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Chromium Speciation of Drinking Waters by IC-ICPMS

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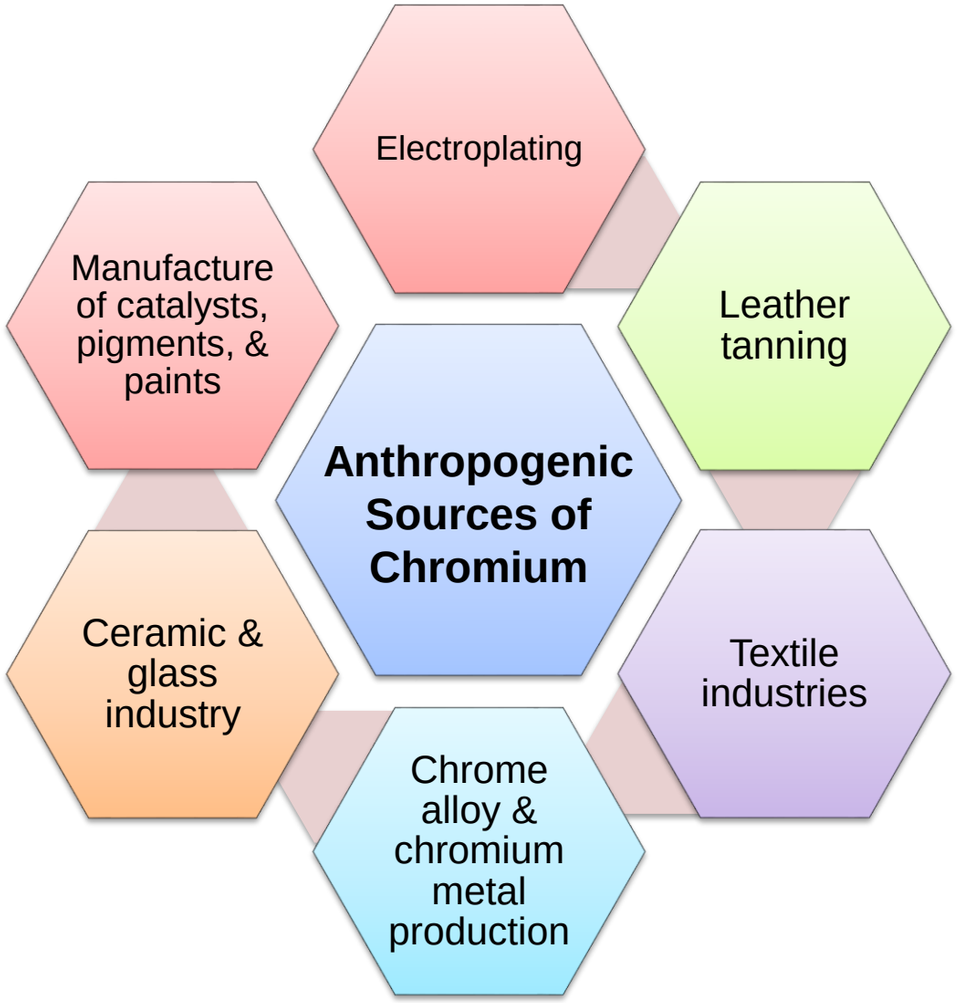
Shimadzu Scientific Instruments

