



Applied Speciation

Analysis Research Consulting

Trace Analysis of Hexavalent Chromium using IC-ICP-DRC-MS

Hakan Gürleyük, Ph.D.

hakan@appliedspeciation.com



APPLIED SPECIATION
www.appliedspeciation.com

info@appliedspeciation.com

Who is Applied Speciation?

- Started in 2005 in a 1000 sqft warehouse space
 - 17,000 sq ft state-of-the-art laboratory since 9/09
 - 4 Elan DRCII, 3 Elan 6000s
 - PE Series 200 HPLC systems, Various Dionex IC Systems, Clarus 600 GC-ICP-MS Interface
 - Access to Agilent 6520 Q-TOF , Bruker MALDI TOF-MS
- Provide routine analyses for compliance purposes (NELAC, CLIA Certified, FDA Compliant)
- Routinely perform research to understand limitations of compliance methods and rectify them
- Routinely perform internal and contract research to better understand the chemistry in the presented sample
- Internal Seminars, Internal Poster competitions
- Strong dedication to client satisfaction and data quality



Analytical Methods for Cr(VI) Analysis

- Method 7196: Colorimetry

- Colorimetric method is prone to interferences. (False positives (Mo, V, Hg) and MnO_4^- , Turbidity, Organic matter)

- Method 7199/218.6: Ion Chromatography - UV

- Ion chromatography is used to separate Cr(VI), detection is achieved by a post column reaction with diphenyl carbazide

- Various preconcentration methods

- Followed by colorimetry, FAAS, ICP-AES, ICP-MS detection
- Preconcentration methods are operationally defined which means what works on one specific matrix may fail on another...



