

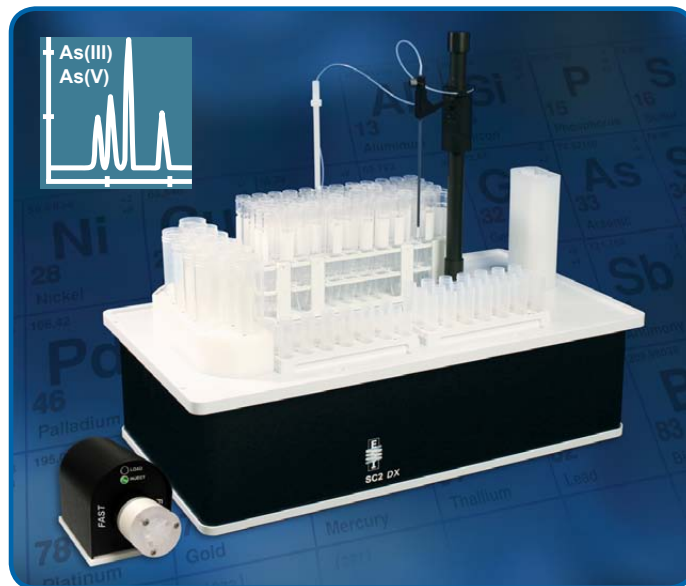
Low-Pressure Arsenic Speciation using the SC-DX chromFAST System with ICPMS Detection

Patrick Sullivan, Thaddeus Kowal, Dan Wiederin – Elemental Scientific

Introduction

Arsenic occurs in both organic and inorganic forms in the environment. Groundwater, for example, often contains inorganic species such as arsenite and arsenate from rock dissolution as well as organic species from agricultural and industrial runoff. Identifying which arsenic species are present in a sample can help determine the source of contamination.

Elemental Scientific's chromFAST arsenic speciation kit, coupled with the SC-DX FAST automated sampling system, is an economical and easy-to-use system that uses a peristaltic pump for low-pressure speciation, allowing researchers to detect a number of As species in a sample.