In today's presentation

1. Why Chromium speciation?
2. Current methods
3. New method
4. Results
5. Conclusions & Benefits
6. Q&A

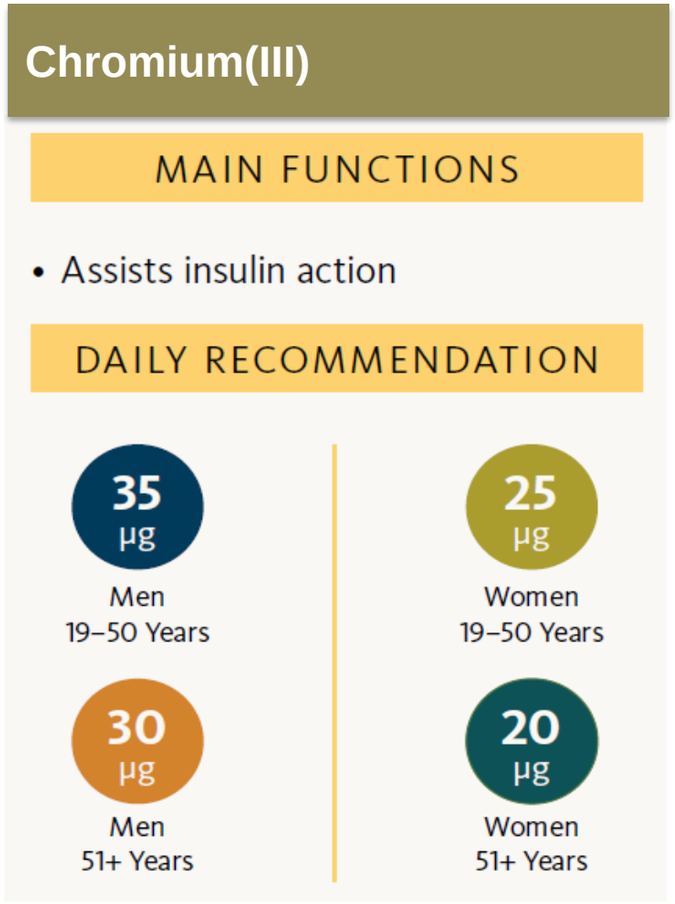
Chromium & Its Sources



- Naturally-occurring element found in rocks, animals, plants, and soil, where it exists in combination with other elements to form various compounds.
- Industrial releases to the air, water, and soil account for the majority of the anthropogenic releases.

  (Johnson et al. The contemporary anthropogenic chromium cycle 2006)
- Occurs in the soluble state in drinking water and mainly presents as Cr(III) & Cr(VI).

Why Chromium Speciation?



- Cr(III) is an essential human dietary element.
- Cr(VI) is an occupational carcinogen, and a reproductive toxicant, and can cause other health issues.

https://www.atsdr.cdc.gov/csem/chromium/standards_and_regulations.html

Chromium Regulations

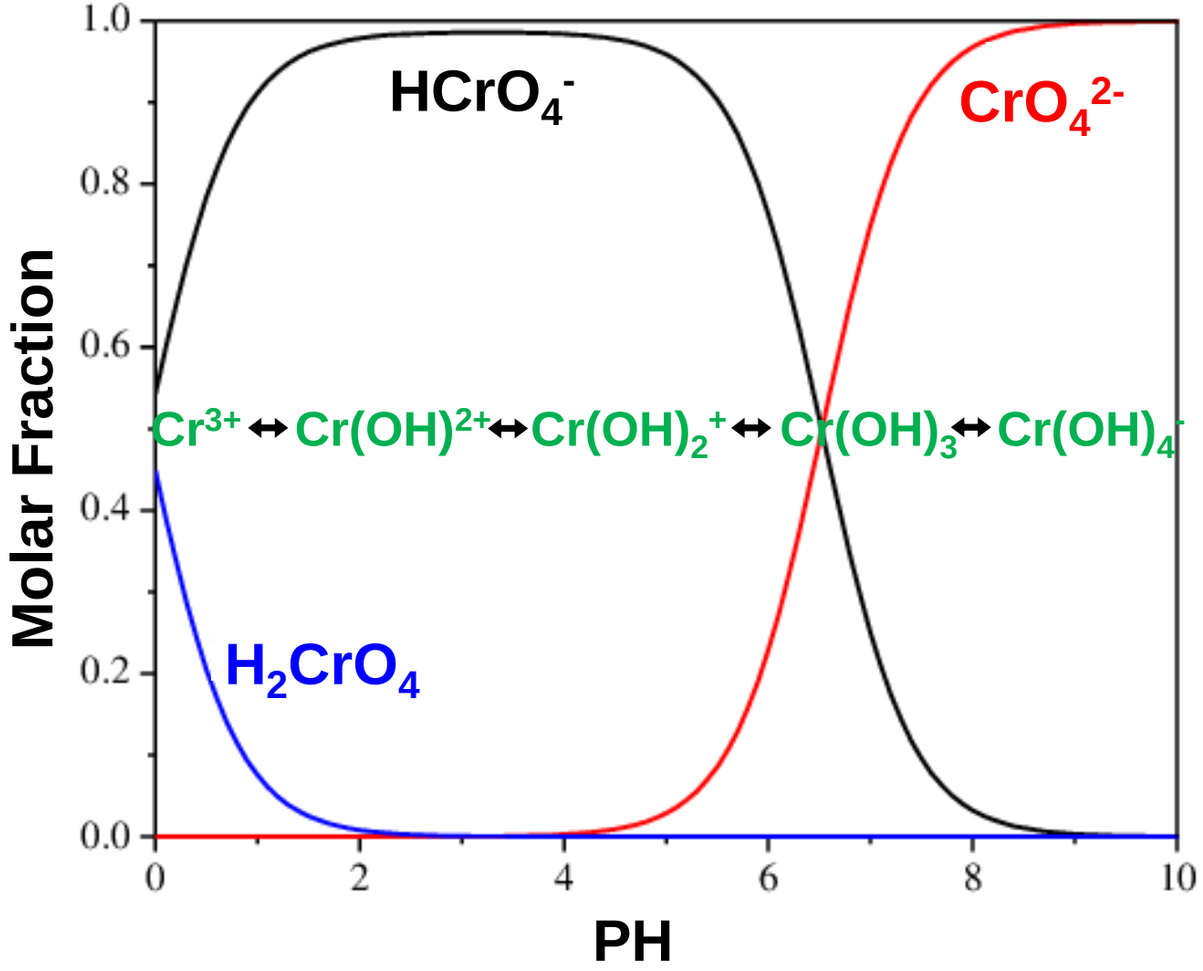
Table 1. Regulations and Guidelines for Chromium

