Agilent ICP-MS Journal

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Agilent Technologies

Direct Analysis of Gases Using a New Gas Sample Intro System and ICP-MS

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Introduction

The direct introduction of gas samples to an ICP-MS isn't a widespread application because of the difficulty of maintaining the plasma and locating suitable calibration standards. It is, however, a desirable method in terms of the potential data quality and speed of analysis. At Sumitomo Seika Chemicals, we have developed a system capable of transferring the particulate substances contained in a gas sample into argon using a gas exchanger. In order to eliminate any changes in the sample gas flow, we used a sample introduction system consisting of an aspirator and a pressure equalizer.
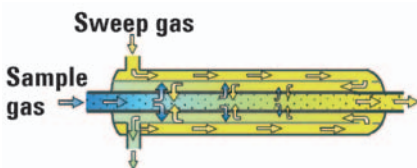
Instrumentation

Figure 1. Schematic of Gas exchanger

The gas exchanger (Figure 1) is designed so that argon flows in countercurrent through the outer side of the porous tube. Sample gas that is introduced into the central tube is dispersed, passes through the porous wall and is eliminated on the outer side. The argon sweep gas passes across the porous wall in the opposite direction and mixes with any particulates within the central tube. Particulates and argon pass along the tube to the outlet and into the plasma. The aspirator and the pressure equalizer smooth any changes in sample gas flow rates due to the pressure differential between the inner and outer sides of the tubes and/or due to the composition of the sample gas. This helps to maintain a constant flow rate of the sample gas.

The standard (reference) element gas generator used in our experiments is capable of supplying a standard gas containing 2.6 µg/m³ of molybdenum

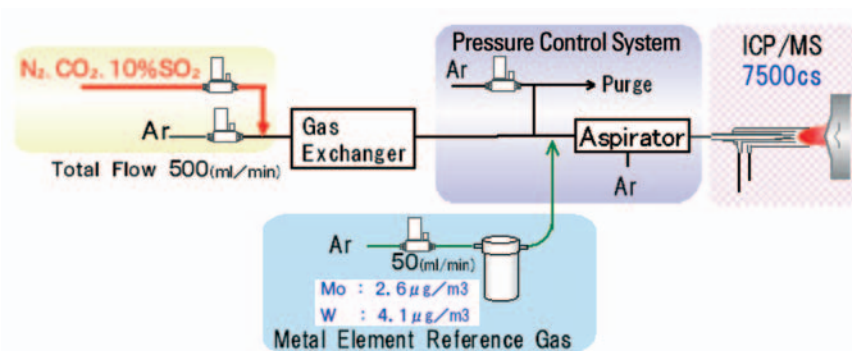**Figure 2. System diagram for direct analysis of gases by ICP-MS**

and 4.1 µg/m³ of tungsten at a flow rate of 50mL/min.

An Agilent 7500cs ICP-MS was used during this study. Because the particulates contained in the gas samples are extremely small, typically 0.01 - 0.1µm, a high sensitivity ICP-MS like the 7500cs is required. A diagram of the gas analysis system is shown in Figure 2.

Results and Discussion

No drop in the reference gas (tungsten or molybdenum) sensitivity was observed even when the sample gas (N_2, CO_2, or 10% SO_2) was introduced at flow rates of up to 500 mL/min through the gas exchanger. Figure 3 shows the signal for the iron isotope (m/z = 56) obtained from introducing the ambient air of the laboratory. The iron contained in the suspended particulates floating in the ambient air was measured in real-time.

This direct introduction method is extremely useful in achieving a higher detection sensitivity than is possible with the indirect method of introducing a solvent into the ICP-MS.

Direct introduction makes it possible to introduce the total amount of micro-particles contained in the sample gas into the plasma. The signals of the elements contained in the particulates are apparent in the form of spikes because of the extremely narrow peak widths.

Conclusion

With the use of the sample introduction system based on a gas-exchanger as described here, it is possible to separate particulates contained in gas samples, including air samples, and introduce the sample gas into the plasma with argon. This opens up the possibility of using ICP-MS effectively in a wide range of applications, including the monitoring of deleterious elements contained in sample gases such as ambient air and exhaust gases.

