prep*FAST* IC

Speciation and Total Metal Analysis

Automated Speciation for Arsenic, Bromine, Chlorine, Chromium, Copper, Gadolinium, Iodine, Mercury, Selenium, and Uranium

Elemental Scientific

ICP | ICPMS | AA

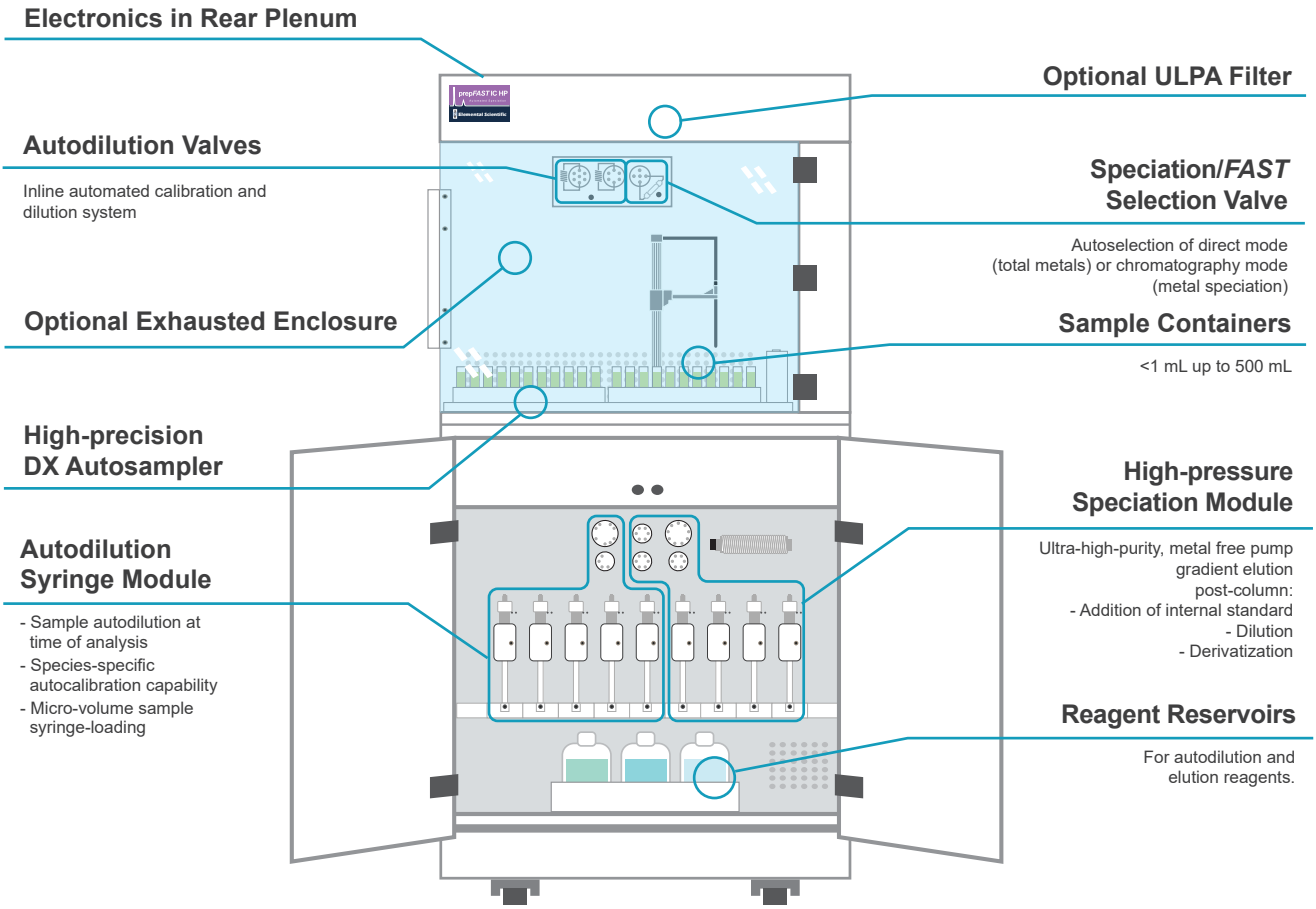
prep*FAST* IC

Autodilution and Speciation System

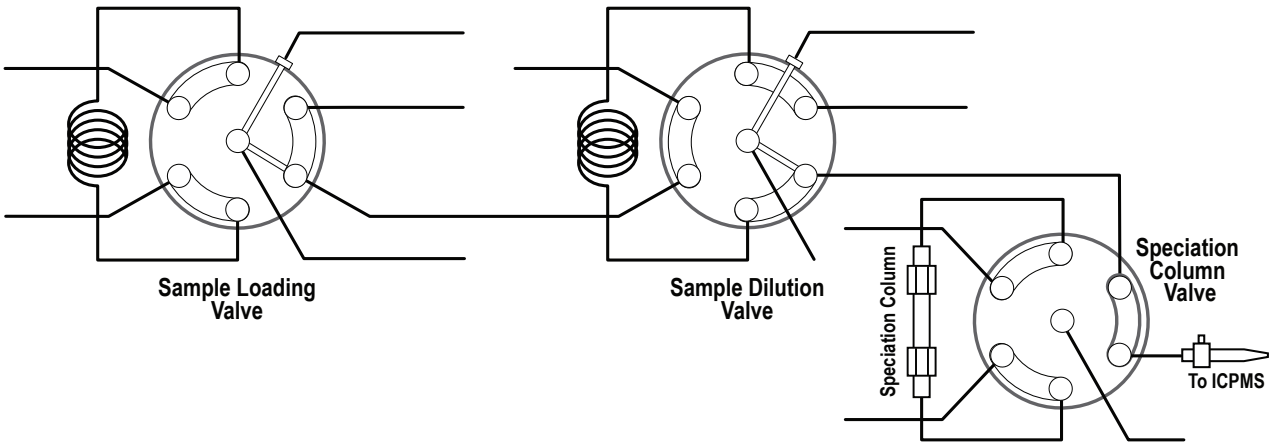
Trace metal laboratories are often required to speciate samples at frequencies that do not require a dedicated LC-ICPMS. As a result, costly LC systems need to be constantly attached and detached from the ICPMS. The prep*FAST* IC is a single platform capable of providing total elemental analysis and elemental speciation. The user can seamlessly switch between total metal analysis and speciation without having to change any hardware, solutions, or samples. In addition the system can autocalibrate from single stock standards and autodilute samples for both total metal and speciation analysis.

Features

- *FAST* uptake, stabilization, & washout
- High Performance P-series valve systems
- SampleSense (optional)
- Superior SC-GX autosampler
- Completely metal free liquid and sample flow path from pump to nebulizer
- Inline autocalibration
  - Total metals
  - Species
- Inline autodilution
  - Total metals
  - Species
- Contamination free
- Integrated chromatography
- Gradient elution
- Operate in total metals or chromatography mode
  - Auto switching
  - Performed with a single instrument
  - No instrument modifications required to switch mode
- Automated tuning
- Syringe loading
  - Viscous samples
  - Allows for all sample types
- Compatible with acids and organic solvents
- Syringe-driven
  - Post-column internal standard addition, dilution or derivatization
- Xceleri - data reduction software



prep*FAST* IC Flowpath



prep*FAST* IC: Total Metals

prep*FAST* IC includes the prep*FAST* autodilution system features which performs precise and accurate inline dilutions for samples and standards. Capable of up to 400x dilution, the prep*FAST* is the fastest, simplest way to ensure high quality data in every run.

Fully Integrated Autodilution

- Autocalibration
- Autodilution
- Intelligent Autodilution
- High performance P-series valves
- Includes SC-GX autosampler
- Includes *FAST* system
  - *FAST* Uptake
  - *FAST* Stabilization
  - *FAST* Washout

prep*FAST* Total Metal Autodilution Flow Path

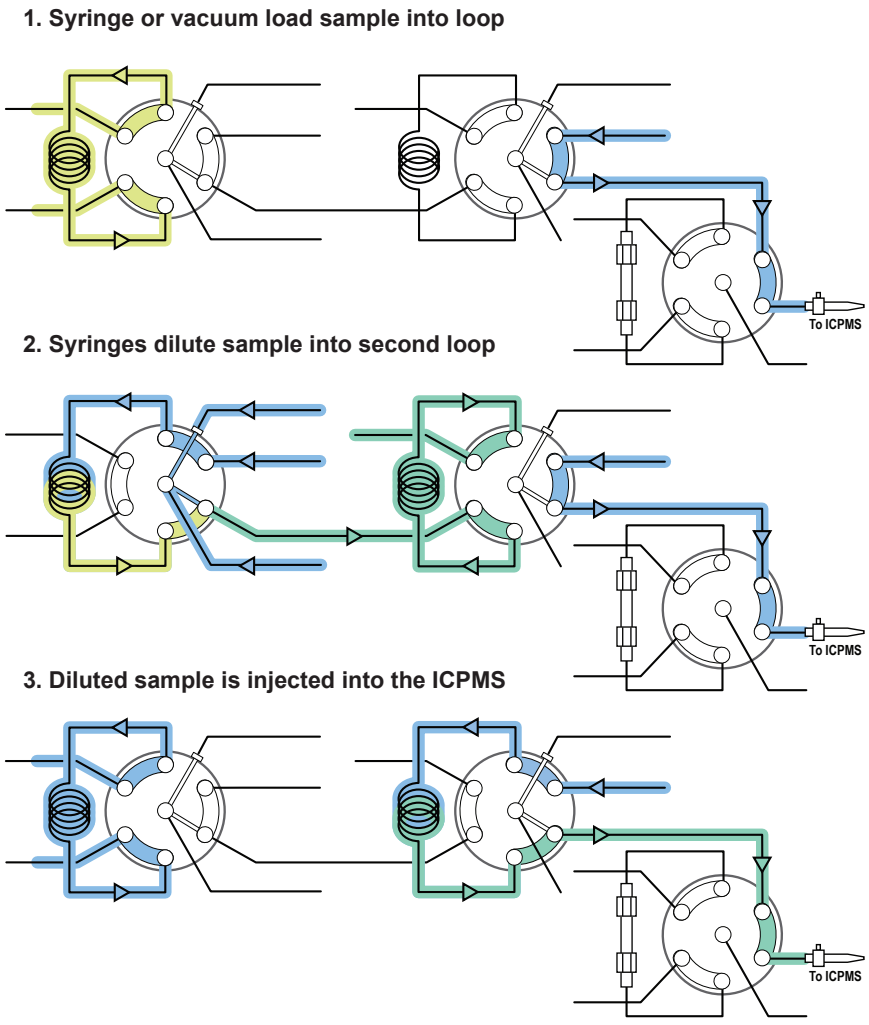


Figure 1. prep*FAST* IC flowpath for total metal analysis. The sample is autodiluted and injected onto the ICPMS without passing through the speciation column.