Agency	Focus	Level	Comments
American Conference of Governmental Industrial Hygienists	Air: workplace	10 µg/m³ as Cr	Advisory; TWA* to avoid carcinogenic risk from insoluble Cr(VI) compounds
		50 µg/m³ as Cr	TWA for water-soluble Cr(VI) compounds
		500 µg/m³ as Cr	TWA for chromium metal and Cr(III) compounds
National Institute for Occupational Safety and Health	Air: workplace	1 µg/m³ as Cr	Advisory; TWA (10-hour) for chromic acid and all Cr(VI) compounds
		500 µg/m³ as Cr	Advisory; TWA (10-hour) for chromium metal and Cr(II) and Cr(III) compounds
Occupational Safety and Health Administration	Air: workplace	5 µg/m³ as CrO3/m³	Regulation; PEL† for chromic acid and chromates, (8-hour TWA)
		500 µg/m³ as Cr	PEL for Cr(II) and Cr(III) compounds (8-hour TWA)
		1,000 µg/m³ as Cr	PEL for chromium metal and insoluble compounds (8-hour TWA)
Environmental Protection Agency	Air: environment	Not available	Chromium is listed as a hazardous pollutant
	Drinking water	100 µg/L	Regulation; current MCL‡ for total chromium

- Different regulations established and in development for Total Cr, Cr(III) and Cr(VI).
- **EPA** currently regulates the **total Cr**. Cr(VI) has been under review since 2008.
- Are new regulations and manufacturing practice about PFAS going to change Cr emissions from electroplating industries?

https://www.cdc.gov/niosh/topics/hexchrom/default.html

Chromium Speciation as f(pH)



- Cr(III) typically exists as cationic aqua-hydroxo complexes
- Cr(VI) exists typically as an anionic chromate species
- Interconversion of Cr(III) & Cr(VI) depending on sample conditions (pH)

Methods for Chromium Speciation

	EPA 7196	EPA 218.7	ISO/CD 24384	New method
Target	Dissolved Cr(VI)	Cr(VI)	Cr(III) & Cr(VI)	Cr(III) & Cr(VI)
Method	Colorimetric	IC	LC-ICP/MS	IC-ICP/MS
Samples	EP/TCLP extracts, groundwater, domestic and industrial waste (limited)	Drinking water	Wastewater, surface water, groundwater, or tap waters	Continue in this presentation!
DL	ppm	ppt	ppt	
Limitations	• Interferences • Laborious sample prep • Lack of sensitivity	• Post-column derivatization required	• Chelating pre-treatment • Laborious sample prep	

