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Analysis for Arsenic and Hexavalent Chromium:

How to avoid false positives and increase data quality

Michelle Briscoe, CEO/President
Hakan Gürleyük, Technical Director
Brooks Rand Labs

Presented April 29, 2015
DoD EMDQ Workshop
Portland, OR

EXCITING ANNOUNCEMENT!

Brooks Rand Labs & Applied Speciation Officially Merged on April 1st!

We will be operating as Brooks Rand Labs as we transition and consolidate into **Brooks Applied Labs** later this year.

Combining our resources to offer an even more comprehensive selection of cutting-edge methods for specialty trace metals and metals speciation

What this Means for You:

- Additional capacity for faster turnaround times
- Added technical capabilities to help you achieve your project goals
- Outstanding customer service through our combined project management staff
- Highest quality data available, supported with an unparalleled internal 3-tier data review process
- All staff from both companies have been retained, ensuring a seamless transition
- Stronger internal research group focused on analytical method development and optimization
- Still a small business enterprise (SBE)

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Total Arsenic

Some labs that utilize HG-AFS, HG-AAS and GF-AAS for total arsenic determination

- May not be TOTAL As
- QA/QC pitfalls = legally indefensible data

ICP-MS should be the first choice for total As analysis

- Wide elemental coverage - virtually all elements can be measured by ICP-MS
- Performance - high sensitivity and low background signals combine to give very low detection limits (sub-ng/L – parts-per-trillion (ppt) in most cases)
- Fast analysis times – with a high speed scanning quadrupole analyzer, measurement of a full suite of elements takes only minutes

Interferences in ICP-MS

Isobaric interferences

- Direct overlap from a different element with an isotope at the same nominal mass (isobars) – known as an isobaric interferences

Polyatomic interferences

- Overlap from a polyatomic ion formed from the combination of species derived from the plasma gas, sample solvent and/or sample matrix e.g. $^{40}Ca^{16}O$ overlap on ^{56}Fe

Matrix interferences

- Presence of matrix components that can enhance or depress the signal for the target analyte (carbon signal enhancement effect on As)

>90% Q-ICP-MS sold with Collision/Reaction Cells

Interferences on Arsenic

Element	Interferences
As	ArCl, CaCl, CoO, ArK, Carbon, Nd^{++}, Sm^{++}, SeH, BaO^{++}, Zr, CaO_2

Interference Removal Technologies

Dynamic Reaction Cell (DRC) Technology is patented by Perkin Elmer instruments
PE ELAN DRCe DRCplus DRCII and Nexion

Reactive Gases NH_3, O_2, CH_4

Collision/Reaction Cell Technology
Agilent and Thermo
Agilent 7500, 7700, 7900
Thermo iCAP Q, X series

Collision Mode NON-Reactive Gas He
(Kinetic Energy Discrimination)
Reaction mode H_2

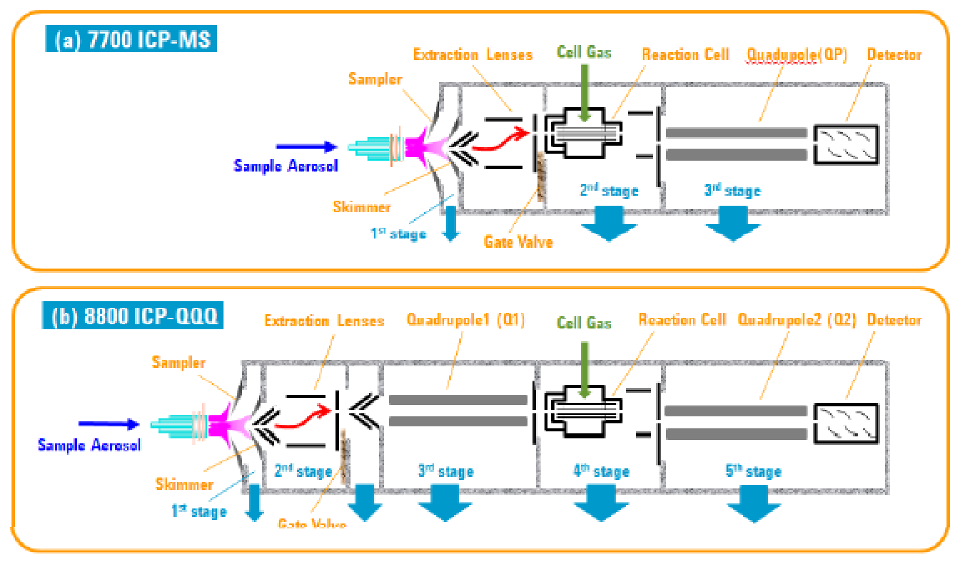
High Resolution ICP-MS
Thermo Element 2, NU Attom

Separation of Polyatomic Interferences
Using Magnetic Sector Field

Triple Quad ICP-MS
Agilent 8800

NON-Reactive Gases He, Xe
Reactive Gases NH_3, O_2, H_2
Controlled Rxn MS/MS Mode

How does ICP-QQQ-MS Work?



With MS/MS, reaction processes in the cell are consistent and predictable, even if sample composition is complex or variable

Consistent cell conditions means reaction mode method development is much easier than on single quad (same method can be used for different samples)

Rare Earth Elements

Not so rare?