Autodilute Samples in Seconds

Tedious manual preparation steps are automatically handled by the prep*FAST* system, making better use of time and resources. Dilution factors are achieved in seconds by using in-valve mixing capabilities. Mixing inline eliminates the need to premix/dilute samples prior to analysis and greatly improves sample throughput.

- Vacuum or syringe loading
- Inline dilution
- Rapid uptake and stabilization of sample

Autodilution Calibration Curve

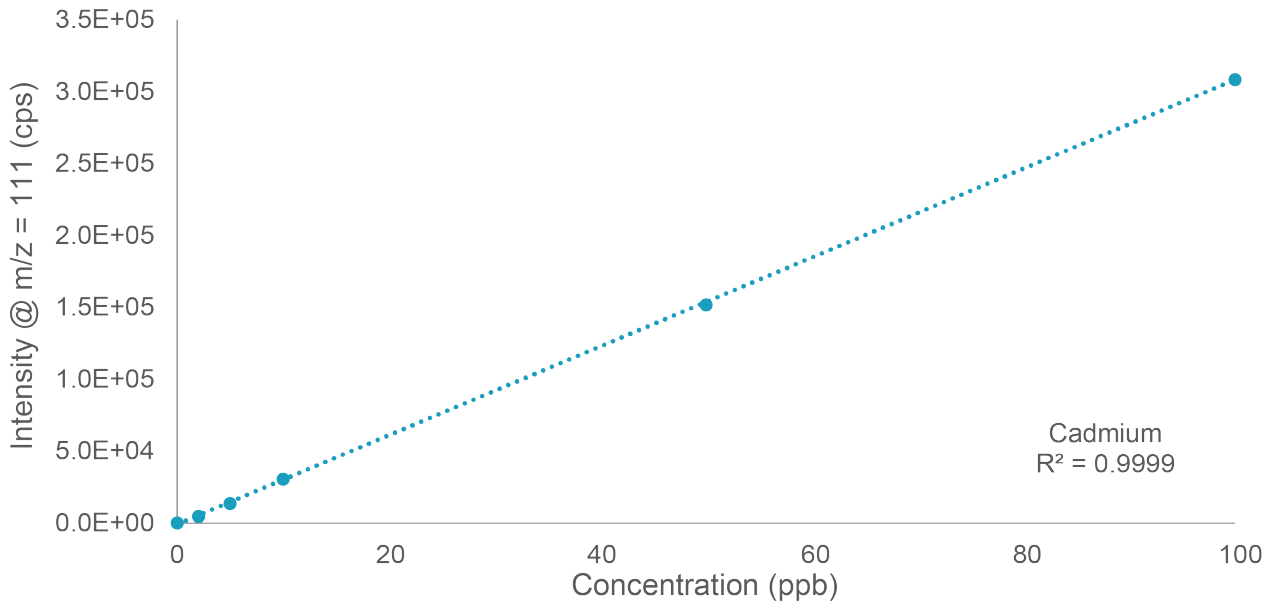
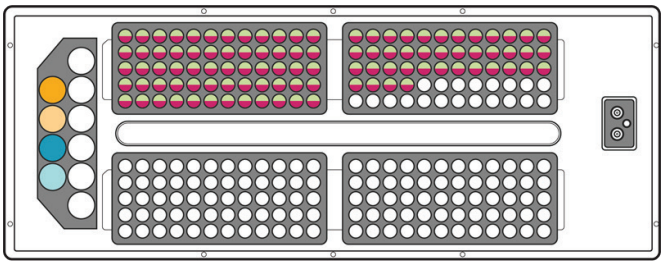


Figure 2. An example autocalibration curve for Cd using the autocalibration function of the prep*FAST*.

User predefined dilution factors for a single multi-element standard are used to build calibration curves. Accuracy of dilution is illustrated by excellent linearity of the calibration curve (R^2 = 0.9999).

- Automatically calibrates the instrument from one or more single standard solution(s)
- Improved linearity vs. calibrations prepared in separate vials
- Easily create calibration curves with more points (weighted curves)
- 1 - 2 vials per method—leaves space in standards rack for other calibration curves and QC
- Eliminate manual dilution errors

prep*FAST* IC: Automated Total Metals and Elemental Speciation



- Samples of Total Metals
- Samples of Speciation
- Speciation Stock Standard
- Speciation Blank
- Total Metals Stock Standard
- Total Metals Blank

Autosampler Location	Dilution Factor	Sample	Action
1	1	Blank - Total Metals	Total Metals
2	50	Standard 1	Total Metals
2	25	Standard 2	Total Metals
2	10	Standard 3	Total Metals
2	5	Standard 4	Total Metals
2	1	Standard 5	Total Metals
101	10	Sample 1	Total Metals
↓	↓	↓	Total Metals
240	10	Sample 100	Total Metals
10	1	Dummy Sample	Prime for Speciation Method
3	1	Blank - Speciation	Speciation
4	100	Standard 1	Speciation
4	20	Standard 2	Speciation
4	10	Standard 3	Speciation
4	5	Standard 4	Speciation
4	2	Standard 5	Speciation
101	10	Sample 1	Speciation
↓	↓	↓	Speciation
240	10	Sample 100	Speciation
9	1	Dummy Sample	Prime for Total Metals

Figure 3. Displays an example autosampler layout for running both total metals and elemental speciation using the same sample set. The sample sequence can be setup to be completely automated, such that one single analytical run can include total metals and elemental speciation analyses.

Arsenic Speciation In Less Than 2 Minutes

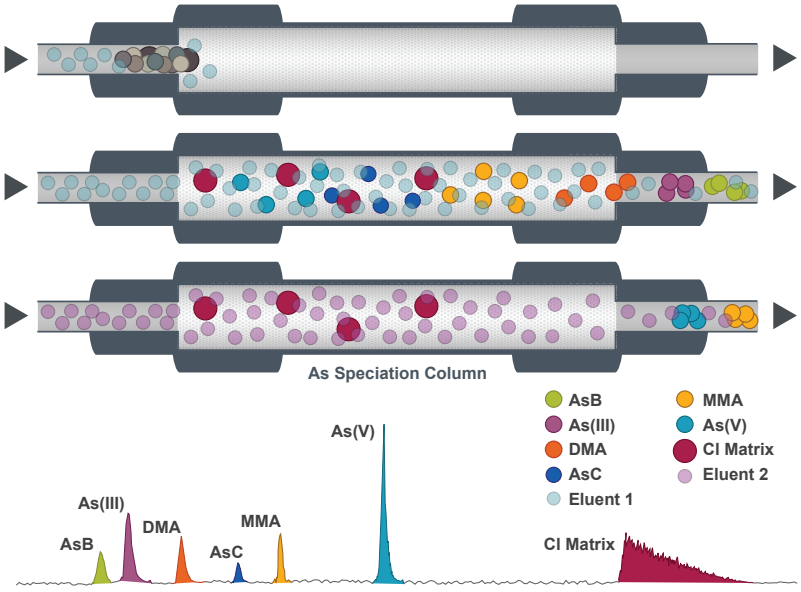


Figure 4. Illustration of the chromatographic separation of AsB, As (III), DMA, AsC, MMA, and As (V) as they elute off of the anion exchange column.

Separation of 6 Arsenic Species in 2 Minutes

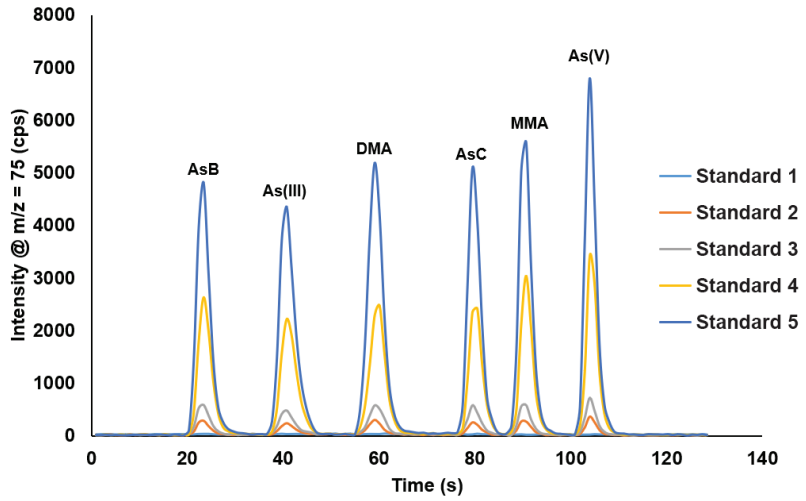


Figure 5. A typical chromatogram for AsB, As (III), DMA, AsC, MMA and As (V) using the prep*FAST* IC.