Evolution of IC-UV Methods

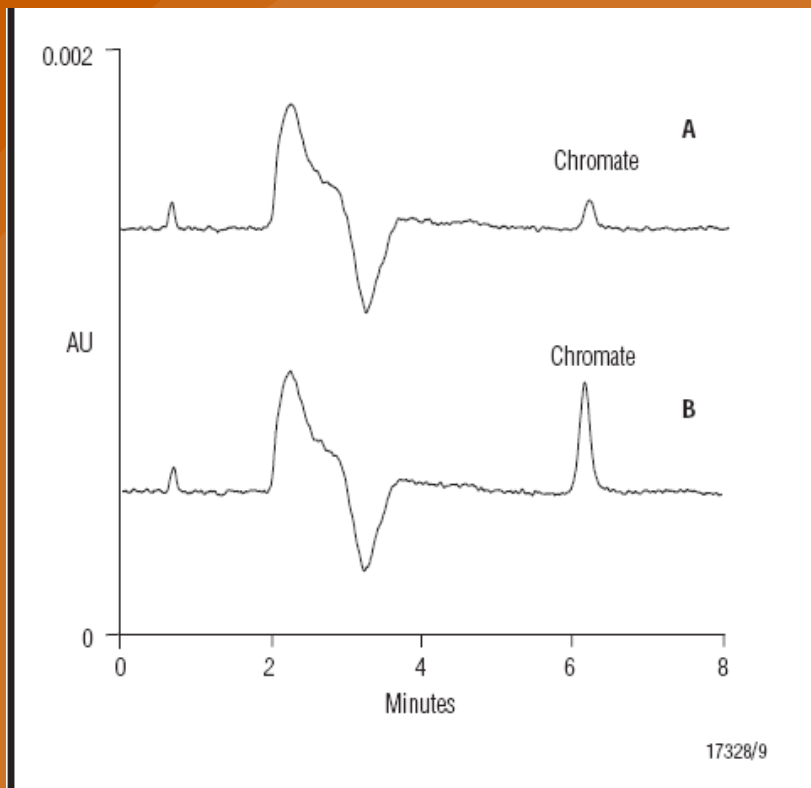


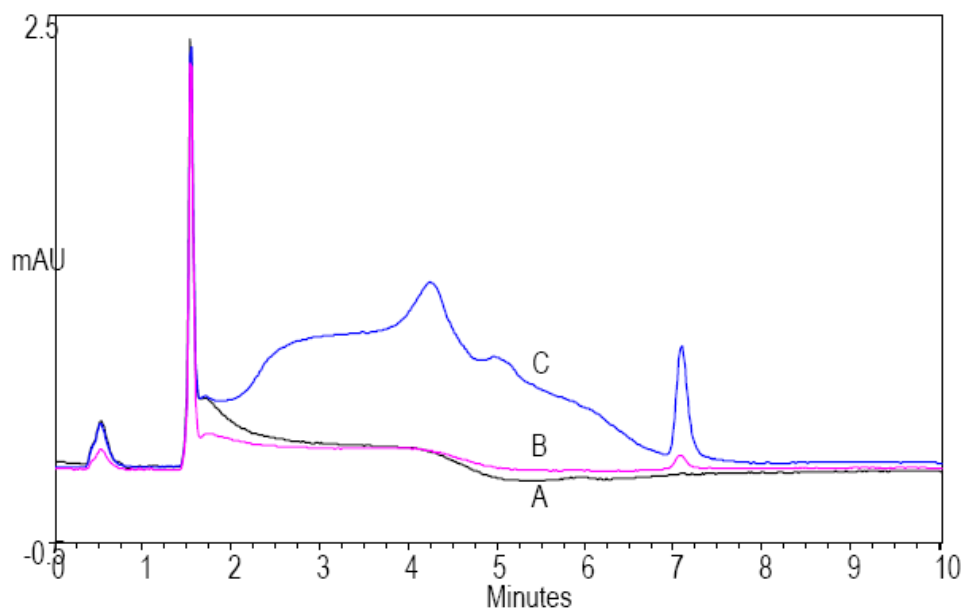
Figure 5. Determination of chromate in drinking water. Conditions: as for Fig. 3, except sample, buffered Sunnyvale, CA drinking water (A) and drinking water spiked with 0.2 µg/L chromate (B); peaks, (A) chromate (0.055 µg/L) and (B) chromate (0.245 µg/L)

- Dionex AS7 4mm Column
- 1mL injection loop
- Detection limit = 0.018ppb



The new method (DL = 0.001ppb)

Cr(VI) Analysis using 2 mm format



Column: IonPacNG1 (2 x 50 mm),
AS7 (2 x 250 mm)
Eluent: 250 mM (NH₄)₂ SO₄,
100 mM NH₄OH
Flow: 0.36 mL/min
Inj. Vol: 1000 µL

Post Column Reagent:
2 mM diphenylcarbazide
10% methanol
1N sulfuric acid

Reaction Coil: 125 µL

A) DI water blank
B) 0.007 µg/L Cr(VI) in DI water
C) Sunnyvale, CA drinking water
0.05 µg/L



AS7 Column Properties

Table 1 IonPac AS7/AG7 Packing Specifications					
Column	Particle Diameter μm	Substrate X-linking %	Column Capacity μeq/column	Functional Group	Hydrophobicity
AS7 4 x 250 mm	10.0	2	100	Alkyl quaternary ammonium	Medium-High
AG7 4 x 50 mm	10.0	2	25	Alkyl quaternary ammonium	Medium-High
AS7 2 x 250 mm	10.0	2	25	Alkyl quaternary ammonium	Medium-High
AG7 2 x 50 mm	10.0	2	6.25	Alkyl quaternary ammonium	Medium-High

The 2mm AS7 Column has 1/4th the capacity of the 4mm AS7

The 4mm AS7 Column has a total internal volume of 3.14 mL

The 2mm AS7 Column has a total internal volume of 0.79 mL

The new and improved method injects 1mL of buffered sample

Not much different than injecting 4mL sample onto a 4mm AS7 column



Matrix Effects for Blanks?

- Most samples contain significant amounts of Ca, Mg, and transition metals such as Fe, Mn, and Al
 - 85% of drinking waters in USA are Hard Waters (>60ppm Ca, Mg)
- Some samples (wastewaters) can contain significantly higher concentrations (upto10,000ppm Ca+Mg for FGD Wastewaters)
- Single injection of a Drinking Water sample may introduce 60ug of Ca
- Single injection of an FGD wastewater may introduce 10mg of Ca and Mg into the column