Instrumentation

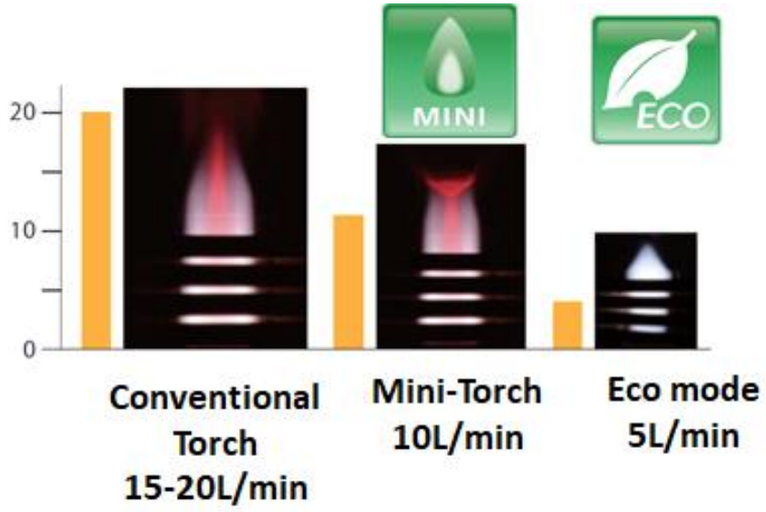
- All analyses were run on a IC coupled to ICPMS.
- The ICPMS is equipped with a collision cell that uses helium (He) to discriminate polyatomic interferences based on kinetic energy.
- Cr was analyzed at 52 m/z with He gas on to remove polyatomic interferences such as ArC and ClOH.

Shimadzu ICPMS-2030

Instrumentation – Inductively Coupled Plasma Mass Spectrometry (ICPMS)

Operating Conditions of ICPMS

Parameter	Setting	Parameter	Setting
Radio Freq. Power	1.20 kW	**Mix Gas**	0.00 L/min
Sampling Depth	5.0 mm	**Cell Gas**	6.0 mL/min
Plasma Gas	8.0 L/min	**Cell Voltage**	-21 V
Auxiliary Gas	1.10 L/min	**Energy Filter**	7.0 V
Carrier Gas	0.70 L/min	**Chamber Temp.**	5°C



- An LC fittings kit was used to connect IC tubing directly to the nebulizer.

Instrumentation – Ion Chromatography (IC)

Shimadzu Prominence IC

- The IC was configured with an inert flow path.

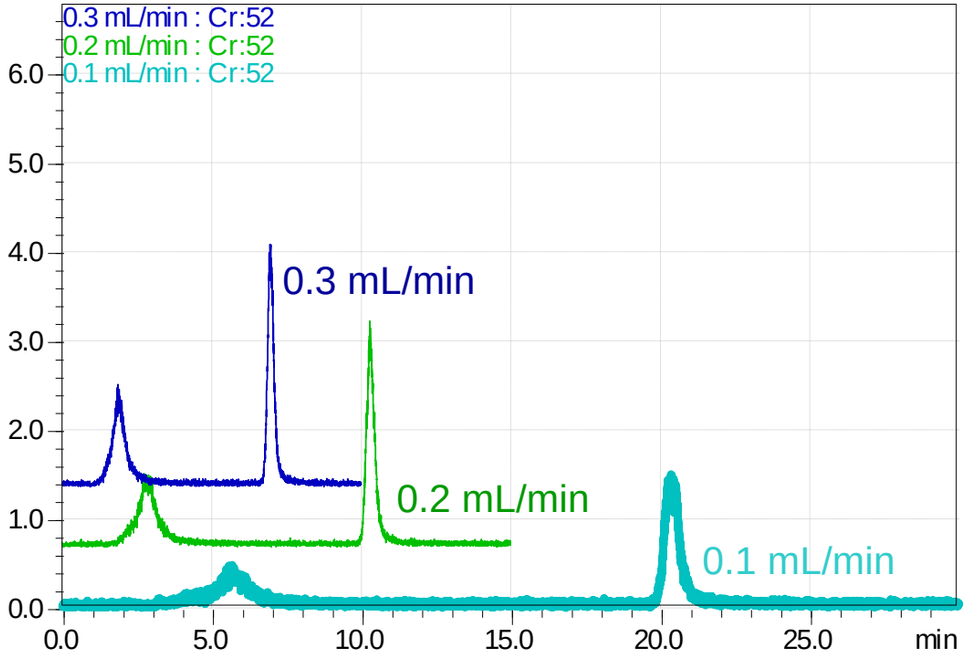
Optimization Studies for Chromatographic Separation of Cr(III) and Cr(VI)