prep*FAST* IC - Total Metals and Speciation

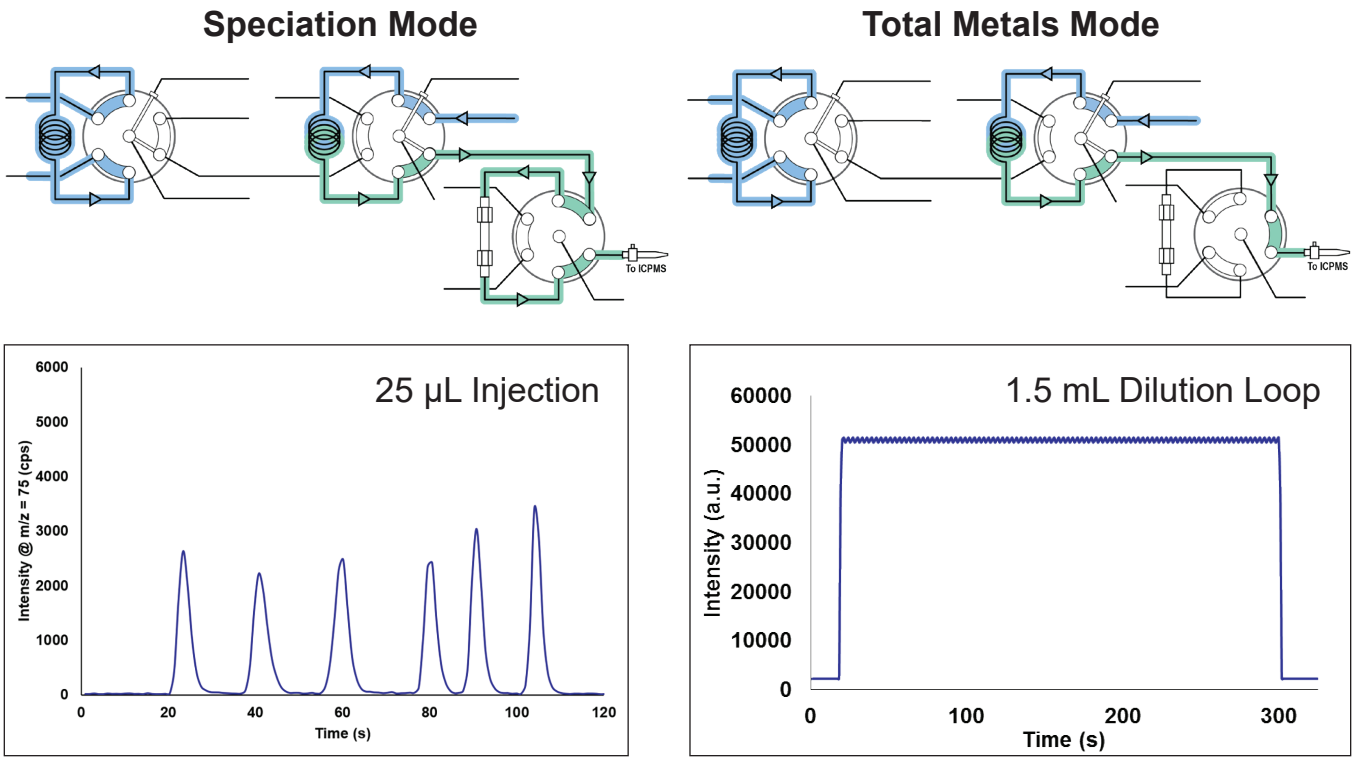


Figure 6. Displays the flow path for speciation mode and total metals mode. In speciation mode the sample is introduced to the column prior to the ICPMS, whereas in total metals mode the sample bypasses the column and is delivered directly to the ICPMS.

Arsenic Speciation

Separating Arsenic Species: AsB, As (III), DMA, AsC, MMA and As (V)

Farming in areas with arsenic enriched soil and groundwater can lead to an increase in arsenic levels found in several dietary staples. Naturally occurring organic and inorganic arsenic are composed of several species with a wide range of toxicity levels. Inorganic As (III and V) is toxic at only 10 mg/kg (Lethal Dose (LD)), while the organic forms (AsB, AsC, DMA and MMA) are much less toxic (LD50 >700 mg/kg). It is therefore important to know the species of As that compose the total As found in a wide variety of food, water and beverages. In clinical toxicology the level of exposure to humans is determined by doing arsenic speciation on urine samples.

Arsenic Elution Profile for Calibration Standards

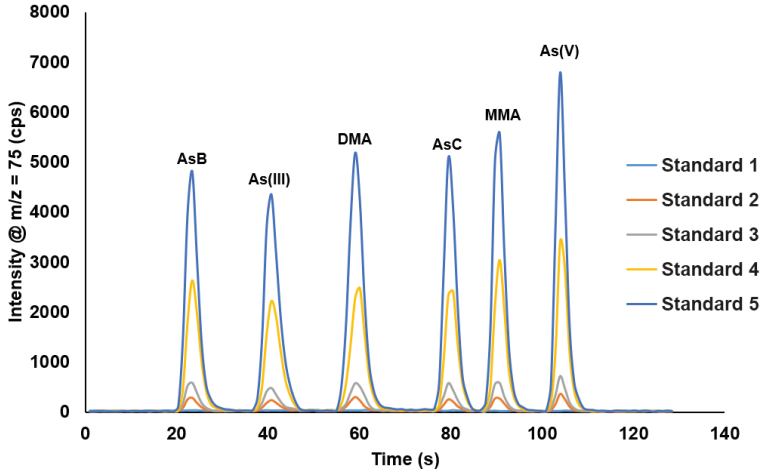


Figure 7. A typical chromatogram for AsB, As (III), DMA, AsC, MMA, and As (V).

Example of Inorganic Arsenic Calibration Curve (As (V))

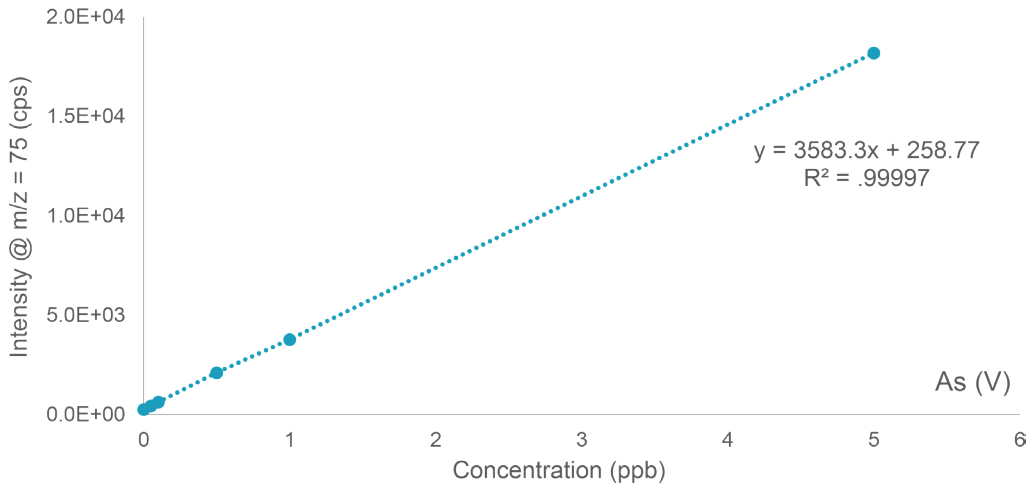


Figure 8. A typical autocalibration curve for As (V) using the prep*FAST* IC.

Inline Dilution Eliminates Species Interconversion

Manual Dilution

30X Manual DF

1 (Urine Spiked with 10 ppb As (III)): 29 (DI H_2O)

Inline Dilution

30X Inline DF

Urine Spiked with 10 ppb As (III)

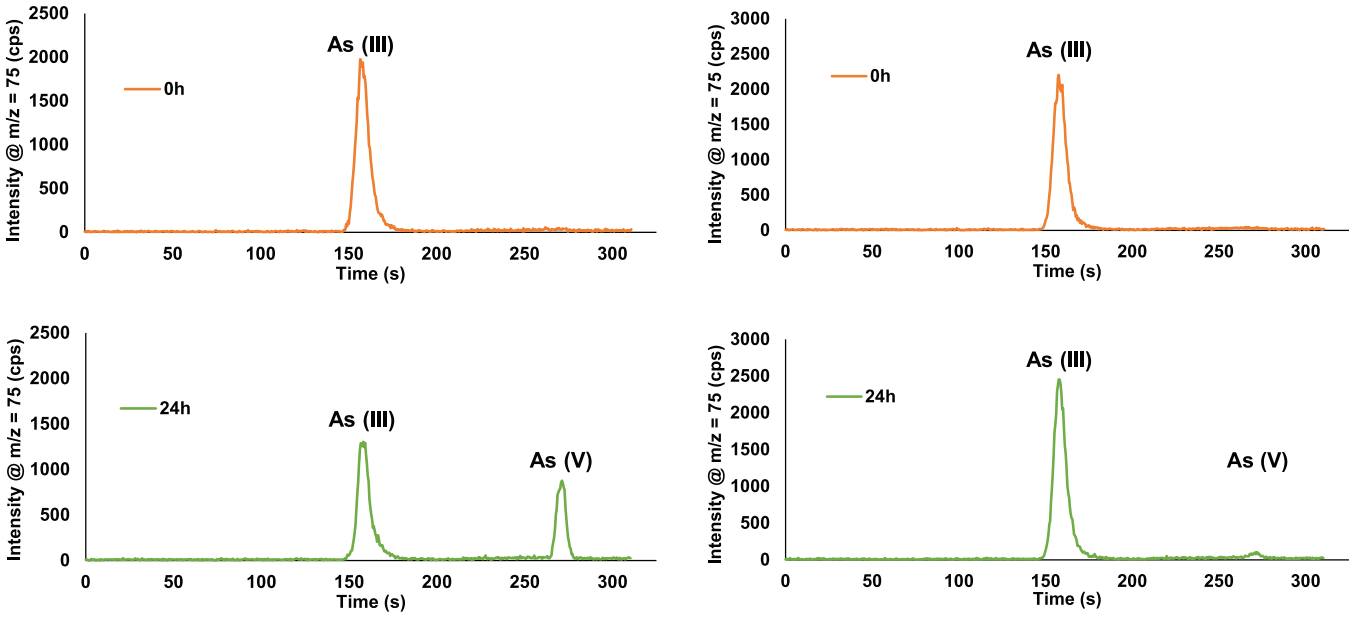
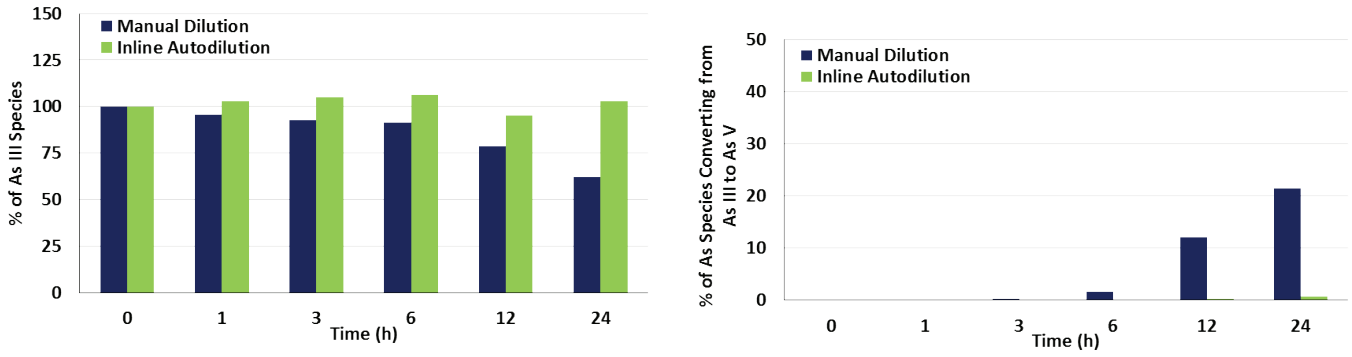


