, 1310 Goshen Parkway, West Chester, PA 19380, USA, 1-610-431-1700,
www.vwr.com

Pall Life Sciences, 25 Harbor Park Drive, Port Washington, NY 11050, 1-516-484-3600, www.pall.com

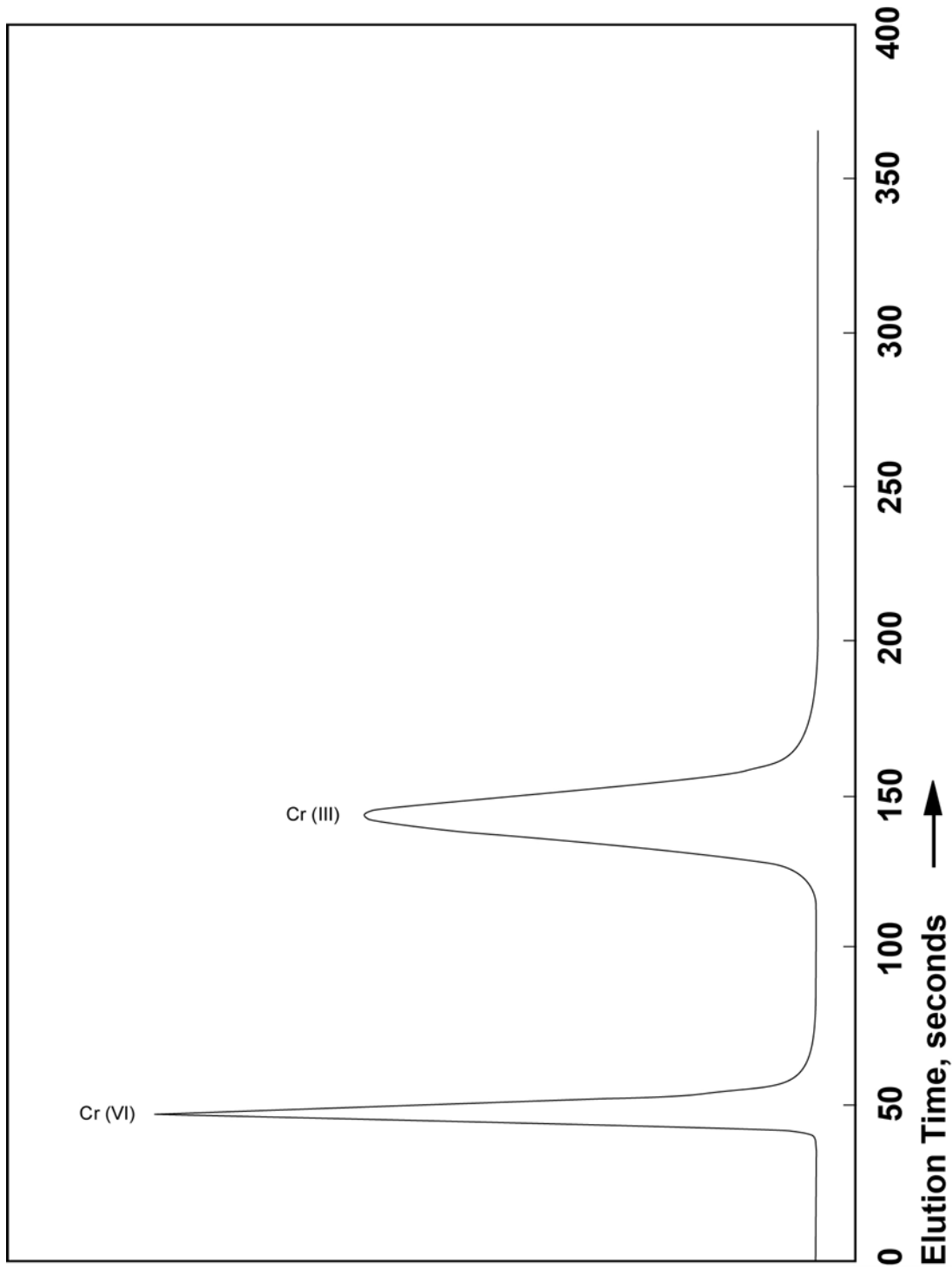


Figure 1

Chromium speciation chromatograph of aqueous solutions of Cr (III) and Cr (VI)