The SC-2 DX FAST Low-Pressure Elemental Speciation System

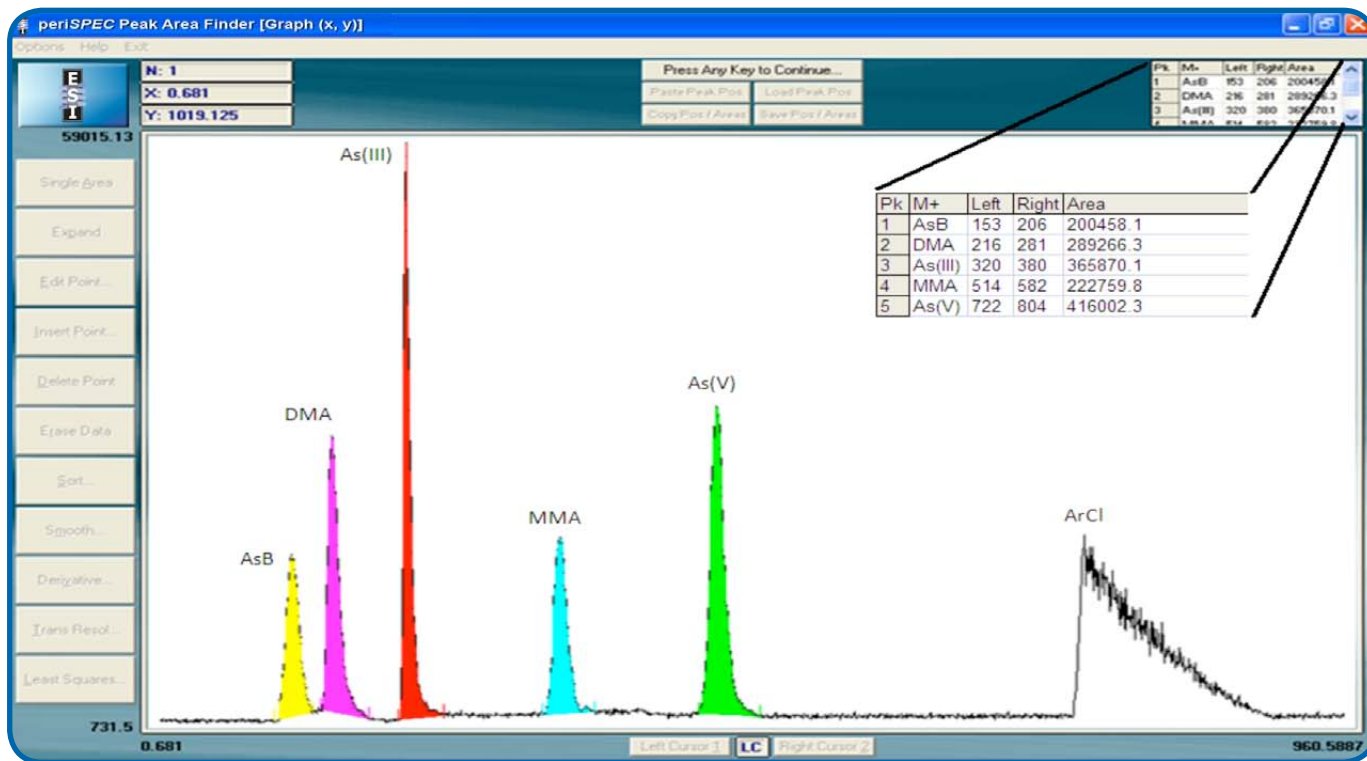


Figure 1. Low-pressure separation and detection of five arsenic species with SC-DX FAST and the ELEMENT2 ICPMS.