Figure 9. A set of urine samples were measured over 24 hours to compare manual dilution to inline dilutions. The manual dilution shows that As (III) interconverts to As (V) due to offline dilution. The inline dilution keeps the sample in its native state until just seconds before being introduced onto the column, which leads to more accurate results.

Manual Dilution vs Inline Dilution



As (III) % = (x h As (III) / 0 h As (III)) * 100, As (V) % = (x h As (V) / 0 h As (III)) * 100, As (III) + As (V) = As (III) % + As (V) %

Figure 10. Displays the manual vs inline dilution results from the aforementioned chromatograms. The overall recovery and As species accuracy is much better using the inline dilution option as compared to offline dilutions. The 24 h As (III) manual dilution results were 62% As (III), 21% As (V), and the sum of As (III) + As (V) was equal to 83%. The 24 h As (III) inline dilution results were 103% As (III), 1% As (V), and the sum of As (III) + As (V) was equal to 104%.

Chromium Speciation

Separating Chromium Species: Cr (III) and Cr (VI)

Chromium exists in the environment in several forms which differ in their effects upon organisms. Chromium enters the air, water and soil as Cr (III) and Cr (VI) through natural processes and human activities. At certain levels, Cr (III) is an essential nutrient for humans. On the other hand, Cr (VI) is detrimental to human health and is considered carcinogenic.

For this reason, there is an interest in measuring the level of Cr (VI) in drinking water. prep*FAST* IC is a robust speciation system that utilizes autocalibration and an anion exchange column to separate, detect, and quantify Cr (III) and Cr (VI) species in water samples.

Chromium Speciation In Less Than 2 Minutes

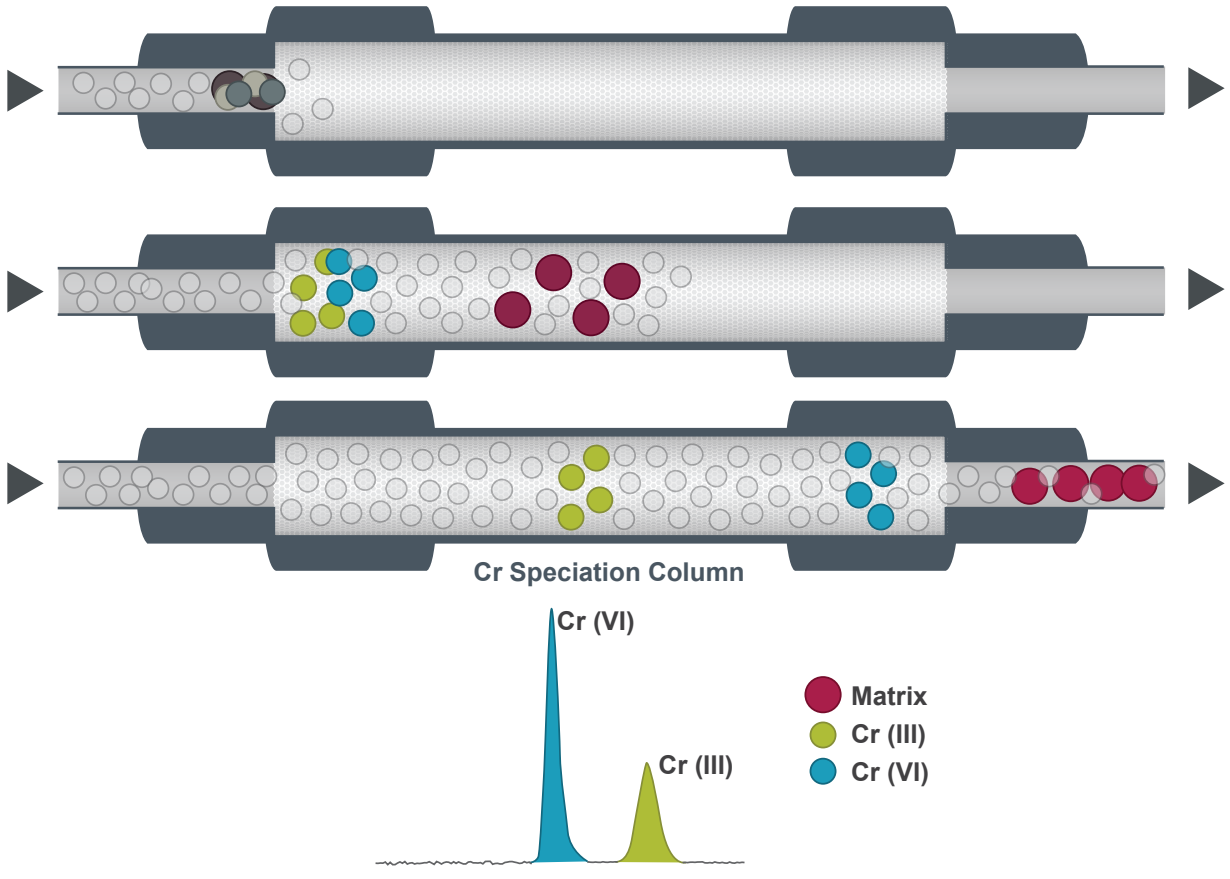


Figure 11. Illustration of the chromatographic separation of Cr (VI) and Cr (III) as they elute off of the anion exchange column.

Cr Elution Profile for Calibration Standards

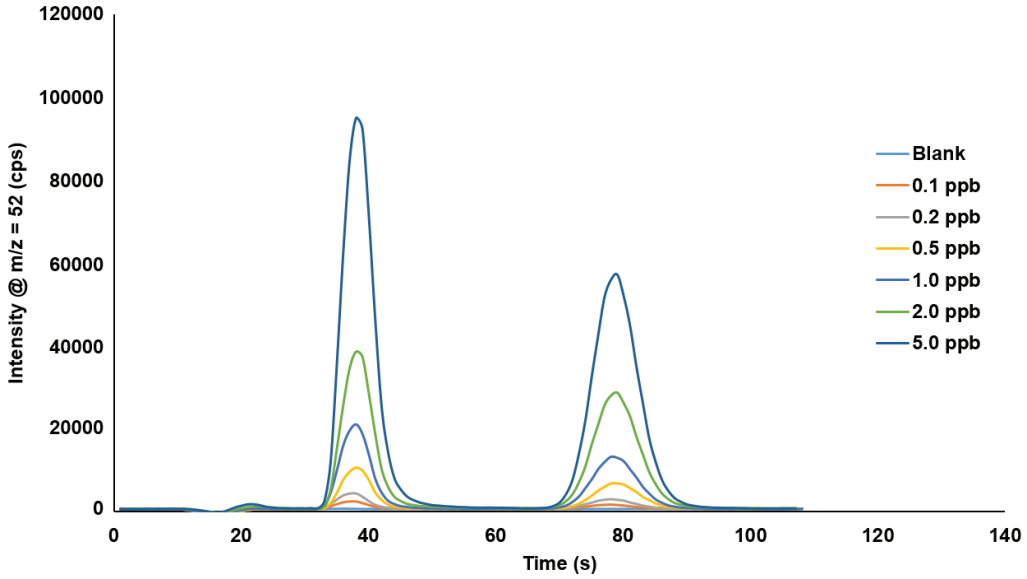


Figure 12. A typical chromatogram for Cr (VI) and Cr (III).

Cr (VI) Autocalibration for Drinking Water

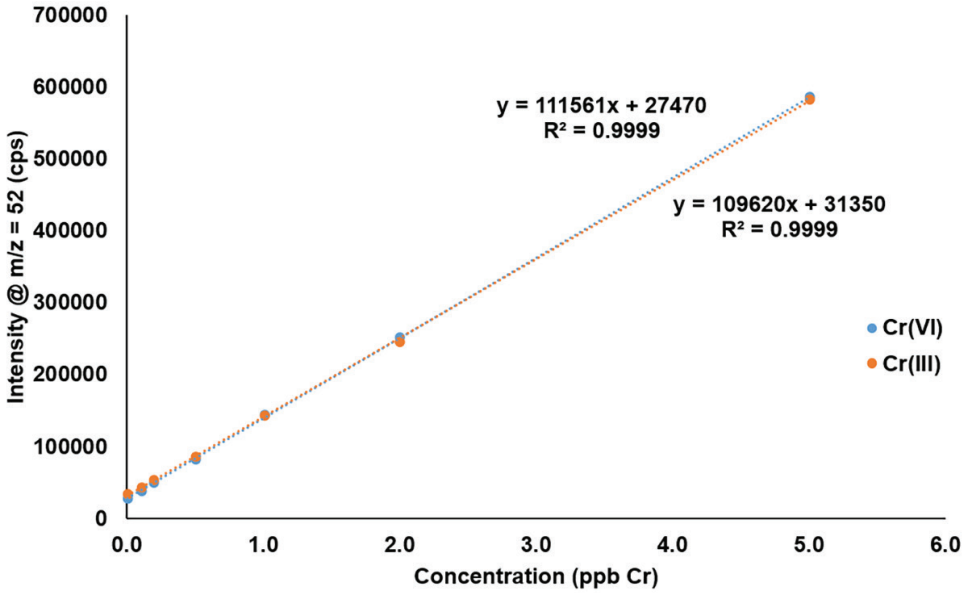


Figure 13. prep*FAST* IC inline preparation of low level standards from concentrated stock solutions eliminates environmental contamination. This provides linear calibration curves in the single digit ppt range.