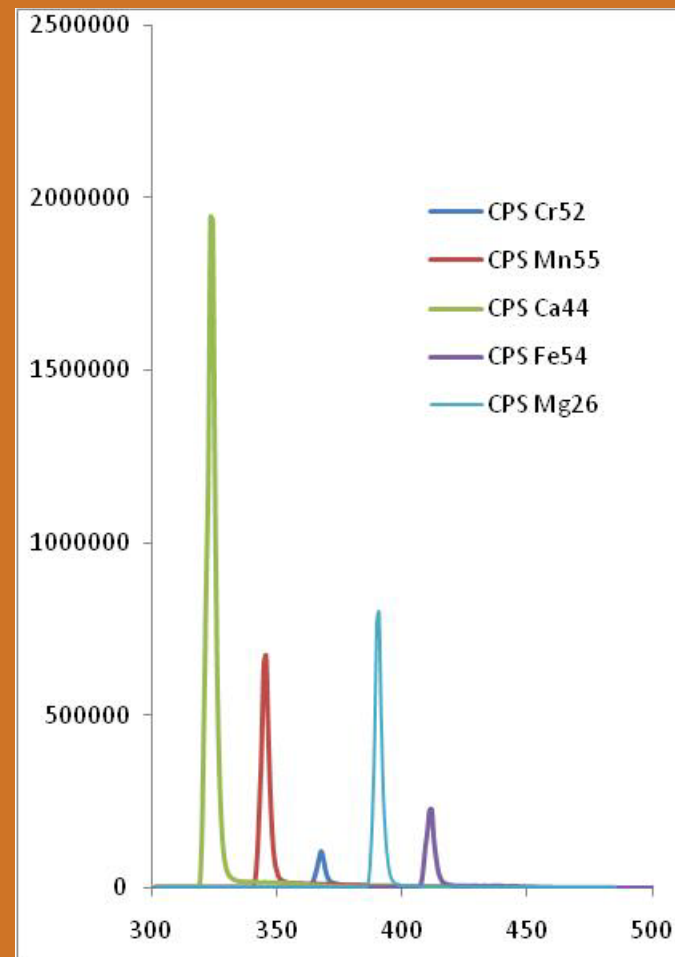


Blank Issues

	Cr(VI) Concentration
Blank Before Samples	0.001 ppt
Blank After 30-40 WW samples	0.018 ppt

Injection of 10% HNO₃ solution after the samples

Percent levels of Ca and Mg removed from column



Cr(VI) Analysis using IC-ICP-MS

JAAS

FULL PAPER

Determination of chromium(III) and chromium(VI) using suppressed ion chromatography inductively coupled plasma mass spectrometry†

Hakan Gürleyük* and Dirk Wallschläger

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First published as an Advance Article on the web 6th August 2001

Table 1 Comparison of detection limits for chromium speciation analyses by LC-ICP-MS (not corrected for injection volume)

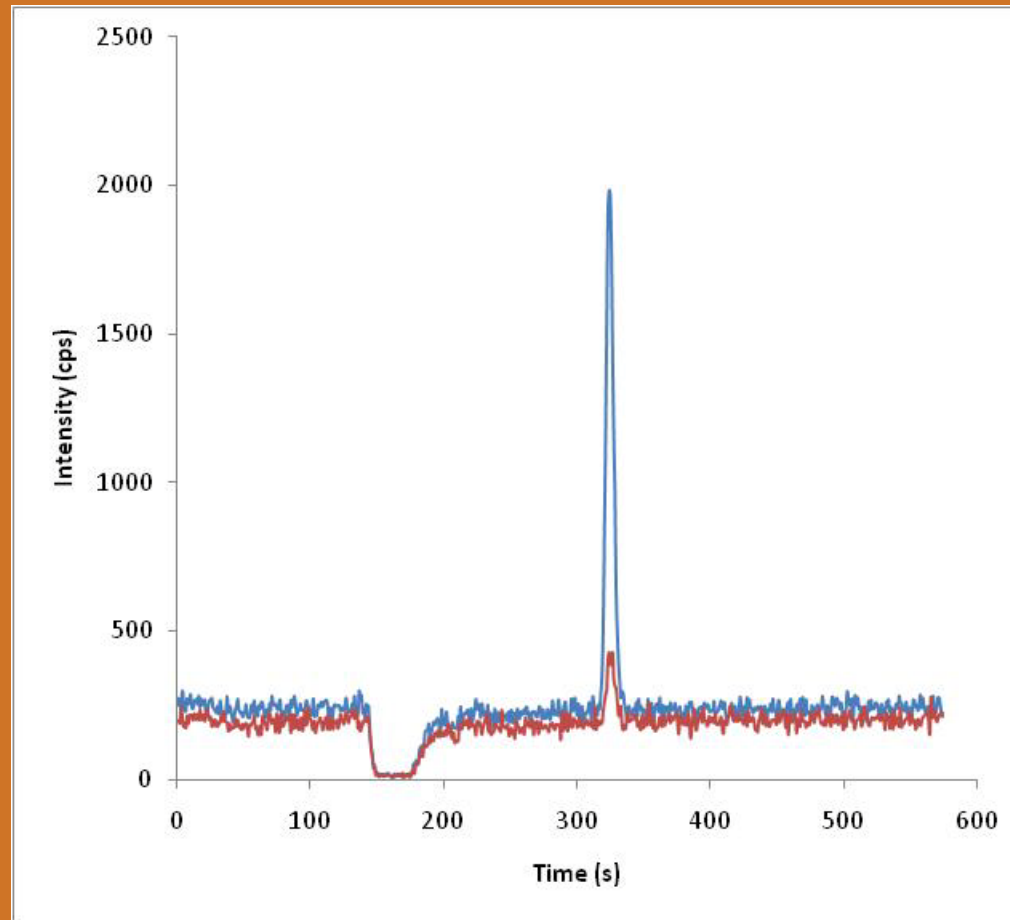
Technique	Detection limit/ng L ⁻¹		Ref.
	Cr(III)	Cr(VI)	
IC-ICP-MS	400	1000	11
IC-HHPN-ICP-MS	100	200	12
IC-ICP-MS	300	500	13
IC-ICP-MS	330	440	16
HPLC-DIN-ICP-MS	60	180	17
IPC-ICP-MS	300	300	25
IC-ICP-MS	5	12	This work