Samarium (Sm) is the 40th most abundant element in the Earth's crust and is 3x more common than arsenic.

Although neodymium (Nd) is classed as a "rare earth", it is a fairly common element, no rarer than cobalt, nickel, or copper.

Interferences from doubly charged species are enhanced in the Collision Cell mode of ICP-MS analysis.

- Doubly-charged ions have double the mass of singly-charged ions at the same m/z; therefore, they have double the kinetic energy, assuming the same velocity.

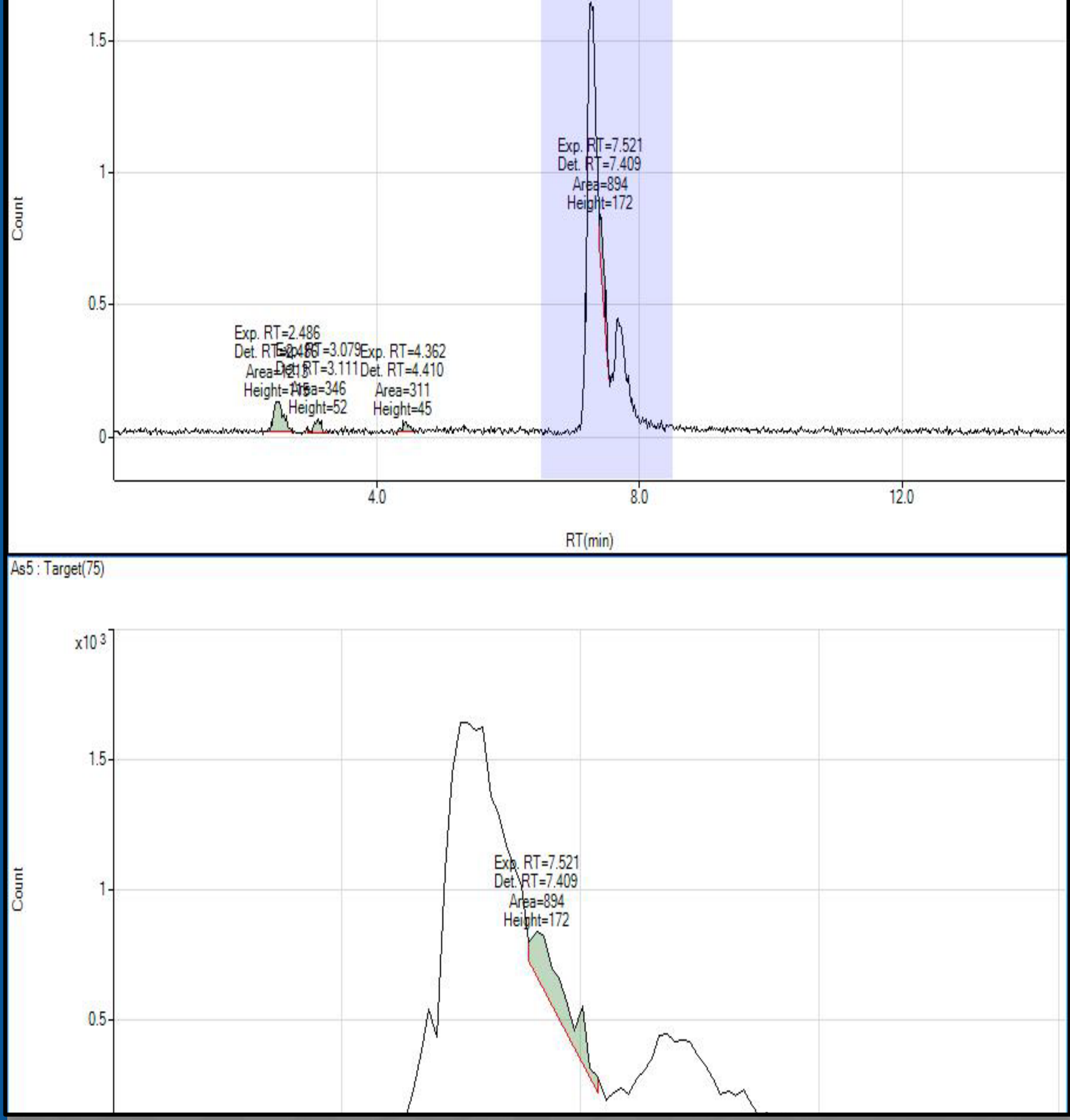
Arsenic treatment doesn’t work???

Client was trying to treat for As, but the treatment was not working.
They requested As Speciation Analysis, which showed << 1 µg/L As.

	Other LAB CRC	CRC (He)	QQQ (O_2)	DRC (O_2)	[Nd]	[Sm]
Sample Name	ppb	ppb	ppb	ppb	ppb	ppb
XX-S	**19.9**	**8.10**	**0.068**	**0.242**	**259**	**46.3**
XX-S Dup		**8.61**	**0.057**		**255**	**45.3**
YY-S	**134**	**73.0**	**0.425**	**1.09**	**2497**	**446**
YY-S Dup		**77.3**	**0.372**		**2406**	**404**

The interference can not be identified unless ^{150}Nd is monitored.
Need to have the QA/QC protocols to identify issues.