Halogen Speciation

Separating Halogen Species: Br^-, BrO_3^-, I^-, IO_3^-, Cl^-, ClO_2^-, ClO_3^-, and ClO_4^-

The treatment of water or wastewater commonly involves the process of ozonation. Ozone is a powerful oxidation technique that can be done onsite, at a low cost, and leaves no residue behind. When included in drinking water treatment it effectively destroys bacteria and/or viruses, degrades organic compounds, eliminates odors or unwanted flavors. However, during the ozonation process bromide can be oxidized leaving the brominated form present in water. This process should be monitored to verify that the bromate species are not being formed (e.g. the by-product bromate is harmful to humans). When disinfectants are used to treat drinking water instead of ozone, chlorine or iodine can be converted to the by-products chlorate or iodate. The following application can detect bromate, bromide, chlorate, perchlorate, chloride, chlorite, iodate, and iodide in less than 3 minutes.

Halogen Speciation

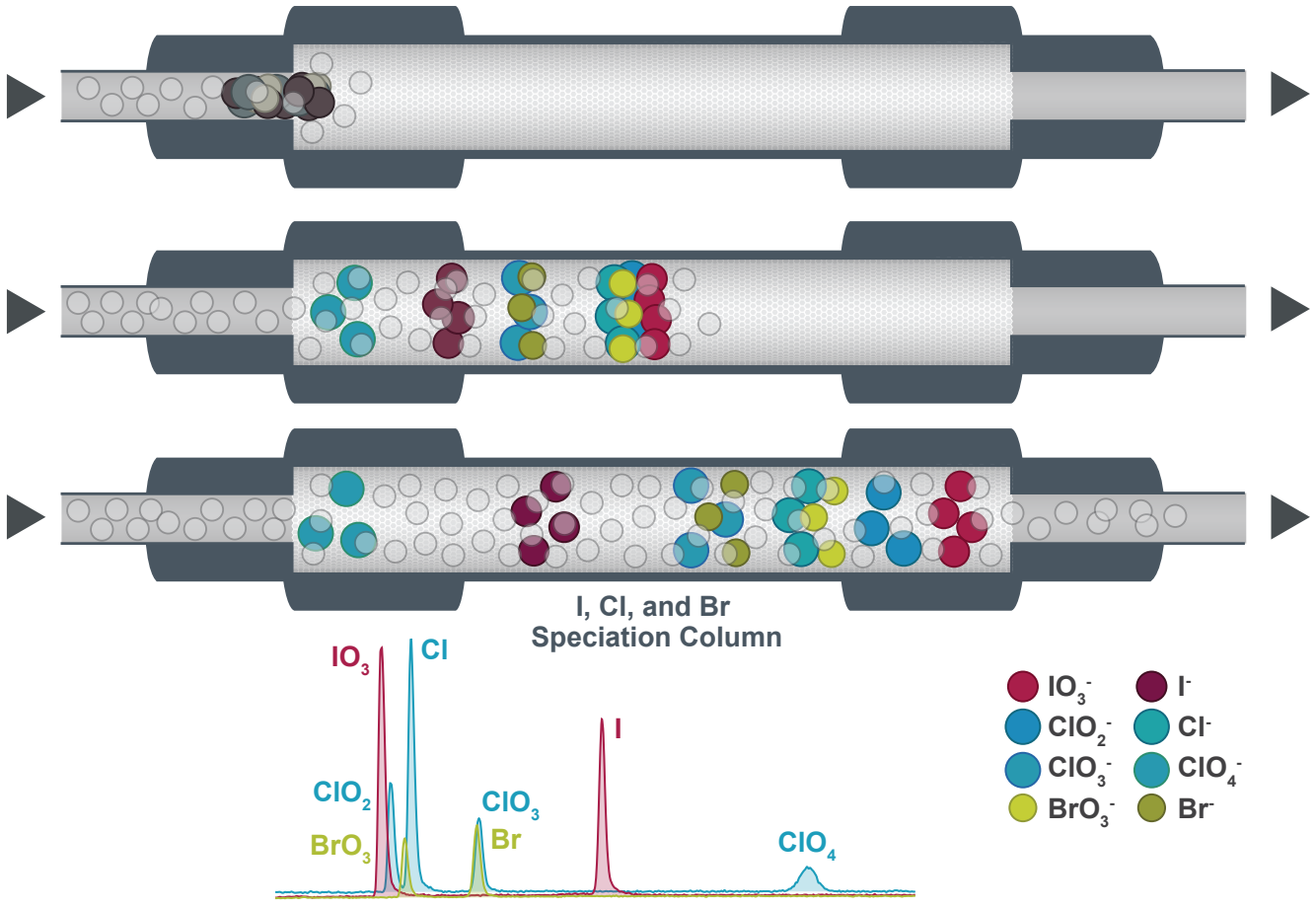


Figure 14. Illustration of the chromatographic separation of iodate (IO_3^-), chlorite (ClO_2^-), bromate (BrO_3^-), chloride (Cl^-), bromide (Br^-), chlorate (ClO_3^-), iodide (I^-), and perchlorate (ClO_4^-) as they elute off of the anion exchange column.

Halogen Speciation

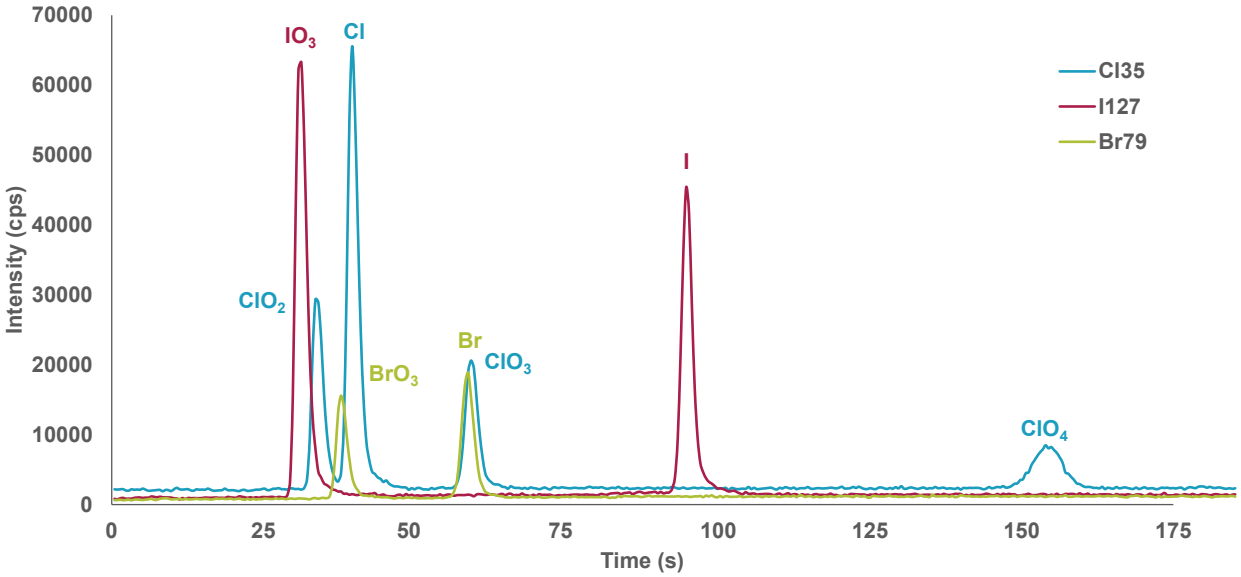


Figure 15. A typical chromatogram for IO_3^-, ClO_2^-, BrO_3^-, Cl^-, Br^-, ClO_3^-, I^-, and ClO_4^-.

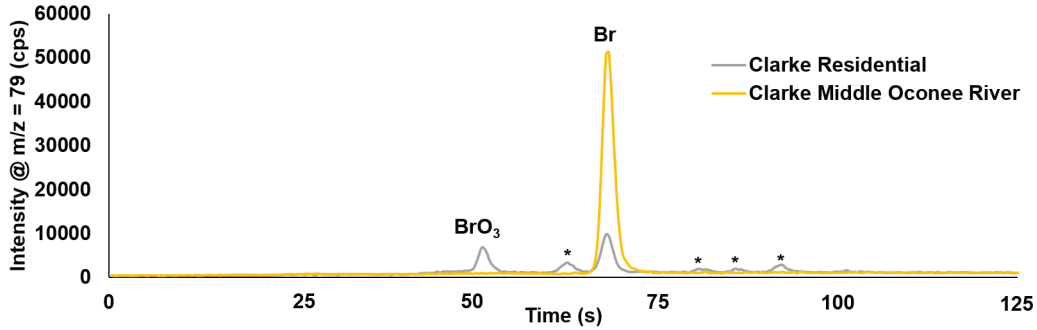


Figure 16. Chromatograms comparing Clarke county residential and Middle Oconee River bromide species results. Bromate plus four other bromide species are present after the water treatment process.