Providing less than 10ppt detection limits for the last 10 years utilizing ion chromatography coupled to an ICP-MS

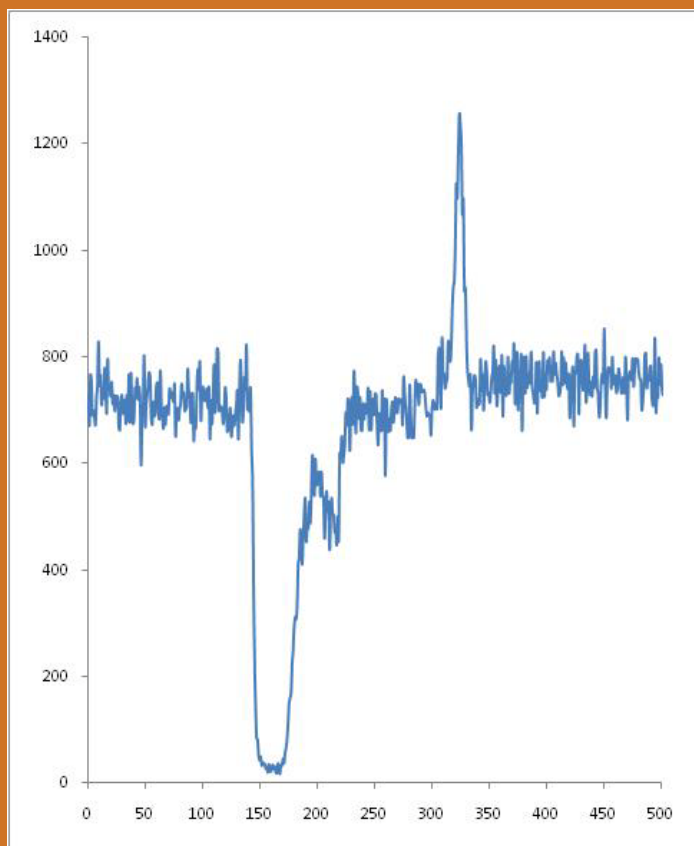


Hexavalent Chromium by IC-ICP-MS

10ppt Cr(VI) standard vs. Blank



Actual Samples



An Actual Ground Water
Sample containing 3.6ppt of
Hexavalent Chromium



Cr(VI) Problems DW Utilities Face

Sample ID	Cr(VI)	Units
Source Water 1	0.017	µg/L
Treated DW 1	0.134	µg/L
Source Water 2	0.021	µg/L
Treated DW 2	1.37	µg/L