Parameter	Setting	Parameter	Setting
Column	Shodex™ VC-50 2D	**Separation Scheme**	Isocratic
Mobile Phase	6-9 mM HNO_3	**Column Temp.**	30-50°C
pH	2-3	**Injection Volume**	5-100 µL
Flow Rate	0.1-0.3 mL/min	**LC Vials**	Plastic, 1.5 mL

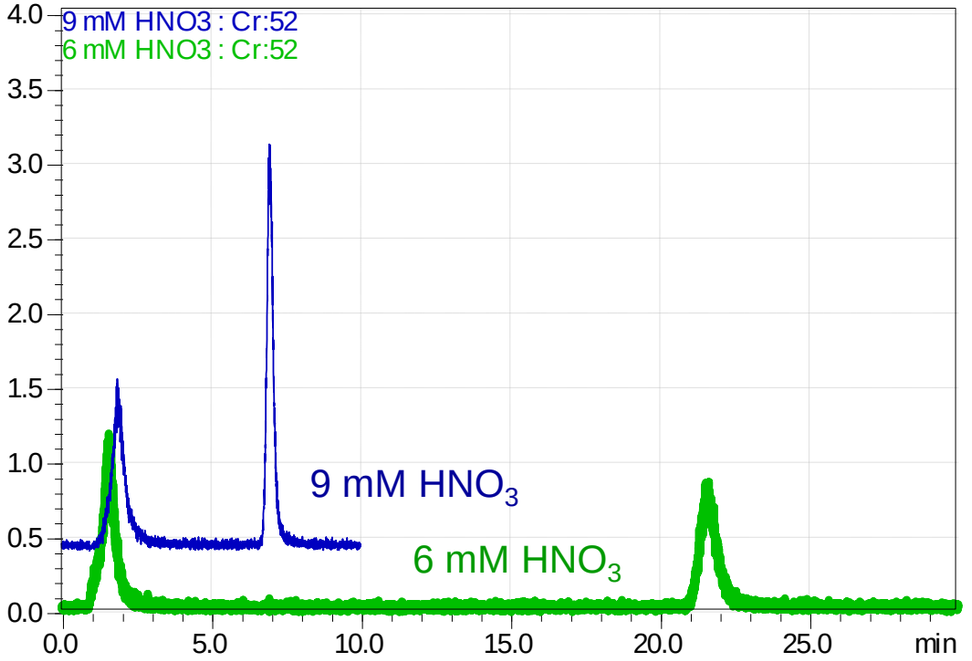
Method - Sample Preparation

- Samples analyzed directly without any pretreatment
  - Tap water
  - Well water
  - Commercially available mixed standards of 22 elements
  - Spiked samples
- Chromium standards
  - Diluting 1000 mg/L stock solutions of trivalent and hexavalent chromium in deionized water
- Mobile phase HNO_3
  - Made from trace metal grade concentrated HNO_3