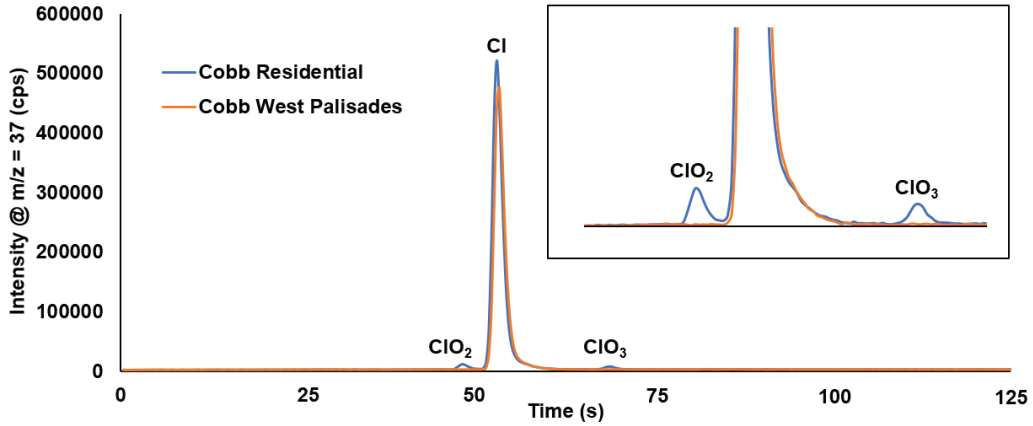


Figure 17. Chromatograms comparing Cobb county residential and West Palisades chloride species results. Chlorite and chlorate both appear after the water treatment process.

Selenium Speciation

Separating Selenium Species: Organic Se, Se (IV), and Se (VI)

Selenium is a naturally occurring element that is widely distributed throughout the environment and is a part of many industrial applications. For example, selenium is a component in the manufacturing of photovoltaic cells, metal alloys, and medical therapeutic agents, as well as an oxidizing agent in drug and chemical manufacturing. Selenium is usually found as a compound with other elements such as copper, silver, lead and nickel and the mining/refining processes for these elements yields a buildup of selenium residue through accidental mobilization. Certain species of selenium have greater toxic effects in higher concentrations, so determination of individual species is of critical importance.

Selenium Speciation

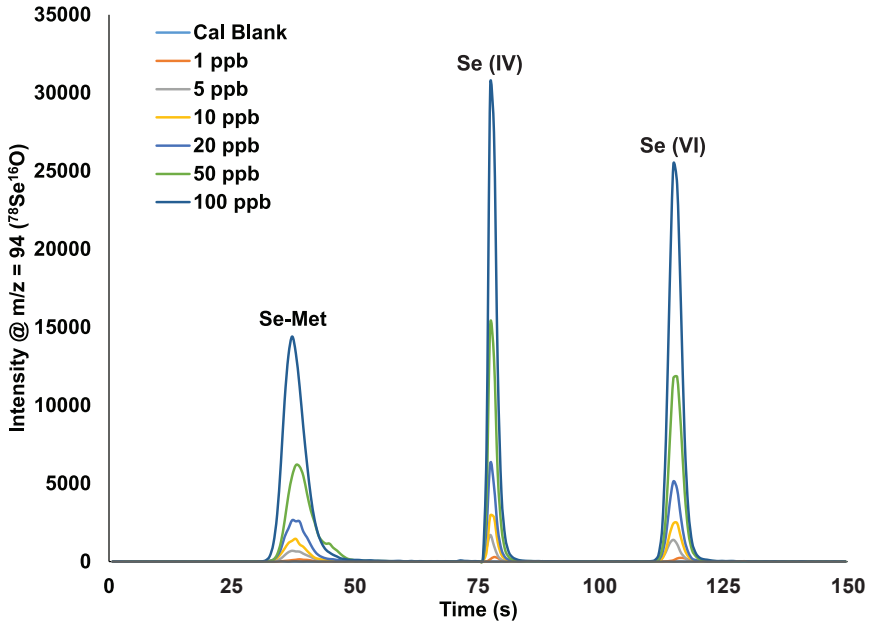


Figure 18. A typical chromatogram for Se-Met, Se (IV) and Se (IV).

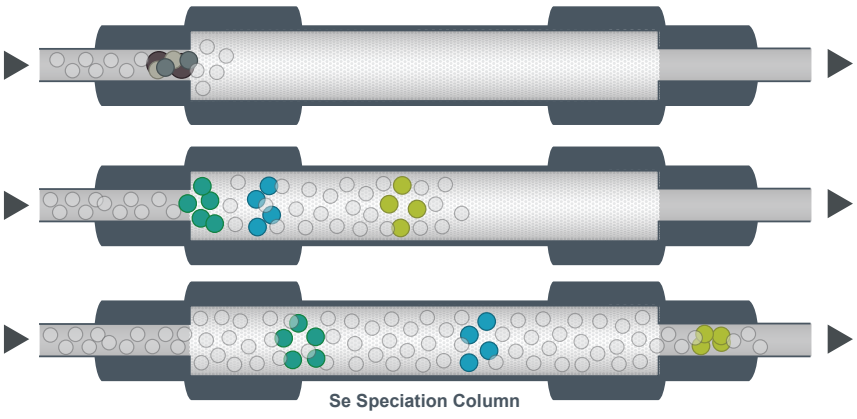
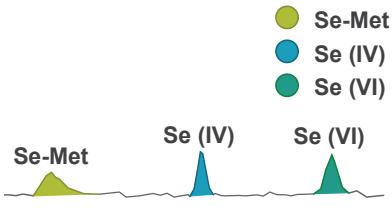


Figure 19. Illustration of the chromatographic separation of Se-Met, Se (IV) and Se (VI) as they elute off of the anion exchange column.



Mercury Speciation

Separating Mercury Species: Organic Hg (e.g. Me-Hg) and Inorganic Hg

Mercury (Hg) exists in the environment in several forms, all of which are toxic to humans to some degree. Obtaining precise, timely measurements of Hg in environmental samples, especially methylmercury (MeHg) in water samples, is essential to monitoring potential toxicity issues. However, detecting trace amounts of the element is an obstacle that can prevent accurate analysis of Hg and MeHg levels. The following method allows for a simple technique to detect mercury and/or methylmercury in under 2 minutes for water, seawater, or fish digest.

Mercury Speciation

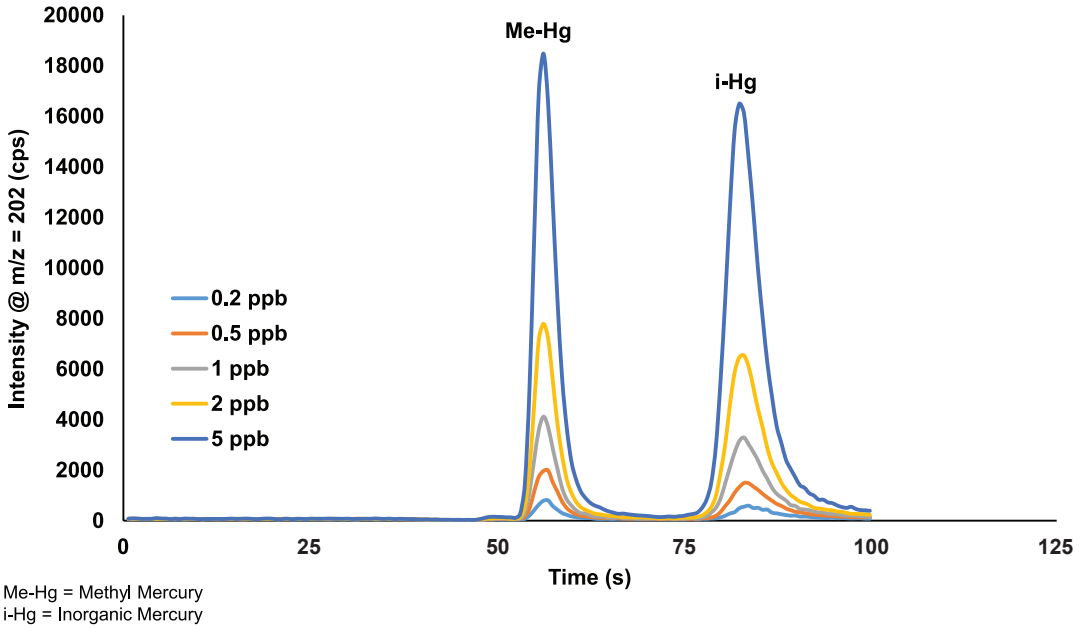


Figure 20. A typical chromatogram for Me-Hg and i-Hg.

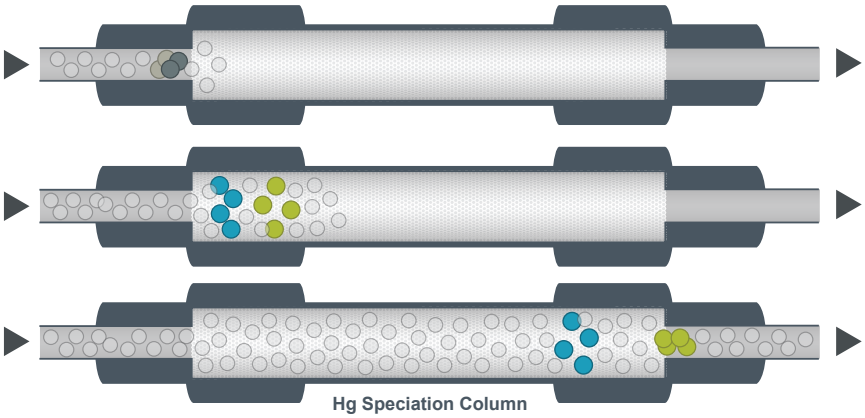
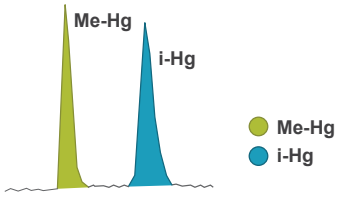


Figure 21. Illustration of the chromatographic separation of Me-Hg and i-Hg as they elute off of the anion exchange column.



Uranium

Separation of Trace Metals from U Matrix

The determination of trace elements in uranium (U) materials are an important step for several areas in the nuclear industry including exploration/mining, refining, fuel production, operational monitoring, decommissioning/storage and environmental monitoring. This method allows the uranium rich matrix to be sent to waste, while the trace elements are detected on an ICPMS or U pre-concentration can be utilized followed by analysis on the ICPMS. In order to analyze trace elements in the presence of uranium by ICP, the emission rich uranium matrix must be removed. We have automated this off-line sample preparation process (commonly done by gravity-fed chromatography) which has reduced the time, sample volume, and reagents consumption required.