INTERFERENCES CAN ALSO AFFECT SPECIATION DATA



Inexperienced operators may miss that the big peak is due to Nd^{++} eluting very close to the As(V) peak. The peak after As(V) is from Sm^{++}.

Suggestions…

Never trust a single isotope or a single mode

- Isotopic match = defensible data
- Always collect more data than needed (monitor elements that can possibly interfere with your target analytes)

QC on every sample?

- Analyze every sample in multiple ICP-MS modes (Std, NH_3 and O_2) and look for matching results between modes

Optimization

- Optimize the instrument for the minimization of interferences rather than highest sensitivity

Arsenic Speciation Analysis

EPA Method 1632

- One of the best methods out there when used by qualified/knowledgeable laboratories
- RLs around 0.010 µg/L in most waters for As(III), As(V), MMAs, DMAs

IC-ICP-MS

- Provides data for almost all As species in the sample
- Requires experienced personnel to analyze samples, understand data, and interpret results

Correct preservation is the key

- The most important aspect of As speciation analysis
- Freezing and not preserving is probably the worst…

Preservation of Arsenic Species

Parameters that affect stability of As species are:

- Sulfide, pH, DO, light exposure, dissolved and precipitated forms of Fe, Mn, Al, Ca, Mg, etc…

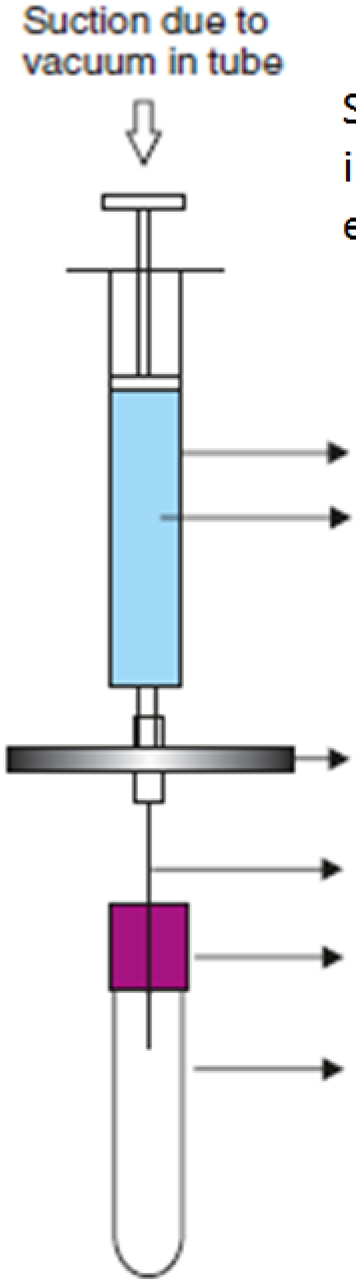
Sulfide

- If sulfide is present, thioarsenic species will be present
- pH is very important and should not be disturbed

Fe, Mn, Ca, and Mg

- They can precipitate out and remove As from solution
- Chelation seems to work pretty well for samples containing up to 10’s of ppm of each interfering element

Sample starts to flow once the needle is inserted in the tube due to the suction effect of vacuum


Suction due to vacuum in tube

Sterile syringe

Sample

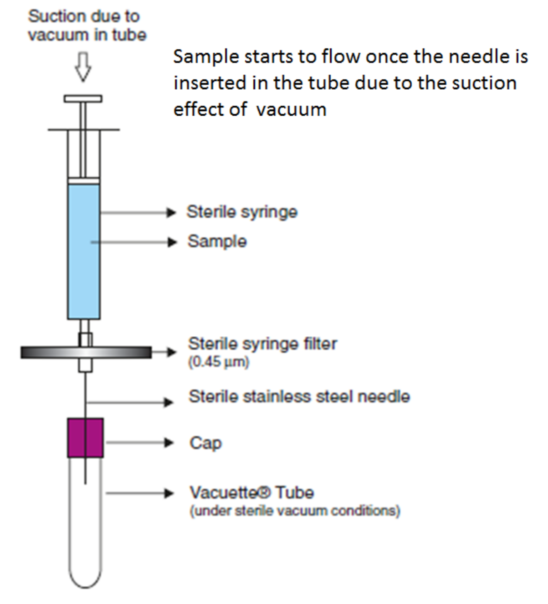
Sterile syringe filter (0.45 µm)

Sterile stainless steel needle

Cap

Vacuette® Tube (under sterile vacuum conditions)

Preservation of Arsenic Species



These tubes are evacuated to create a vacuum inside the tube, facilitating the draw of liquid, and may contain different additives designed to stabilize and preserve the specimen prior to analytical testing.