Results – Optimized Chromatographic Conditions

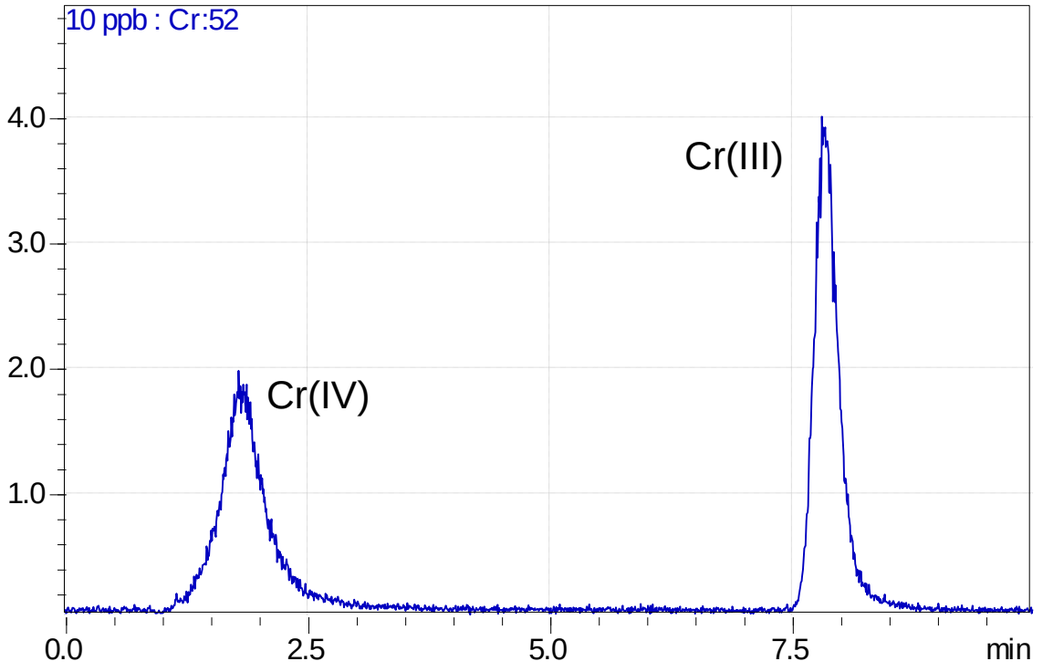


Chromatograms at different flow rates



Chromatograms with different concentrations of mobile phase

Results – Optimized Chromatographic Conditions



Chromatogram of 10 ppb Cr(III) and Cr(VI)

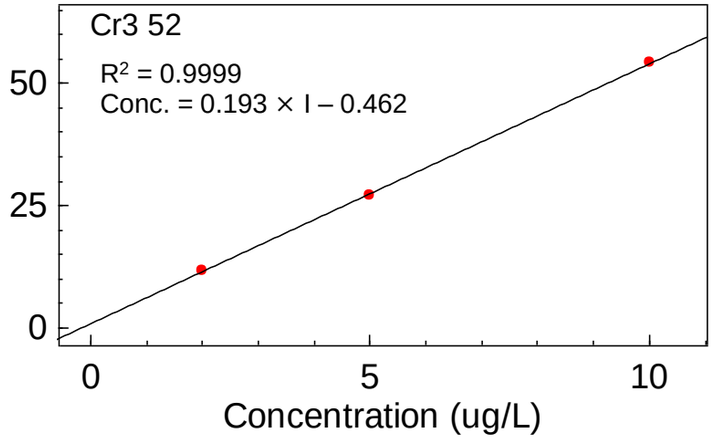
- Chromium species, Cr(III) and Cr(VI), are well separated and elute within 10 minutes.

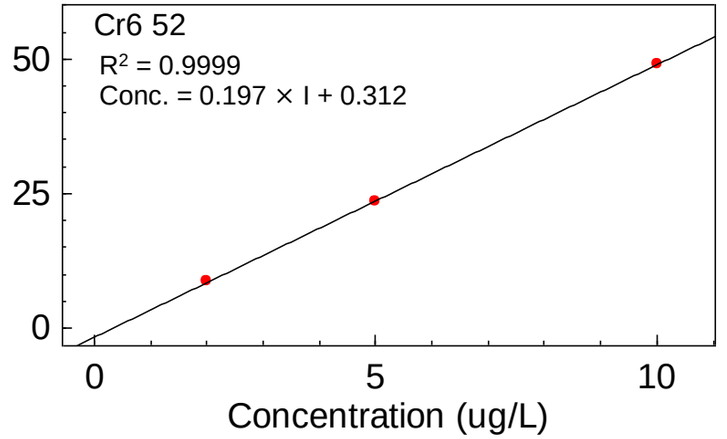
Operating Conditions of IC

Parameter	Setting
Column	Shodex™ VC-50 2D
Separation Scheme	Isocratic
Mobile Phase	9mM HNO_3
Column Temp.	50°C
pH	2.0
Injection Volume	20 µL
Flow Rate	0.3 mL/min
LC Vials	Plastic, 1.5 mL