URANIUM MATRIX REMOVAL

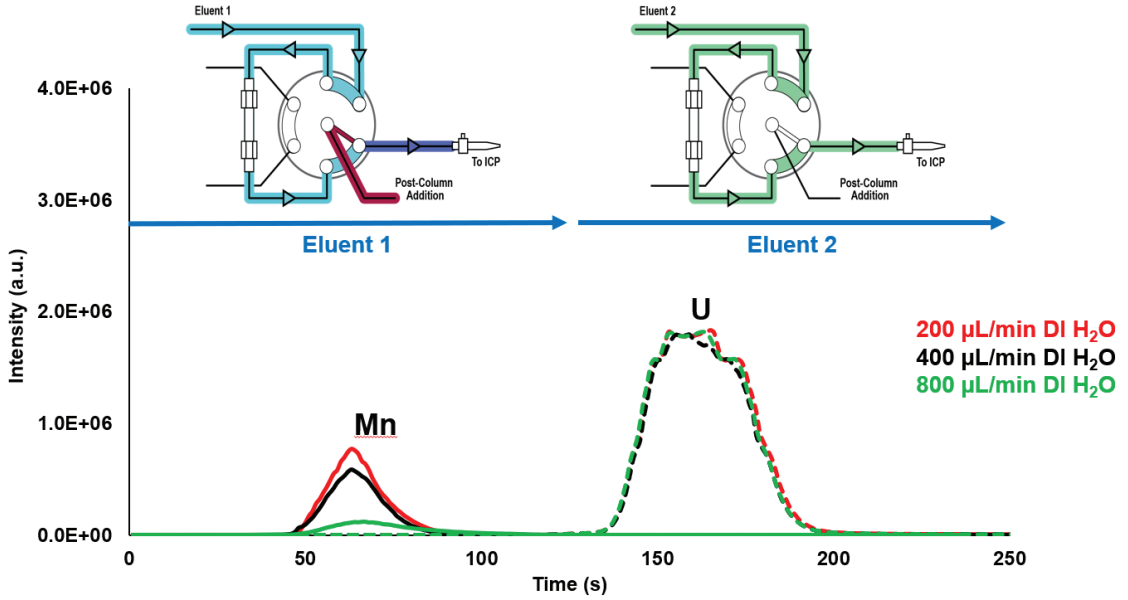


Figure 22. Separation of trace element impurities (e.g., 5 µg/mL Mn) from uranium matrix (1 vol. % U) using three post-column addition flow rates (200, 400, and 800 µL/min DI water). The arrows depict the timing for switching the method from eluent 1 to eluent 2.

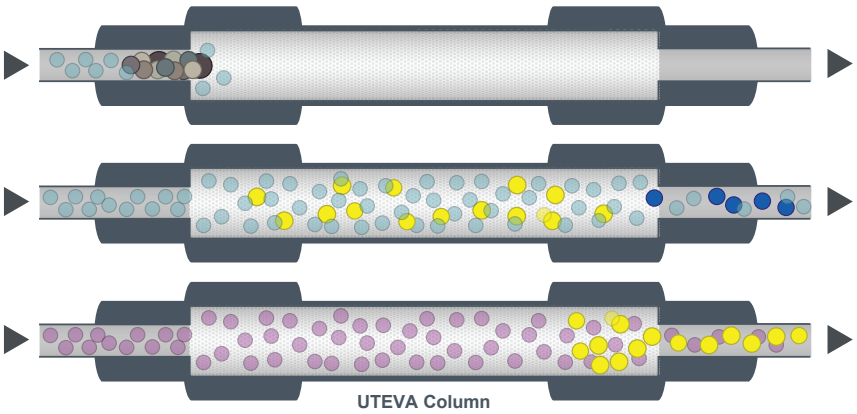
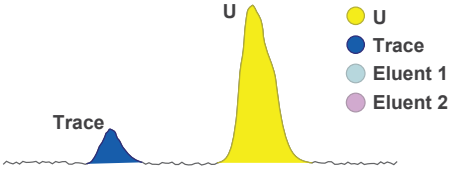


Figure 23. Illustration of the chromatographic separation of trace metals and uranium matrix using an UTEVA resin column.



Copper

Separation of Bound Cu and Free Cu in Serum

Copper is an essential element required for melanin, bone, and connective tissue production. Copper is transported in blood by ceruloplasmin or albumin and is stored in the liver. Several diseases (Menkes or Wilson's disease) account for either excessive or deficient amounts of copper in the body. Typical clinical testing includes total copper in blood, serum ceruloplasmin, and urine copper. Patients with urine copper levels > 40 µg/dL and serum ceruloplasmin < 20 mg/dL are typically associated with Wilson's disease. Healthy patients have ~ 5-20% free copper (not bound) and is determined by an indirect method: (serum copper – ceruloplasmin)/(serum copper). Currently, there is no direct method in the medical/clinical arena that can determine free Cu in patient samples. The work below offers a direct method to determine the amount of Cu bound to proteins and free Cu in serum.

BOUND COPPER VS FREE COPPER

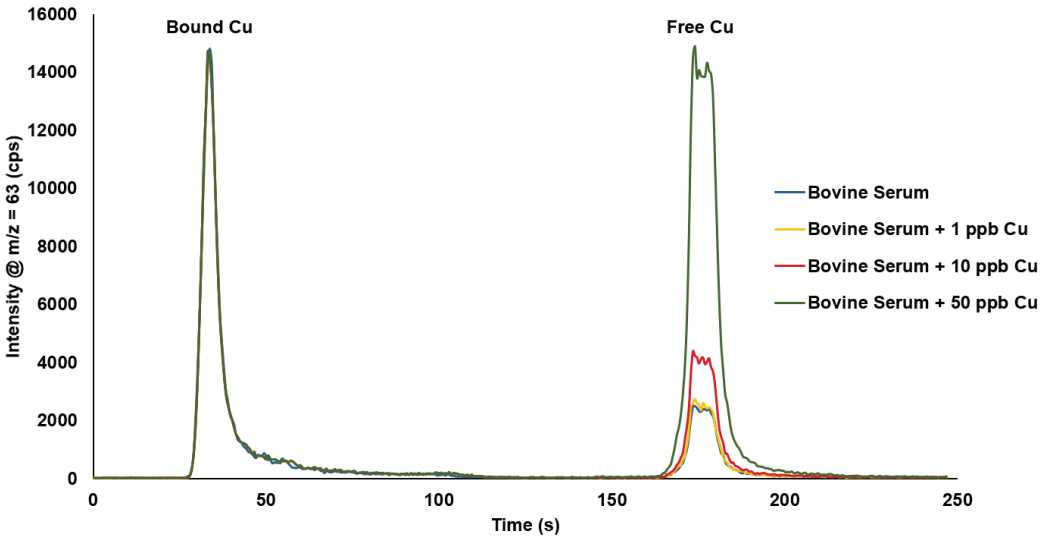


Figure 24. Displays the separation of bound Cu and Free Cu in bovine serum that was spiked with excess inorganic Cu.

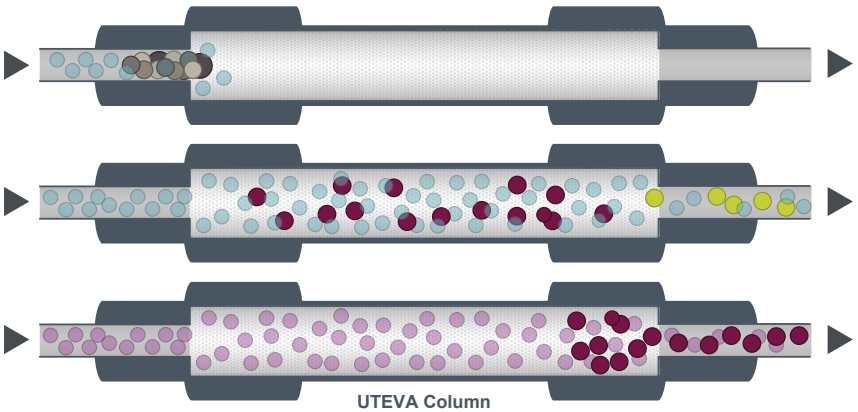
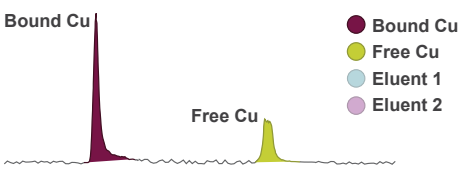


Figure 25. Illustration of the chromatographic separation of bound copper and free copper using an ESI copper column.



Gadolinium-Based Contrast Agents

Separation of Gd-Based Contrast Agents and Free Gd^{3+}

Diagnostic techniques such as magnetic resonance imaging (MRI) play a crucial role in current medicine. The administration of contrast medium to patients, such as gadolinium-based contrast agents (GBCA), can enhance the image quality, aiding more accurate diagnosis. Gd (III) has a similar ionic radius to Ca (II), which means Gd (III) could block voltage-gated Ca (II) channels or exchange with Ca based proteins within the body. In 2017 the FDA listed 8 FDA-Approved GBCAs, while the European Medicines Agency (EMA) took a different approach with only 4 of these agents being approved for full use. There are ongoing concerns about the stability of these compounds in the body and in the environment. The separation below provides a chromatographic separation to detect the GBCAs and free Gd^{3+} in tissue, urine, or the environment (drinking water, rivers, lakes, etc.).