Gürleyük *et. al.*, J. Environ. Eng. 2013.139:1080-1088

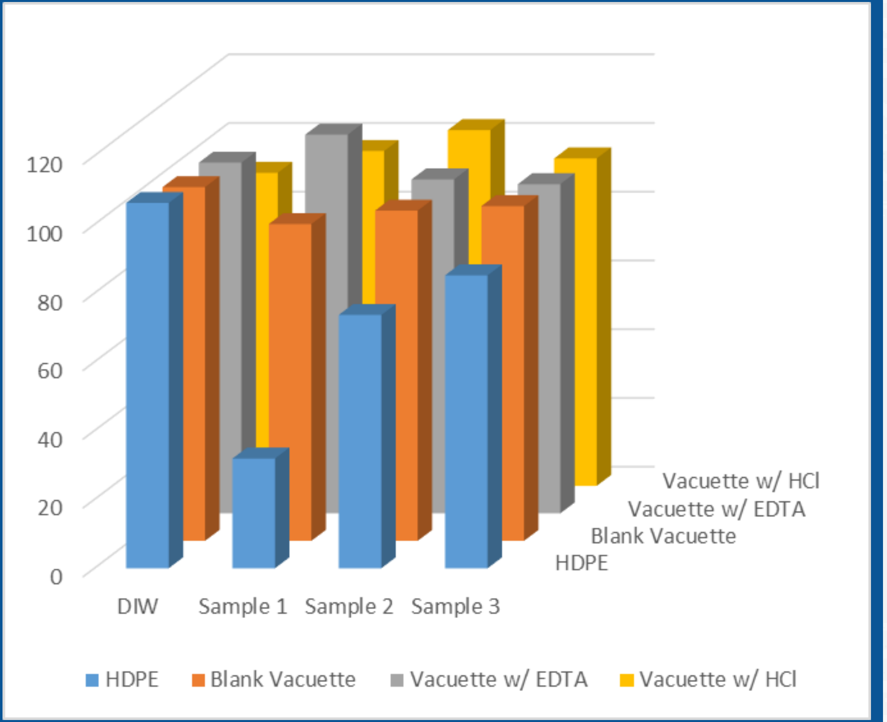
Preservation of Arsenic Species

3 groundwater samples, as well as a reagent water (DIW) sample, were spiked with As(III) in the field

Samples were then transferred to HDPE and 3 different types of Vacuette tubes

Samples in the HDPE bottles were not stable during transport to the lab

- All Vacuette tubes preserved the spiked As(III) concentration



Gurleyuk et. Al., J. Environ. Eng. 2013.139:1080-1088.

Hexavalent Chromium

DoD Applications

Used in metal finishing pre-treatments, primers/paints, and sealants

Ground and amphibious vehicles (Army and Marine Corps)

Ships/landing craft (Navy)

Aviation and missiles (Army, Air Force, and Navy)

Being replaced by alternatives

Analytical Methods for Cr(VI) Analysis

Method 7196: UV-Vis Colorimetry

- Colorimetric method is prone to interferences/false positives caused by Mo, V, Hg, MnO_4^-, turbidity, organic matter, etc.

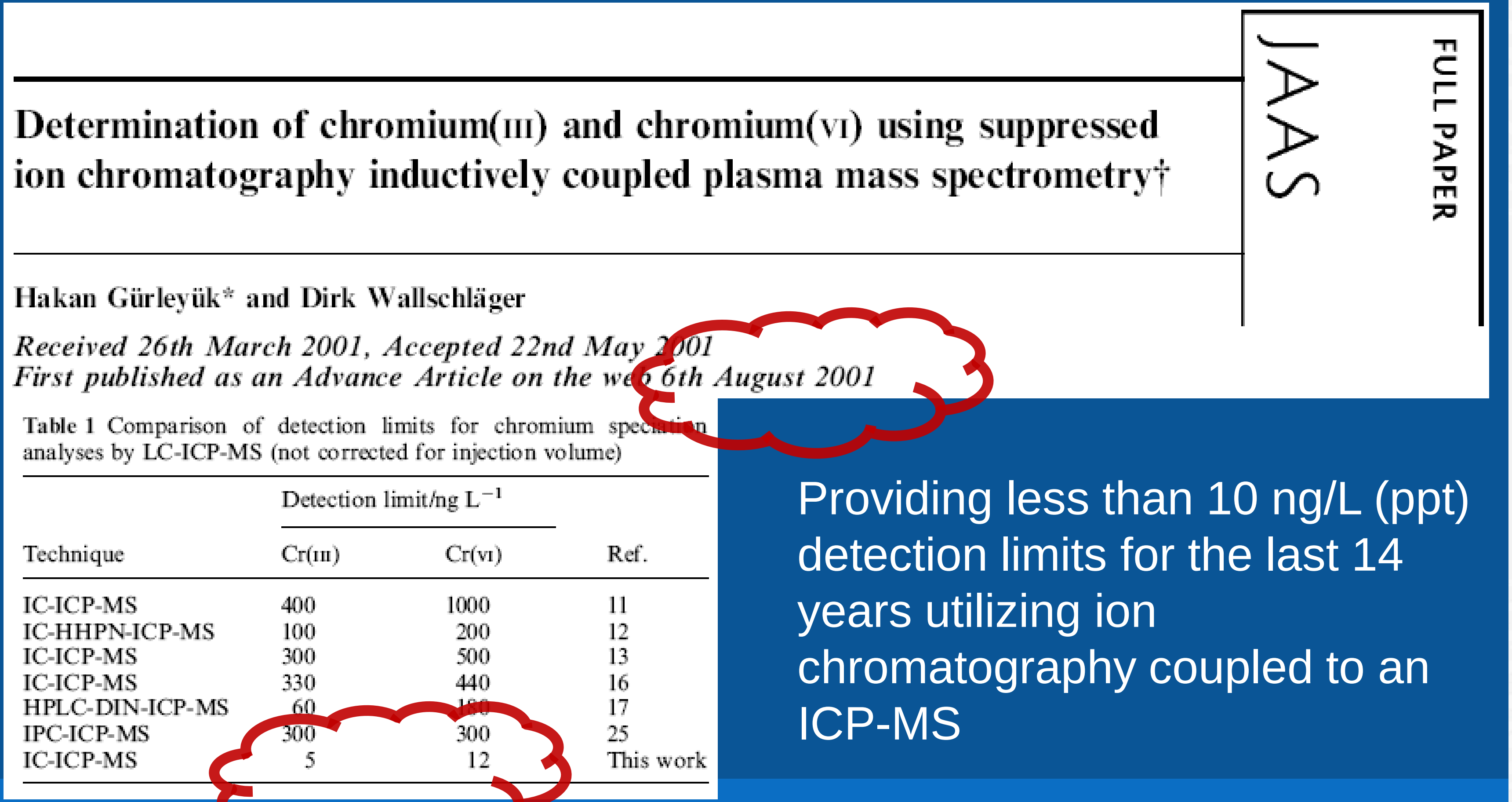
Method 7199: Ion Chromatography/UV-Vis Colorimetry