Results – Calibration Curves

Calibration curves of Cr(III) and Cr(VI) in the range of 2-10 µg/L





Characteristics for Chromium Speciation Determined

	Cr(III)	Cr(VI)
Retention Time (min)	7.79	1.84
Limit of Detection (µg/L)	0.20	0.35
Limit of Quantitation (µg/L)	0.67	1.67
Correlation Coefficient (R^2)	0.9999	0.9999
Equation	Conc. = 0.193 × I -0.462	Conc. = 0.197 × I + 0.312
Residual Range (µg/L)	-0.005 - 0.001	-0.03 - 0.02
Relative Standard Error (RSE, %)	0.05	1.22

Results – Sample Analysis

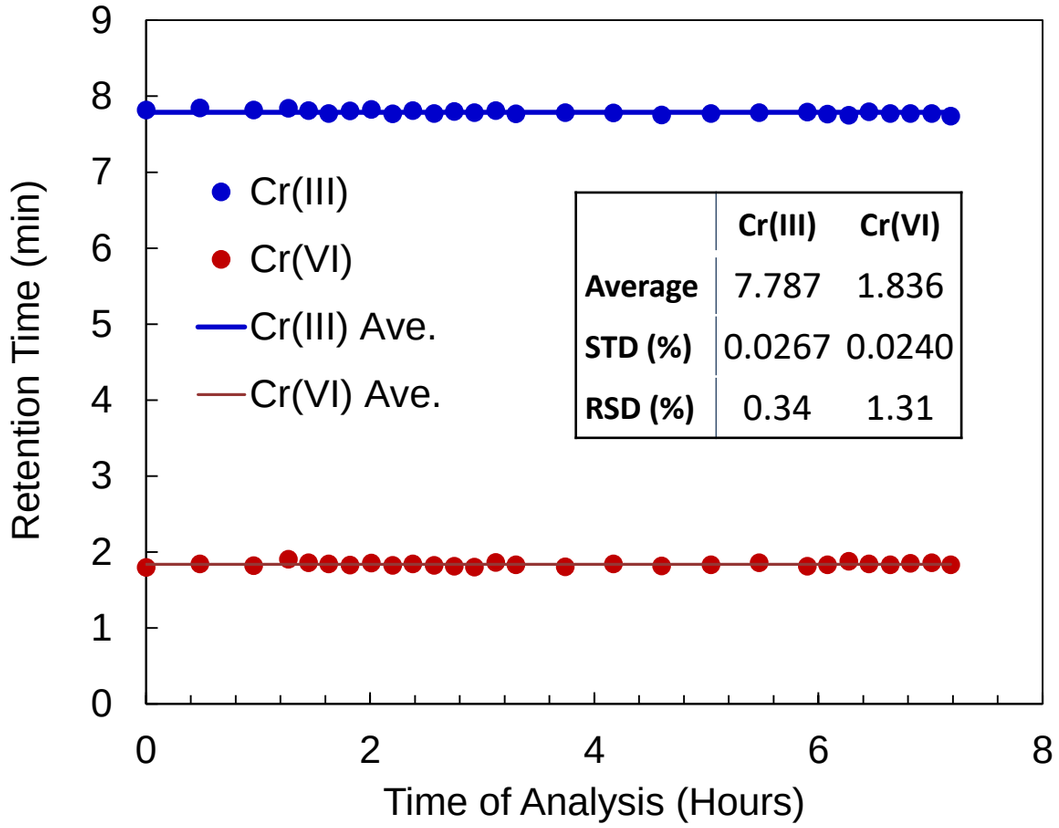
Concentrations of Cr in µg/L in Original and Fortified Samples as well as Recovery Yields in Percent

Sample	Cr(III)	Cr(VI)
Tap water	n.d.	n.d.
Fortified tap water	5.05	5.16
Recovery (%)	**101**	**103**
Well water	n.d.	0.738
Spiked well water	5.15	5.61
Recovery (%)	**103**	**97**
Commercial Standard	3.92	n.d.
Fortified commercial standard	9.06	4.77
Recovery (%)	**103**	**95**

n.d. = not detected. Cr(III) < 0.20 µg/L, Cr(VI) < 0.35 µg/L.