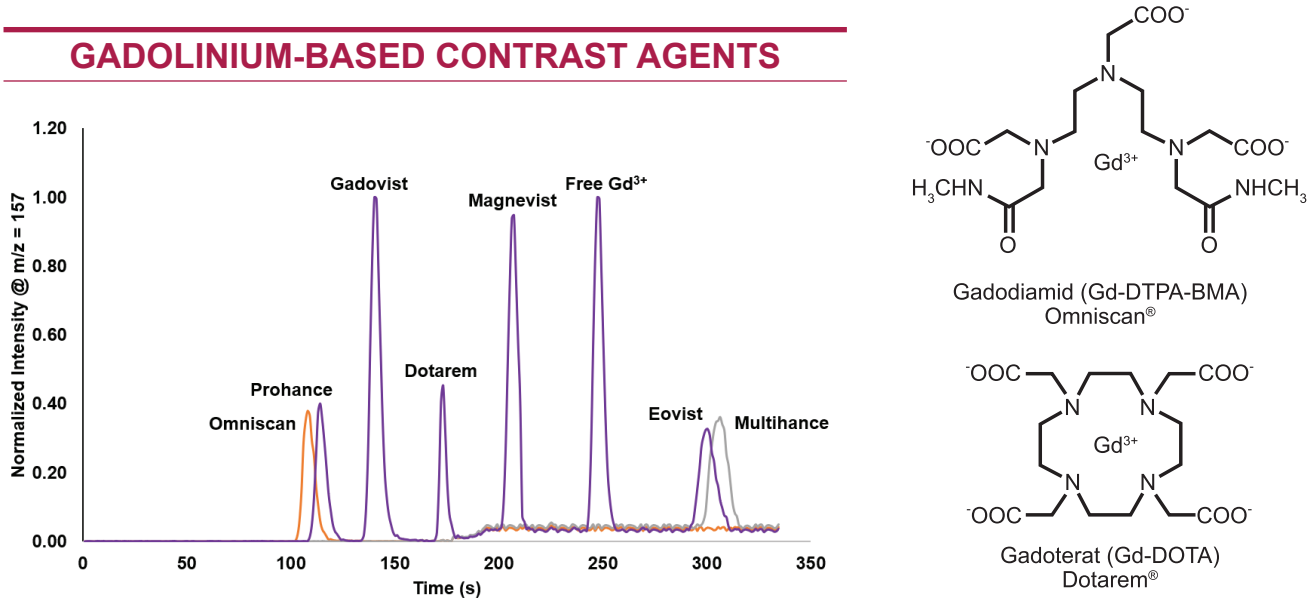


Figure 26. (Left) Displays the separation of Omniscan, Prohance, Gadovist, Dotarem, Magnevist, Eovist, Multihance, and Free Gd^{3+}. (Right) An example of a linear compound (Omniscan) and a macrocyclic compound (Dotarem).

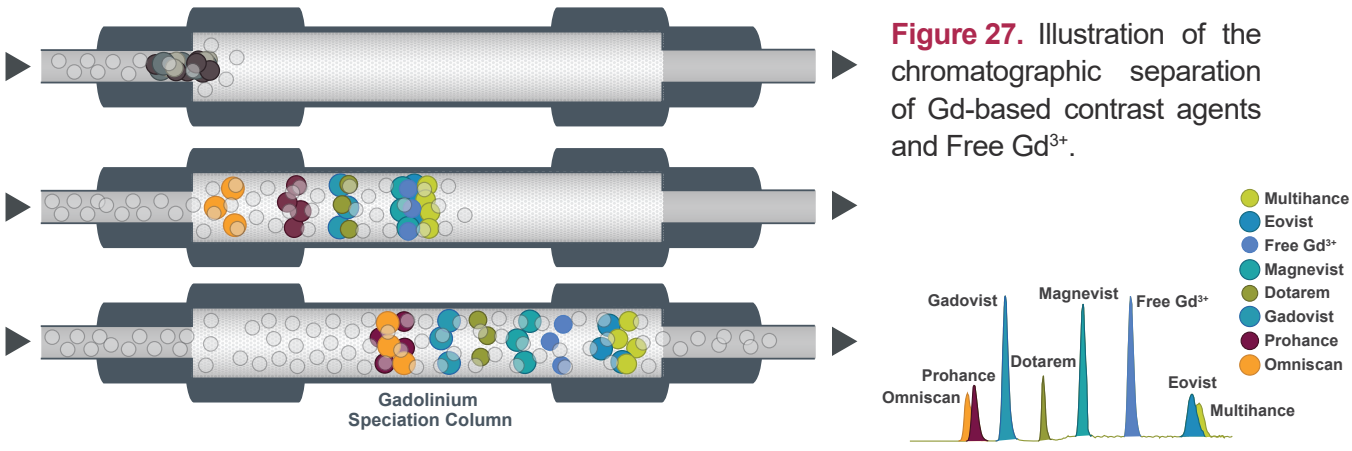


Figure 27. Illustration of the chromatographic separation of Gd-based contrast agents and Free Gd^{3+}.

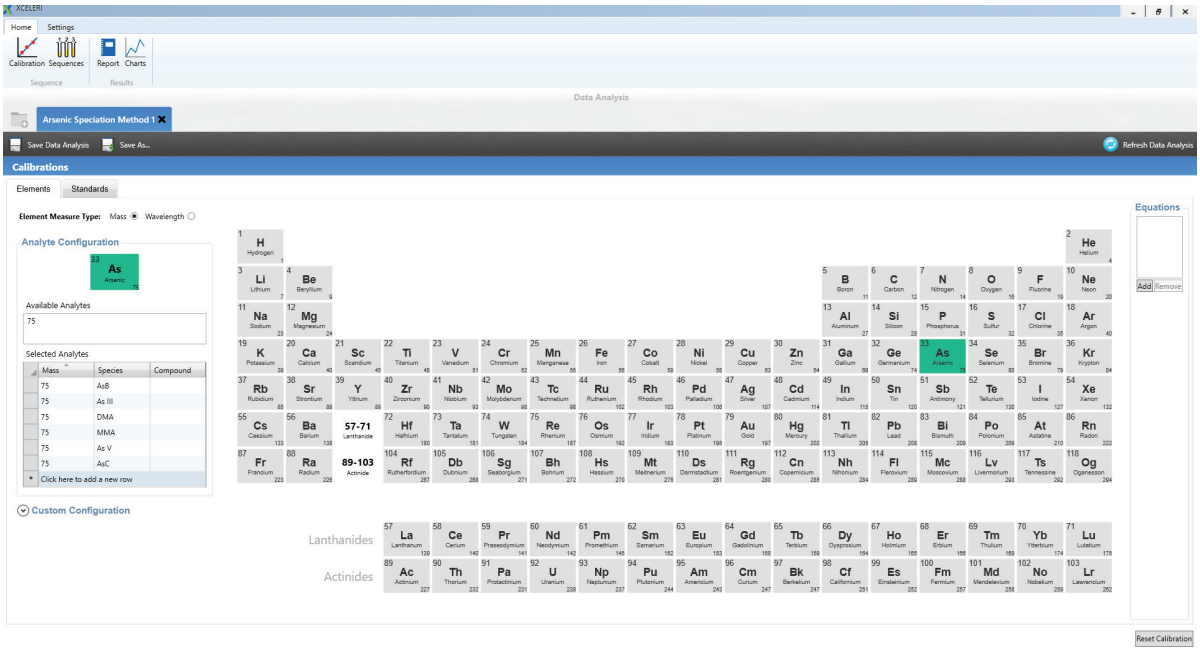


Figure 28. Screen shot example of the arsenic speciation method. Element(s) of interest are selected then assigned the desired species that will be monitored. For example here AsB, As III, DMA, MMA, As V and AsC have been selected for this method. More than one element can be selected if the method requires monitoring of multiple elements and species simultaneously.

CHROMATOGRAM VIEWING

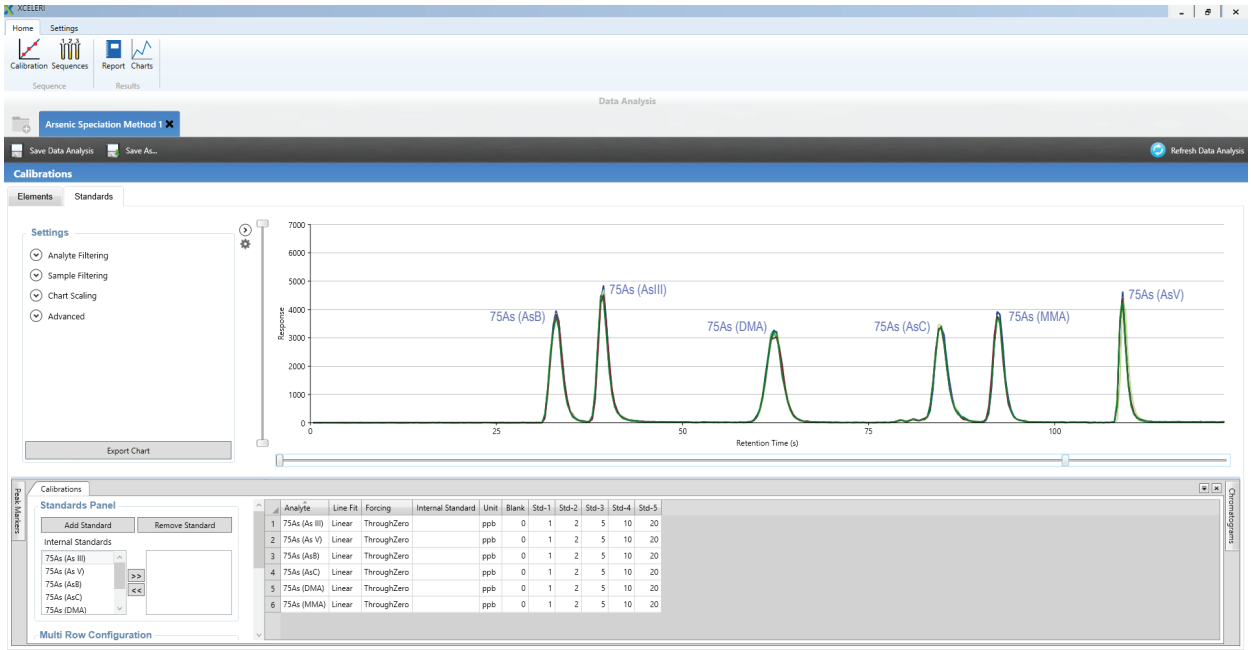


Figure 29. An example arsenic species method (AsB, As III, DMA, AsC, MMA, and As V). Data from standards or samples can be easily overlaid for comparison purposes.

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