- Ion chromatography is used to separate Cr(VI), and detection is achieved by a post column reaction with diphenylcarbazide
- Detection limits for water samples are 0.02 – 1 µg/L, depending on the lab

Solid samples require an alkaline extraction of Cr(VI)

- EPA Method 3060a - solubilizes adsorbed and precipitated forms of Cr(VI) compounds
- The method allows for analysis of the extracts by **IC-ICP-MS**

Cr(VI) Analysis using IC-ICP-MS



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

Hakan Gürleyük* and Dirk Wallschläger

Received 26th March 2001, Accepted 22nd May 2001
First published as an Advance Article on the web 6th August 2001

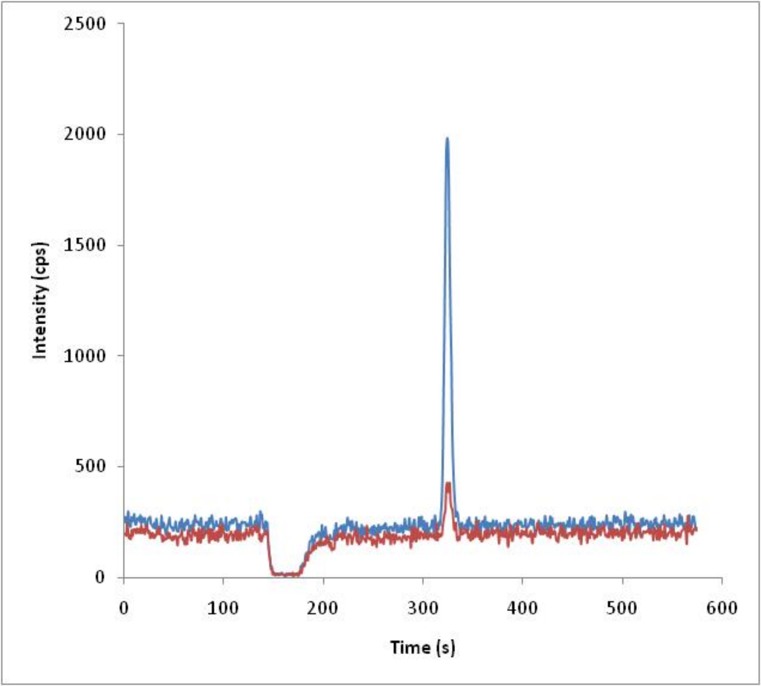
Table 1 Comparison of detection limits for chromium speciation analyses by LC-ICP-MS (not corrected for injection volume)

	Detection limit/ng L^{-1}		
Technique	Cr(III)	Cr(VI)	Ref.
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

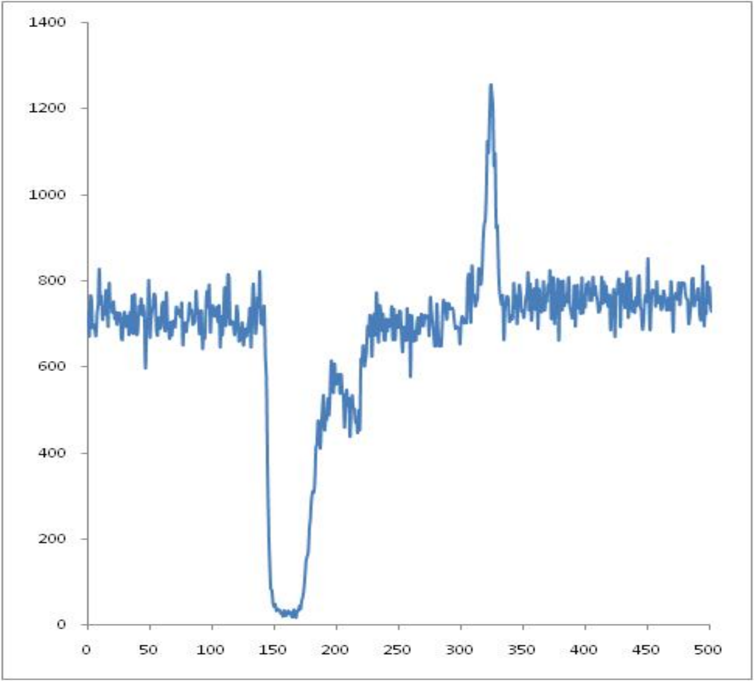
Providing less than 10 ng/L (ppt) detection limits for the last 14 years utilizing ion chromatography coupled to an ICP-MS