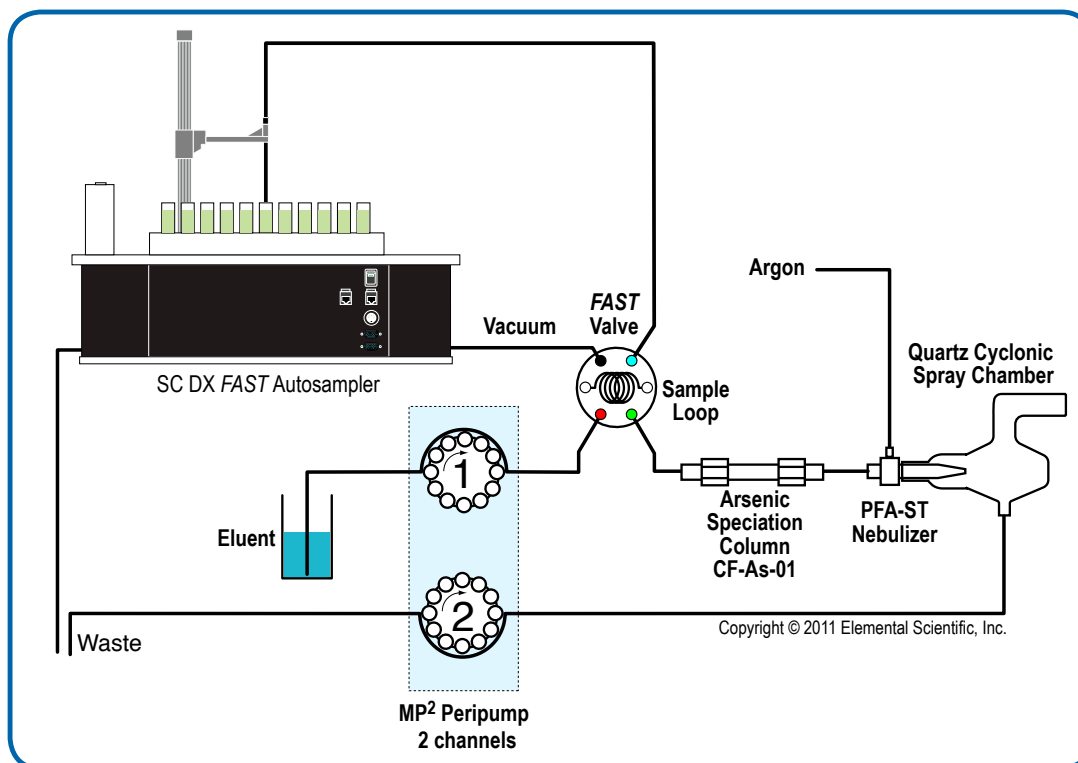


Figure 2. A diagram of the addition of a chromFAST speciation column to an existing SC-DX FAST system for separation of arsenic species by step-gradient elution anion exchange chromatography.

Instrumentation, Sample Introduction, and ICPMS Parameters

- ESI chromFAST speciation kit (CF-KIT-As35) with the As anion exchange column (CF-As-01)
- periSPEC software (ES-2999-4001)
- Thermo Scientific ELEMENT2 ICPMS
- Carrier flow rate: 170 $\mu\text{L}/\text{min}$
- Sample Volume: 20 μL

Procedure

Using an existing SC-DX FAST system, samples and standards are loaded into the sample loop via the PTFE vacuum pump. Once loaded, the valve switches and the peristaltic pump pushes the sample through the column for 7 seconds, introducing 20 μL of the sample into the column. The As species are separated on the column using a step gradient process and then nebulized using a low dead volume PFA-ST nebulizer.

Data Analysis

The collected data are analyzed with the ESI periSPEC Peak Area Finder software. This simple and relatively inexpensive software utilizes an Excel-based spreadsheet to integrate the chromatographic peak areas. The resulting data can then be used for calibration and determination of As species.

Separation and Calibration Studies

Species-specific standards of arsenite (As(III)), arsenate (As(V)), arsenobetaine (AsB), dimethylarsinous acid (DMA) and monomethylarsinous acid (MMA) were used to perform separation and calibration studies. The separation of the 5 arsenic species was obtained by using a step gradient elution, where eluent 1 washed the column for 3 minutes for the separation of AsB, DMA and As(III) (**Fig. 1**). Eluent 2 is then passed through the column for the elution of MMA, As(V) and Cl⁻. The calibration graphs were found to be linear to at least 10 ppb (**Fig. 3**).