Sample ID	Cr(VI)	Units
Lime Source 1	14.5	mg/kg
Lime Source 2	1.76	mg/kg

For some utilities, the problem arises from their treatment system

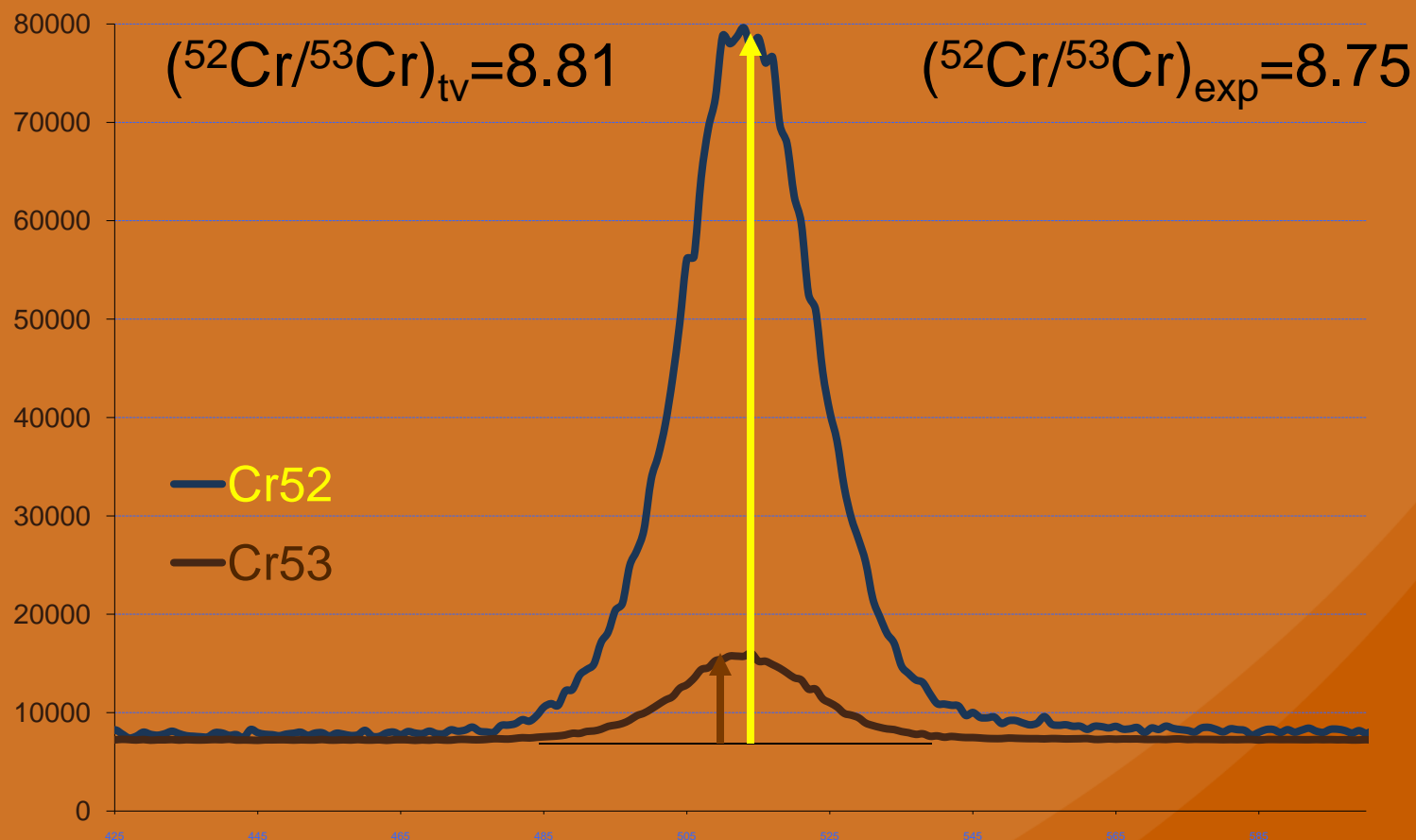


Field Spikes

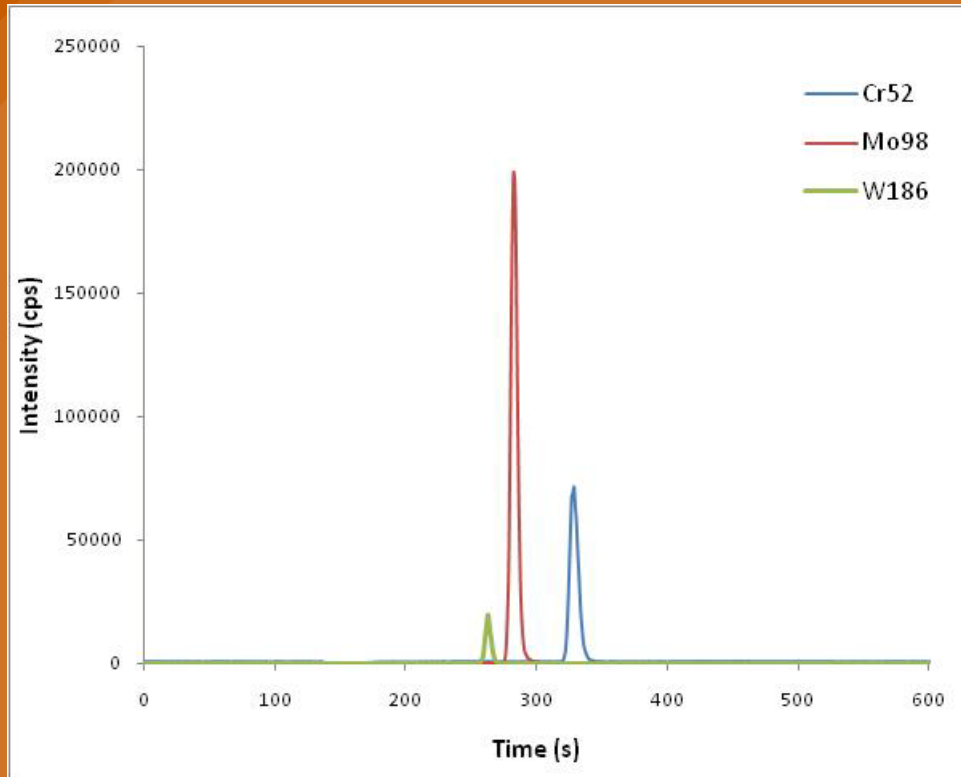
- Applied Speciation also utilizes field spikes to confirm preservation of species information.
- A stock solution of Cr(VI) standard is added to specific samples
- These samples are analyzed to determine if any oxidation or co-precipitation reactions occur during sampling and shipping