Cr(VI) by IC-ICP-MS

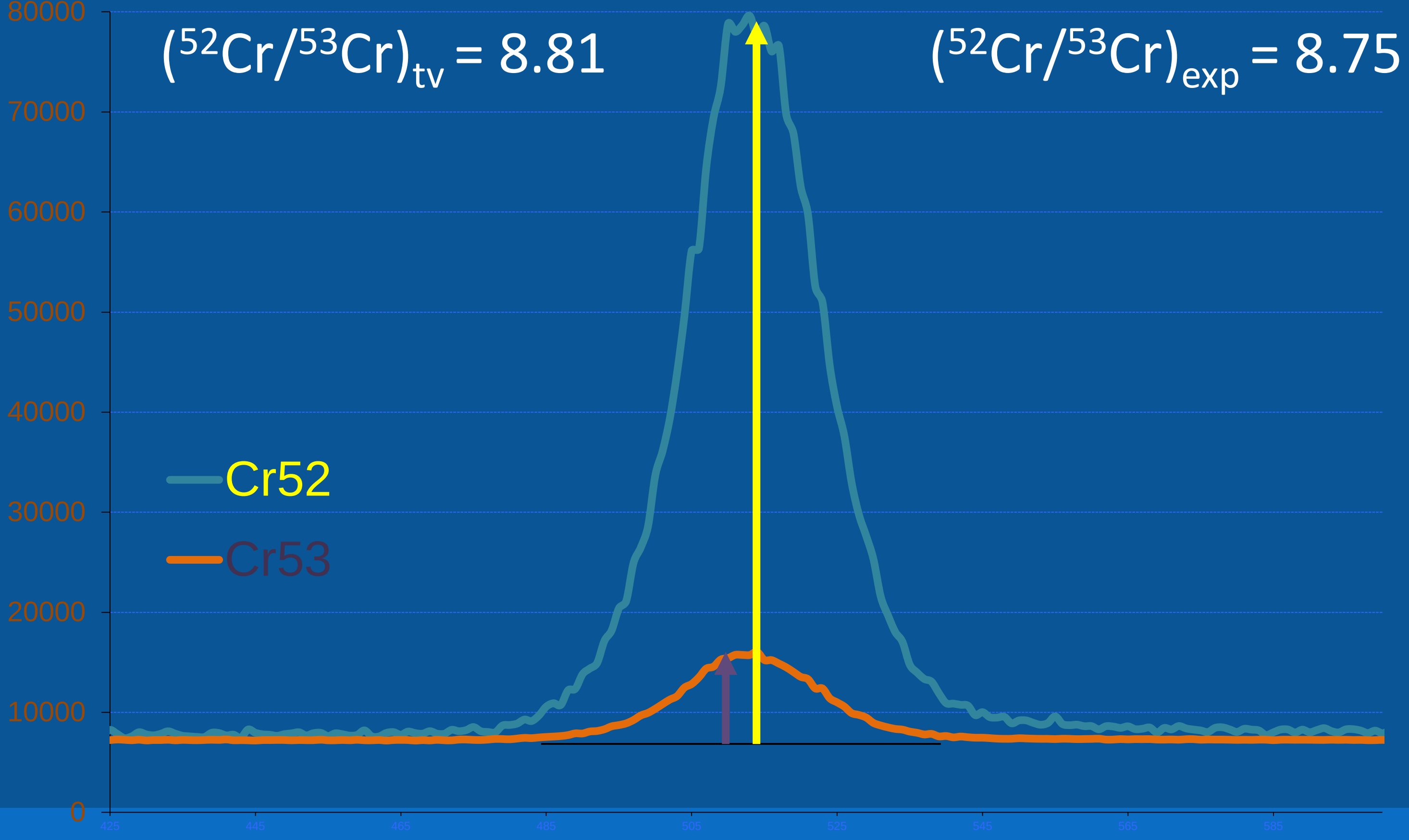
10 ng/L Cr(VI) Standard vs. Blank



Groundwater Sample Containing 3.6 ng/L Cr(VI)