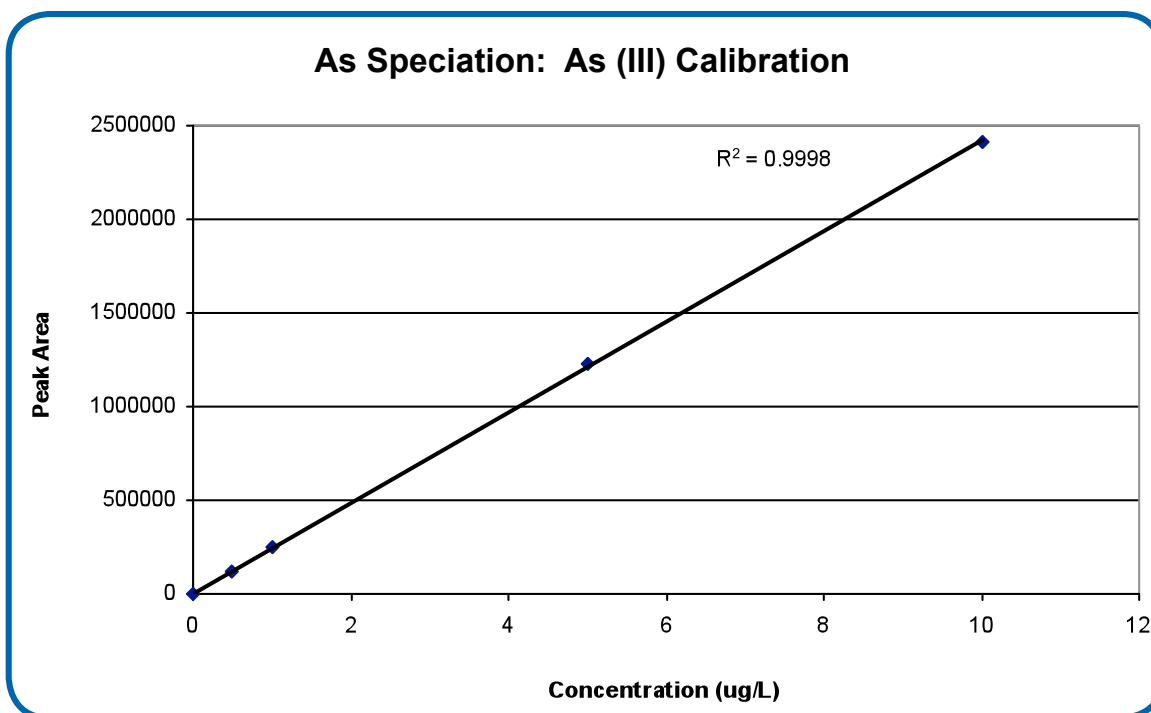


Figure 3. Calibration curve for inorganic As(III) species.

Matrix Effect Study

The effect of sample matrix on chromatographic retention time was measured for a variety of sample matrices, ranging up to 10% seawater, 1000 ppm chloride, and 100 ppm sulfate. 10 ppb spikes of DMA, As(III) and As (V) were added to each matrix and peak retention times were compared with the aqueous calibration standards. The retention time for the three arsenic species were constant for all sample matrices tested (**Fig. 4**).

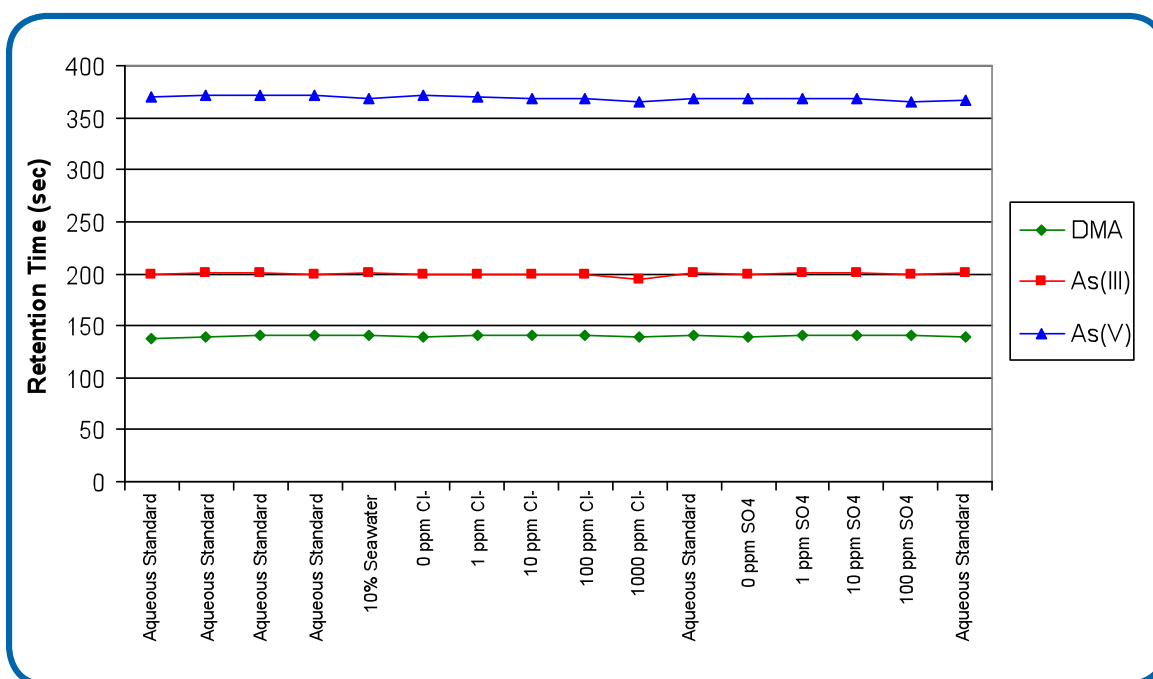


Figure 4. Effect of sample matrix on retention time.