Identification by Isotopic Ratios



Internal Standards?



Molybdate and Tungstate as
Internal Standards

Best Internal Standard is the
enriched $^{53}\text{Cr(VI)}$ but they
have $^{52}\text{Cr(VI)}$ impurities



Cr(VI) in Soils and Sediments

- Method 3060a for extraction
 - Alkaline extraction that stabilizes Cr(VI)
- Oxidation and/or reduction can happen concurrently
- ASC utilizes Cr(III), Cr(VI), and $\text{Pb}(\text{CrO}_4)_2$ spikes
 - MDL for 3060a/7199 = 0.0013 mg/Kg
- We can also perform Speciated Isotope Dilution Mass Spectrometry
 - Uses enriched Cr isotopes
 - Legally defensible
 - Applied Speciation is one of only 2 labs in the world certified to perform this method



Isotope Dilution Mass Spectrometry (IDMS)

- Has been around for a long time
- Applicable to a variety of elements
 - Pb, Hg, U, Re, Fe, Zn
- DRC technology offers unique advantages
 - Collisional Damping of the ICP noise in the dynamic reaction cell
 - This damping allows precise measurement of isotope ratios on a sequential quadrupole analyzer.
 - Internal precision is shown to be limited by counting statistics only.

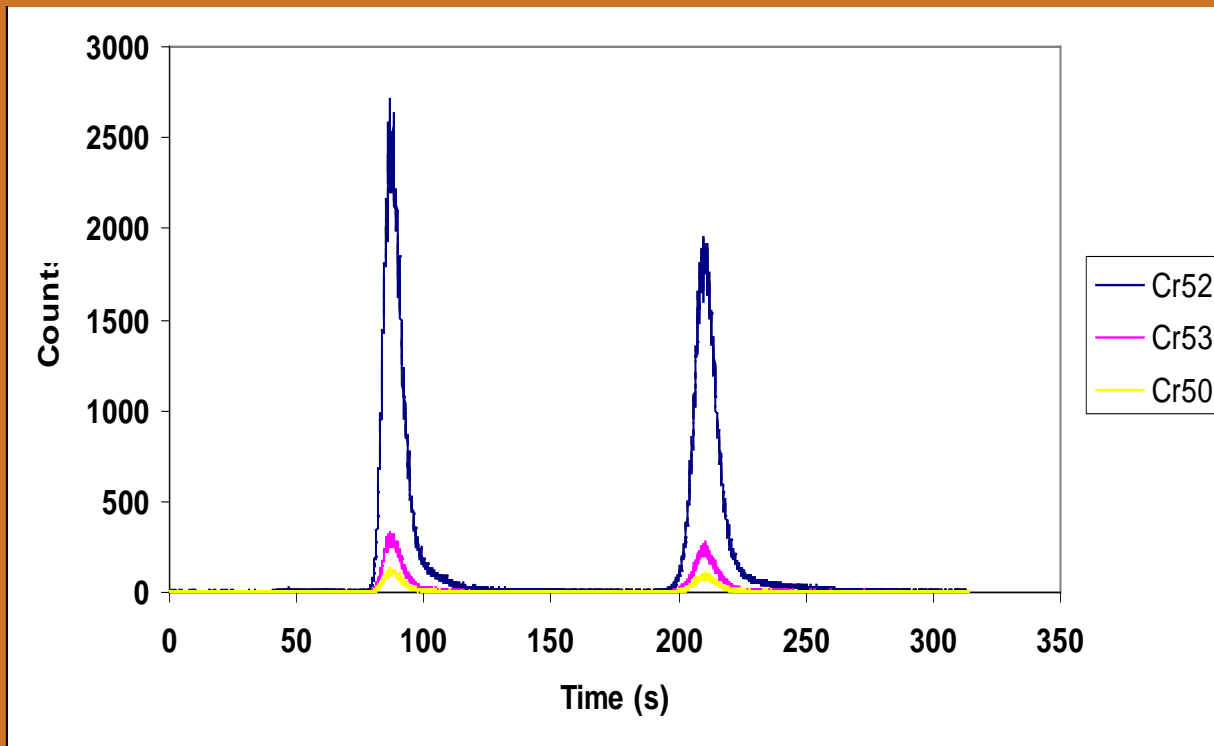


Speciated Isotope Dilution Mass Spectrometry (SIDMS)

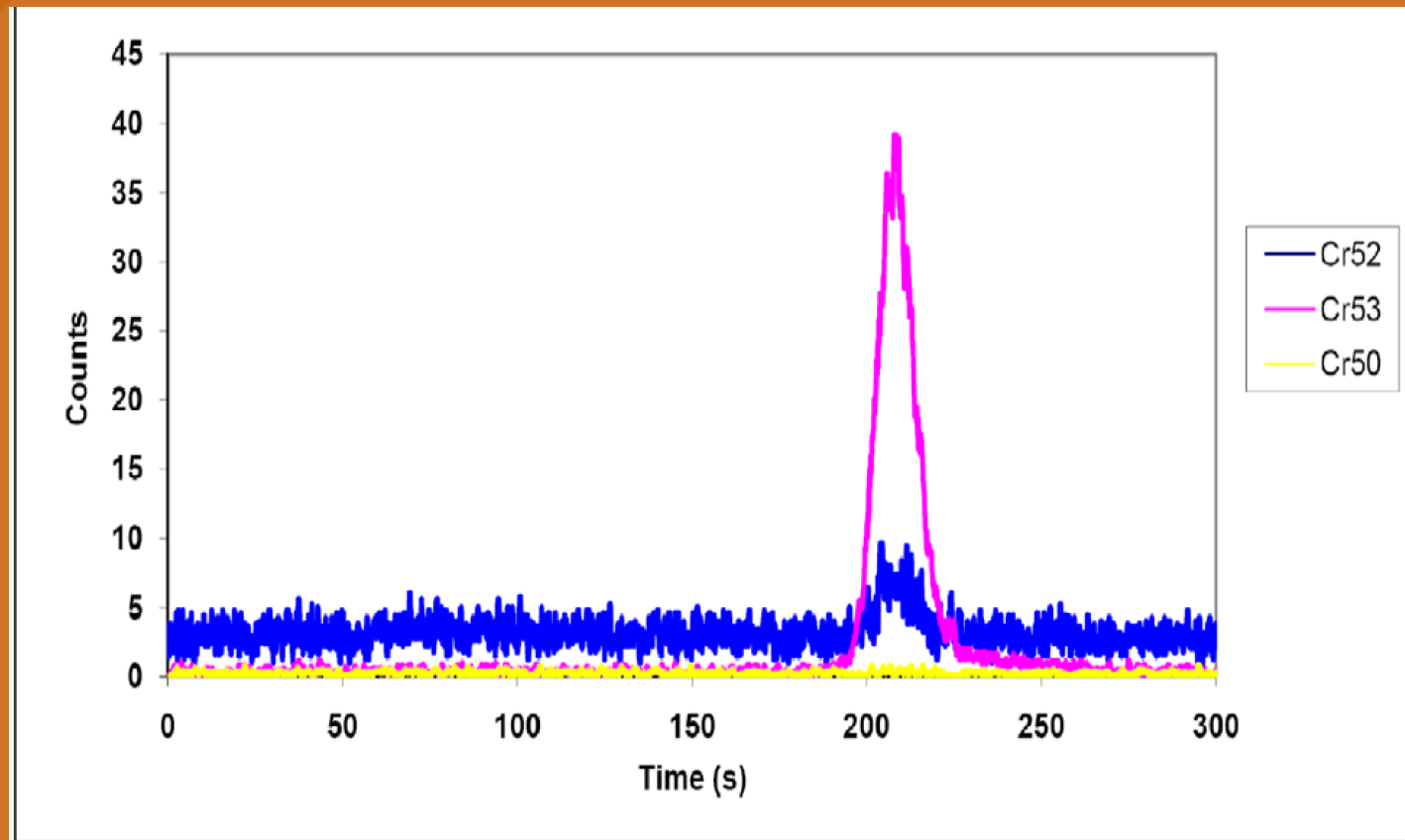
- Traditional speciation methods attempt to hold each species static while making the measurement.
- In SIDMS, each species is “labeled” with a different isotope-enriched spike in the corresponding species form.
- Thus, the interconversions that occur after spiking are traceable and can be corrected.
- SIDMS is also a diagnostic tool that permits the evaluation of species altering procedures and permits evaluation and validation of other more traditional speciation analysis methods.