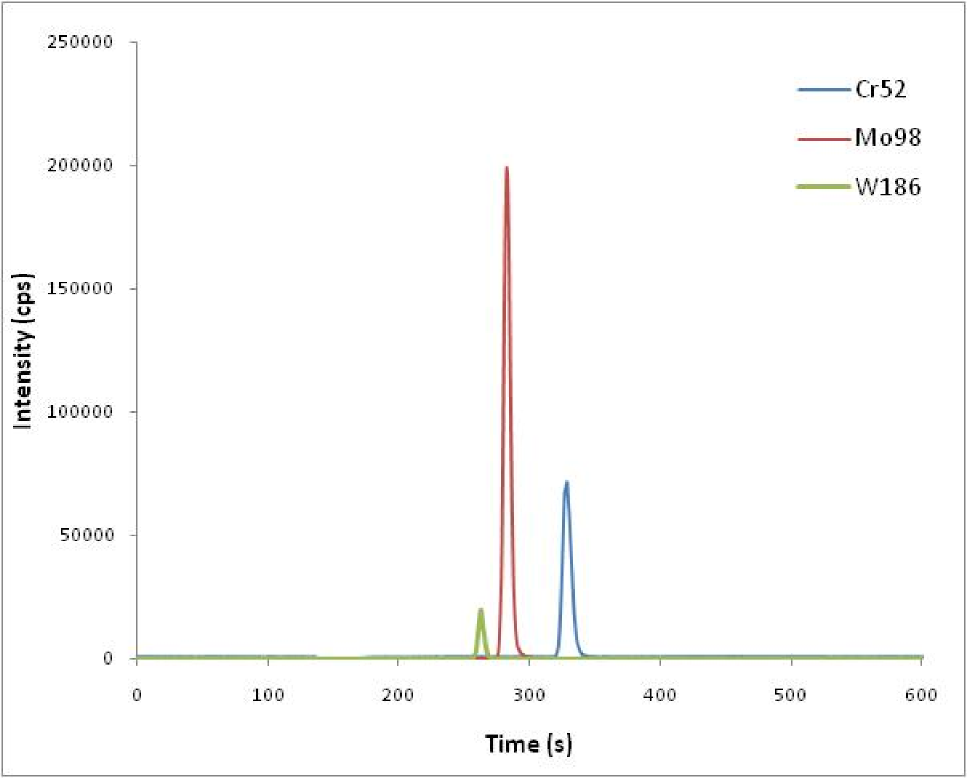
Identification by Isotopic Ratios



$(^{52}\mathrm{Cr}/^{53}\mathrm{Cr})_{tv} = 8.81$

$(^{52}\mathrm{Cr}/^{53}\mathrm{Cr})_{exp} = 8.75$

Internal Standards for Cr(VI)



Internal Standards:
Molybdate, Mo(VI)
Tungstate, W(VI)

Best Internal Standard is the enriched ^{53}Cr(VI), but this has ^{52}Cr(VI) impurities

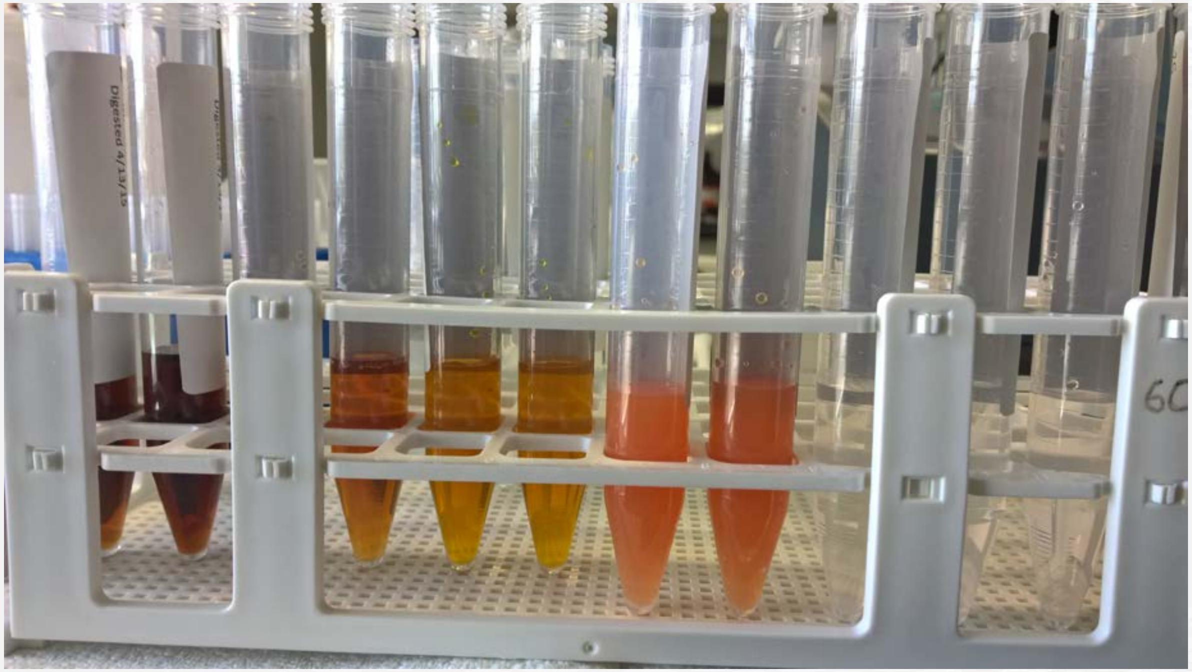
Using similar analytes, we can not only correct for drift, but also identify chromatographic issues during analysis

Cr(VI) in Soils and Sediments

- Oxidation and/or reduction can happen concurrently
- Quality control samples help to understand redox reactions
- Utilize Cr(III), Cr(VI), and $Pb(CrO_4)_2$ spikes

Reporting Limits		
3060a/7196 (UV-Vis)	3060a/7199 (IC/UV-Vis)	3060a/7199mod (IC-ICP-MS)
4 mg/kg	0.4 mg/kg	0.01 mg/kg

Cr(VI) in Soils and Sediments



Almost all 3060a extracts come out colored due to organics.