Unspiked and Spiked High-Matrix Groundwater Measurements

The following graphs show As chromatographs of groundwater unspiked (**Fig. 5**) and spiked with 10 ppb each of DMA, As(III), MMA, As(V) (**Fig. 6**)

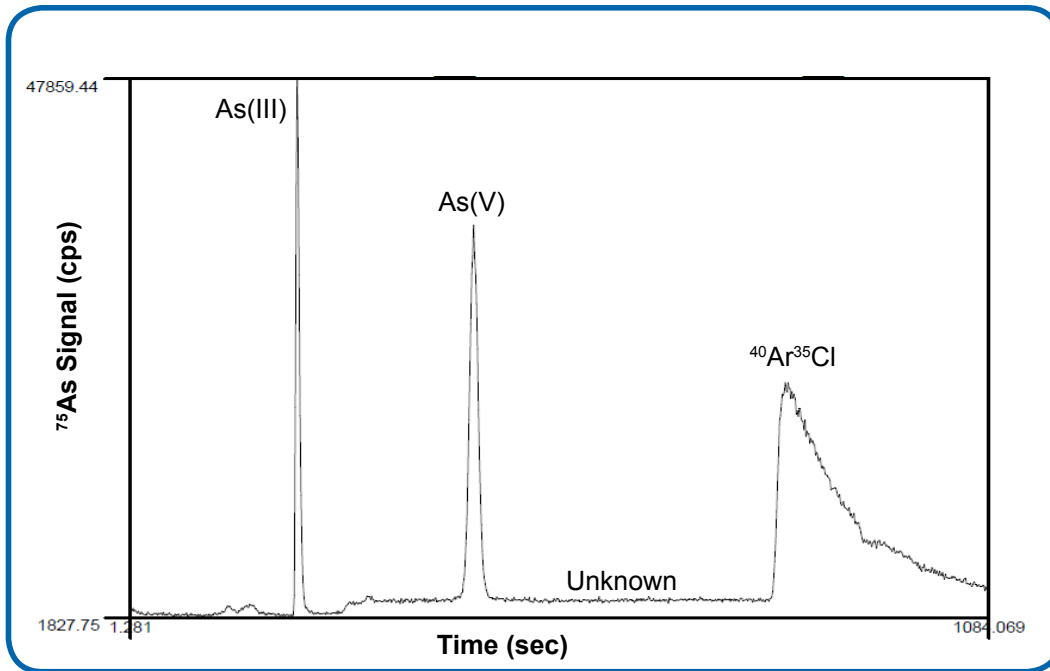


Figure 5. Low-pressure As chromatographs of an unfiltered and unspiked high mineral groundwater sample using step gradient elution.

