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Use of an Inline Dilution Method for Measuring Arsenic Species in Urine Utilizing the prepFAST IC-HP in Combination with ICP-MS

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Improve Laboratory Efficiency for Total Metals and Speciation Analysis Using prep*FAST* IC-HP

Introduction

Trace element analysis is vital for industrial, government, and academic communities. Knowing the total concentration of an element in a given sample is important, but it does not tell the whole story. The chemical species (e.g., As(III), As(V), or AsCH5O3) plays an important part in understanding how it can affect the environment, its bioavailability, or its toxicity. For example, inorganic arsenic (As(III)) is more toxic than organic arsenic (monomethylarsonic acid, MMA), whereas organic mercury (methylmercury) is more toxic than its inorganic form (Hg(II)).[1]

The most common technique for trace metals analysis is inductively coupled plasma (ICP) coupled with either an optical emission spectrometer (-OES) or mass spectrometer (-MS). However, to determine the species of an element the chemical forms need to be selectively separated and the most common technique for this has become liquid chromatography (LC). Combining the two techniques, LC-ICPMS has become a very powerful and important tool for speciation of clinical, biological, food, pharmaceutical, and environmental based samples.[2]

Typically, trace elemental analysis measurements are done by acidifying the sample (e.g., 2% HNO3) and introducing it into an ICPMS (or ICP-OES). When determining the chemical species in a given sample, the sample integrity is paramount, and thus the sample must be kept in its native form. Species interconversion (the process of a chemical species changing form) becomes more likely during sample preparation as it is handled and exposed to external conditions. Yet most analytical columns used for chromatography have a low mass loading capacity which require diluted samples and/or small sample volumes (µL's).

In order to address this issue, we at Elemental Scientific (ESI), have demonstrated an all-inclusive autosampler instrument, prep*FAST* IC, which can be used for both total metals analysis and speciation analysis.

Recently, ESI has made advancements in the aforementioned technology and has introduced a higher-pressure unit, prep*FAST* IC-HP. This unit is capable of much faster chromatographic separations but also keeping the same advantages previously described. The improved performance will be demonstrated using the previously published arsenic speciation method for urine.

Instrumentation

ESI's prep*FAST* IC-HP

- Allows for faster separations, higher throughput, and the ability to use higher back pressure columns as compared to the previous version.

- Completely metal-free liquid and sample flow path from pump to nebulizer.

- Compatible with concentrated acids or organic solvents.

- Inline dilutions of samples and autocalibration functions.

- Ability to operate in "total metals" or "speciation" mode with a fully automated single platform instrument.

- Syringe-driven, post-column dilution, standard addition, or derivatization.

- Syringe loading (e.g. 200 µL of undiluted blood) or vacuum loading (e.g. 1 mL of undiluted urine) of samples.

- On-deck autosampler mixing of samples prior to loading.

- Xceleri Software for data processing and QC report building.

Highlights

Some of the key features that have been recently demonstrated include inline dilutions of undiluted urine samples for the measurement of arsenic species. It was shown that inline dilutions can eliminate arsenic species interconversion that is observed when manual offline dilutions are performed (Table 1).[3] The Eurofins Environmental Testing Sweden laboratory validated the prep*FAST* IC chromium speciation method by demonstrating a good agreement between results obtained with the prep*FAST* IC and their traditional HPLC-ICP-MS measurements.[4] In addition, this laboratory combined a total metals, aqua regia digest method with their chromium speciation method by taking advantage of the automated functions that allow unattended switching between total metals analysis and speciation analysis. Furthermore, it was revealed that having a completely metal free sample introduction system for chromium speciation provided a ~ 43X improvement in the limits of detection compared to their older method. The prep*FAST* IC has a post-column dilution option, that was used to couple a traditionally offline separation method that requires 8M HNO3 to remove trace elements from uranium, directly to an ICP-OES.[5]

Table 1. Manual dilution vs inline dilution of 10 ppb As(III) spiked urine samples.