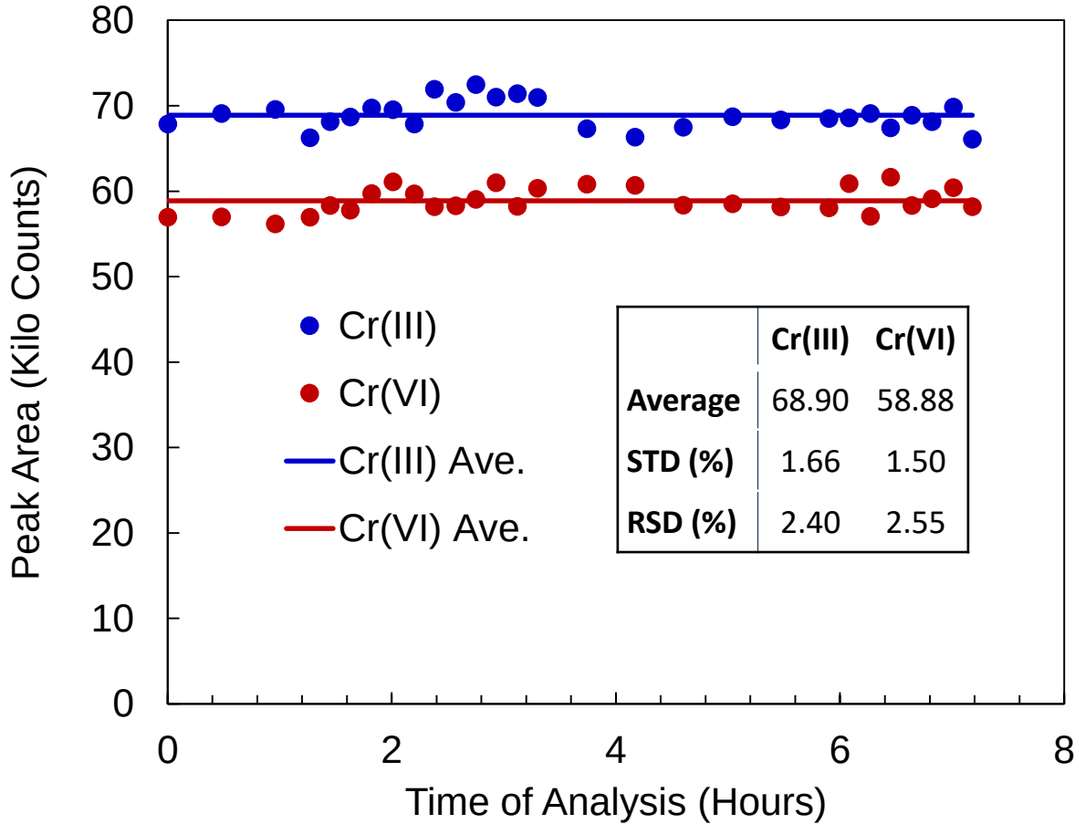
Results – Instrument Stability & Precision

Variation of Retention Time for Multiple Injection of 10 µg/L Cr(III) and Cr(VI) Standard Over 7 Hours



	Cr(III)	Cr(VI)
Average	7.787	1.836
STD (%)	0.0267	0.0240
RSD (%)	0.34	1.31

Variation of Peak Area for Multiple Injection of 10 µg/L Cr(III) and Cr(VI) Standard Over 7 Hours



	Cr(III)	Cr(VI)
Average	68.90	58.88
STD (%)	1.66	1.50
RSD (%)	2.40	2.55

Conclusions

- ICPMS coupled with IC provides excellent sensitivity, precision, accuracy, stability, fast time response and high sample throughput for determination of chromium speciation in waters.
- The use of 9 mM nitric acid other than salt solutions as mobile phase reduces background signal and possible interference.
- The use of a column to separate both cations and anions enables fast separation of chromium speciation without any sample pretreatment with complexing agents.
- Eliminating sample preparation avoids any possible risk of contamination as well as maximizes sample throughput.

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