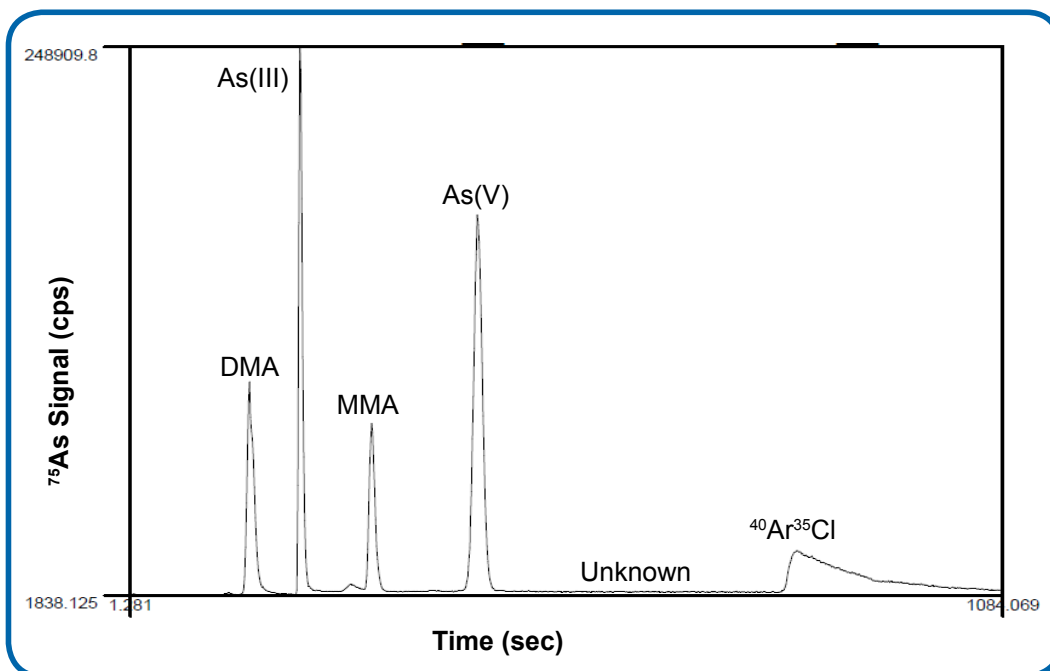


Figure 6. Low-pressure As chromatographs of a spiked (10 ppb each of DMA, As(III), MMA, As(V)), unfiltered high-mineral groundwater sample. Note the vertical scale compared with the unspiked sample. (Fig. 5)

Spike Recovery Studies

Spike recoveries were measured by spiking 5 ppb each of DMA, As(III), MMA, and As(V) into a groundwater sample (**Table 1**). Spike recoveries ranged from 100% to 115%.

Table 1. Arsenic species spike recovery data from high mineral content groundwater sample (HMGW). DUP = Duplicate; MS = Matrix Spike; MSD = Matrix Spike Duplicate.

	DMA		As(III)		MMA		As(V)	
	Concentration (ppb)	% Recovery	Concentration (ppb)	% Recovery	Concentration (ppb)	% Recovery	Concentration (ppb)	% Recovery
HMGW Filtered	0.05		1.07		0.02		0.97	
HMGW Filtered DUP	0.05		1.08		0.02		0.96	
HMGW Filtered MS	5.82	115	6.42	107	5.48	109	5.99	100
HMGW Filtered MSD	5.76	115	6.49	108	5.59	111	6.09	103
HMGW Unfiltered	0.07		1.22		0.03		1.27	
HMGW Unfiltered DUP	0.07		1.30		0.03		1.27	
HMGW Unfiltered MS	5.70	113	6.82	112	5.14	103	6.91	112
HMGW Unfiltered MSD	5.76	114	6.84	112	5.26	105	6.84	111

Table 2. Arsenic speciation in high mineral content groundwater samples.

Arsenic Species	Concentration (ppb)					
	Sample 1		Sample 2		Sample 3	
	Filtered	Unfiltered	Filtered	Unfiltered	Filtered	Unfiltered
DMA	0.053	0.068	0.152	0.208	1.085	1.429
As(III)	1.075	1.224	1.540	2.303	0.088	0.204
MMA	0.017	0.027	0.077	0.093	0.324	1.317
As(V)	0.970	1.271	0.232	0.303	0.006	0.655

Conclusion

The chromFAST low-pressure anion exchange arsenic speciation kit (CF-KIT-As35) and SC-DX FAST system for ICPMS is an economical alternative to HPLC-ICPMS systems. The fully-automated and easy-to-use system produces quick separations, as fast as four minutes for inorganic As species. The flexible system can switch between multi-element ICPMS sample analysis to elemental speciation detection modes in minutes. The unique periSPEC peak finder software provides a straightforward method for data analysis. The robust anion exchange column can be used for multiple samples and efficiently separates As species in difficult matrices, providing a cost-effective solution for As speciation needs.