A turbidity blank should be analyzed for every sample.

Colorimetry vs IC-ICP-MS

Oxidation and/or reduction can happen concurrently

Quality control samples can help us understand redox reactions

Utilize Cr(III), Cr(VI), and $Pb(CrO_4)_2$ spikes

mg/kg	**3060a/7196**	**3060A/IC-ICP-MS**	**Bias Ratio**
Client1-Sample1	23.04	0.331	70
Client2-Sample1	11.66	0.005	2248
Client2-Sample2	4.49	0.039	116
Client3-Sample1	2.57	0.326	8
Client3-Sample2	2.33	0.360	6

It is not uncommon for some samples to have failing QC due to reducing nature of these samples.

Speciated Isotope Dilution Mass Spectrometry (SIDMS)

Produces legally defensible data by correcting for oxidation and reduction that may happen during sample preparation.

Traditional speciation methods attempt to hold each species static while making the measurements.

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 for.

What is Needed?

License from Applied Isotope Technologies (Pittsburgh, PA) to use the SIDMS method

Isotopically enriched Cr(III) and Cr(VI) standards

- ^{50}Cr(III) and ^{53}Cr(VI)
- EXPENSIVE!!! ~ $4,000,000 per gram

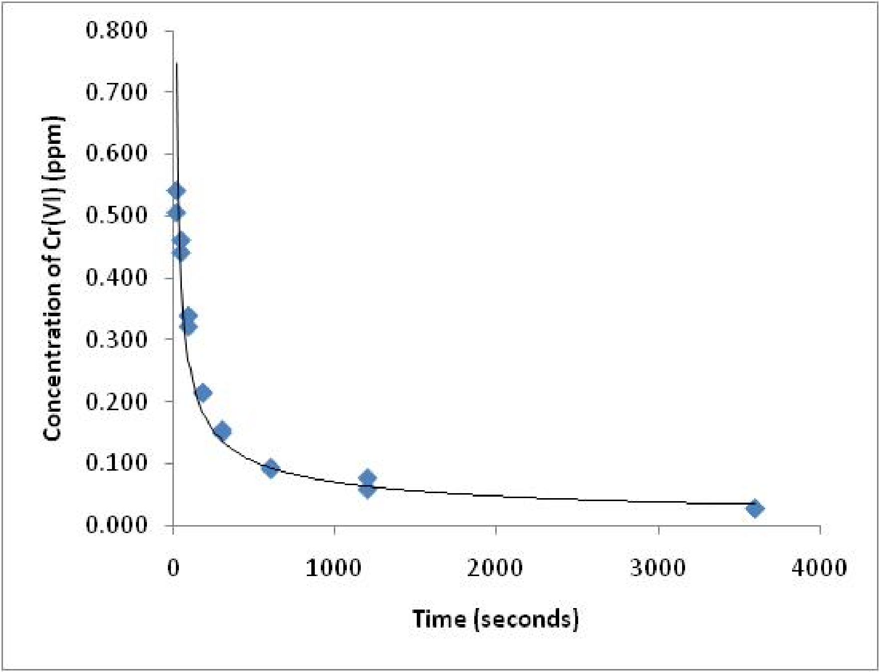
IC method that can separate Cr(III) and Cr(VI)

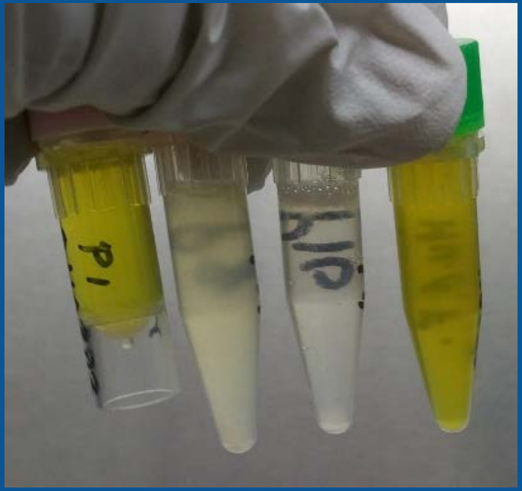
ICP-MS that can accurately monitor all 3 Cr isotopes (m/z 50, 52, 53)

- CRC, DRC, QQQ, or HR-ICP-MS

Fate of Cr(VI) After Ingestion

Human Gastric Fluid (diluted 10x)





Spiked with 1 ppm 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 SIDMS Perfect?

Nothing is perfect!

The SIDMS 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
- Usually multiple extractions and analyses are required

If there is 100% conversion, the concentration can not be calculated.

- For extremely reducing or oxidizing samples, it may not work

Conclusions

Always collect more data than needed

- Monitor elements that can possibly interfere with your target analytes.
- Use your LIMS to identify possible interferences
- QC on every sample? Run every sample with multiple isotopes and modes (Std, NH_3 and O_2) and look for matching results between modes

ICP-QQQ-MS can solve most of the spectroscopic interference problems

Choosing the right preservative for the right sample type is crucial for successful speciation analyses

- Talk to the project managers of your lab for guidance

IC-ICP-MS should be the first choice to generate high quality Cr(VI) data

Consider SIDMS for high profile or litigation cases