		10 ppb As III Spiked Urine Samples		
Manual Dilution	Time (h)	As(III) %	As(V) %	As(III) % + As(V) %
	0	**100.0**	0.0	100.0
	1	**95.7**	0.0	95.7
	3	**92.8**	0.2	93.0
	6	**91.3**	1.6	92.9
	12	**78.5**	12.0	90.6
	24	**61.9**	21.4	83.4
		10 ppb As III Spiked Urine Samples		
Inline Autodilution	Time (h)	As(III) %	As(V) %	As(III) % + As(V) %
	0	**100.0**	0.0	100.0
	1	**102.8**	0.0	102.8
	3	**105.2**	0.0	105.2
	6	**106.4**	0.0	106.4
	12	**95.1**	0.5	95.6
	24	**102.9**	1.3	104.2

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) %

In the previously published method ammonium phosphate was used as the eluent for the separation of AsB, DMA, As(III), MMA, and As(V). This method was susceptible to high arsenic backgrounds due to poor quality phosphoric acid. The switch to ammonium carbonate as the eluent has led to a cleaner eluent, but allows for the separation of AsB, As(III), DMA, AsC, MMA, and As(V) which was not possible with the previous method. Figure 1 shows the separation of six arsenic species using the ammonium carbonate method with the prepFAST IC and the prepFAST IC-HP. The prepFAST IC is a low-pressure system that was capable of separating the six arsenic species in ~ 4 min 20 s, whereas the prepFAST IC-HP is able to separate the six arsenic species in < 2 min.
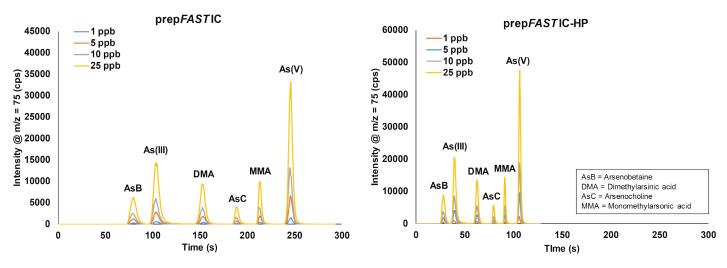

Figure 1. Comparison of the arsenic chromatograms obtained from the prepFAST IC and prepFAST IC-HP instruments in combination with an ICP-MS. The prepFAST IC chromatogram was obtained using 0.5 mL/min ammonium carbonate, while the prepFAST IC-HP chromatogram was obtained using 1.5 mL/min ammonium carbonate.

Data Processing - *Xceleri*

Elemental Scientific has developed a simple chromatographic software (Xceleri) for processing the type of transient data obtained from LC-ICP-MS measurements.

The software features include:

- Easy user interface for building new methods.

- Customizable and intelligent integration parameters for each elemental species.

- Prepares calibration curves.

- Visual overlay of chromatograms for comparison purposes.

- Easy review of chromatograms from standards and samples.

- Report generation includes chromatograms for each sample, intensities and integration parameters, concentrations, calibration curves, and calibration statistics.

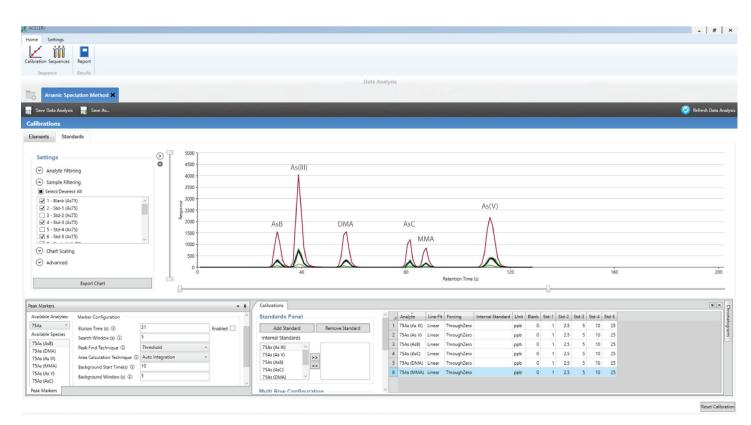- All report data can easily be exported to Excel.

Figure 2. Screenshot from Xceleri Software showing the overlay of As species chromatograms. In addition, the automated peak identification and integration parameters are found in the bottom left corner. The calibration curve values for each species are defined in the bottom right corner.

References

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