Separation of Cr(III) and Cr(VI)



Isotopically enriched Cr(VI) standard

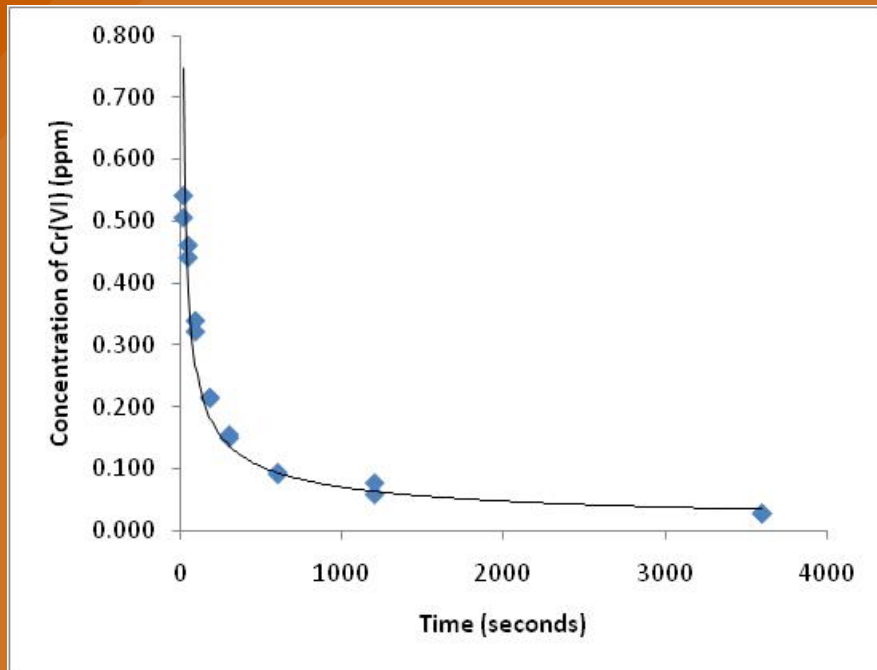


What is needed?

- License from Applied Isotope Technologies to use the SIDMS method
- Isotopically enriched Cr(III) and Cr(VI) standards
 - $^{50}\text{Cr(III)}$ and $^{53}\text{Cr(VI)}$
 - EXPENSIVE!!! ~ \$4,000,000 per gram
- IC method that can separate Cr(III) and Cr(VI)
- ICP-DRC-MS that can accurately monitor all 3 Cr isotopes (m/z 50, 52, 53)



Fate of Cr(VI) After Ingestion



- Human Gastric Fluid (diluted 10X) from a volunteer
- Spiked with 1ppm of Cr(VI) at $t=0$
- At each time point, an aliquot is collected and spiked with enriched Cr(III) and Cr(VI) standards



Is it perfect?

- Nothing is perfect!
- The method requires that the added spike concentrations are within 0.1 – 10 times the native concentration of each species
 - Need to somehow know approximate concentrations of each species before analysis
- If there is 100% conversion, the concentration can not be calculated
 - For extremely reducing or oxidizing samples, it may not work



Conclusions

- Instead of patching the problem, we should try to fix it once and for all...
- ICP-MS is a powerful technique
 - Has been used for speciation analysis of As, Se, Cr, Hg, V, Sb, Sn, Pb for the last 20 years.
- Every lab seems to have at least one or two ICP-MS instruments...
 - Only people crazy about providing the highest quality data will dedicate an \$150K instrument for Cr(VI) analysis ...
- IC-ICP-MS can achieve the detection limit requirements without jeopardizing data quality
- IC-ICP-MS has the capability of incorporating important QA/QC measures that ensure data quality
- Experience is very important
 - Knowledgeable project managers, experienced analysts who are familiar with the chemistry of metals and metalloids, Knowledge of both IC/LC and ICP-MS systems, Analysts that can interpret and report the data



Acknowledgements

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