Investigations are now in progress with regard to calibration methods, including the calibration of standard metal element gases. We are confident that it will soon be possible to perform real-time monitoring of gaseous samples using ICP-MS.
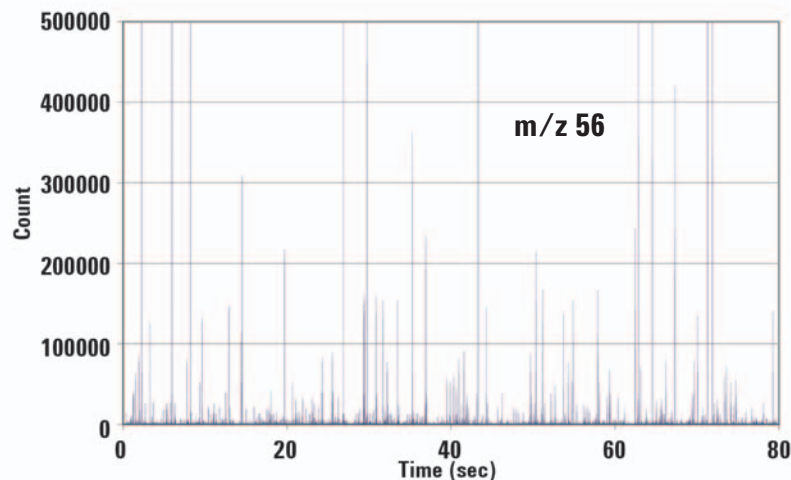

Figure 3. Iron in ambient air

Success Story: Nestle Waters: Certification of 7500ce Method for Trace Elements in Water

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Nestlé Waters manage a portfolio of 75 brands, bottled at 103 production sites. With sales accounting for almost 10% of the Nestlé Group's consolidated sales, quality of product is top priority. All of Nestlé Waters' bottled waters undergo the same strict quality controls and adhere to different local and international regulations.

Nestlé's worldwide center for water science is housed in the Product Technology Centre (PTC), based near the Vittel and Contrex bottling plants in France. Areas of expertise include:
• Bottled water
• Water resources control
• Bottling technology
• Packaging technology
• Industrial practices

The Central Laboratory, which forms part of the PTC, carries out over 200,000 chemical and microbiological analyses every year. It is equipped with the latest instrumentation to detect, identify and qualify water quality parameters, even at low concentrations.

All waters are also subject to taste testing in the sensory evaluation room. The panel of carefully selected tasters establishes organoleptic profiles – subjective, sensory judgments based on the experience of the evaluator – on finished products and new products.

Evaluation of ICP-MS

In 2003, the inorganic testing facility within the Central Lab, was equipped with ICP-OES for major elements (calcium, magnesium, sodium, potassium, sulfur and silicon) and GFAAS for trace elements analysis in bottled waters. With the large workload, operating two instruments in order to assay one sample for the desired suite of elements was labor intensive. To relieve the strain on

Nestlé Waters Product Technology Centre (PTC), based near the Vittel and Contrex bottling factories, France

the lab, ICP-MS was evaluated, as a replacement technique for the existing technologies.

The Agilent 7500ce ICP-MS was installed in the lab in 2004 and it was soon apparent that the new instrument could easily accommodate the workload, with additional advantages:
• Better limits of detection
• More reliable results with Octopole Reaction System (ORS) interference removal capability
• Faster throughput with ISIS and CETAC ASX-520 autosampler
• Spare capacity to analyze non-routine and urgent samples (new wells, new products, water treatment, and process improvement)

Quality Certification for ICP-MS 7500ce

The chemistry department within PTC was awarded COFRAC (French Committee of Accreditation) Certification in 2005 for its trace element analysis of drinking waters by ICP-MS. The COFRAC certificates are equivalent to those issued by European and international bodies e.g. ISO 17294-2:200 (Water Quality – Application of ICP-MS-Part 2: Determination of 62 elements), and provide assurance about the quality and reliability of analysis.

Fifty-six trace elements are now routinely and simultaneously monitored in the PTC chemistry laboratory below 1 µg/L (ppb) in waters coming from any of the 103 production sites within the Nestlé Waters group. Samples can contain total dissolved solid (TDS) content up to 3 g/L.

Method Validation for Major Elements in Water

Although currently all major and minor isotopes are analyzed in the same analytical run using the 7500ce ICP-MS, external validation for the major components (major cations: calcium, magnesium, sodium, potassium and major anions: silicon expressed as silica and sulfur expressed as sulfates) will follow later in 2006.

Future Projects

Now that the 7500ce ORS is taking care of the day-to-day workload of mineral analysis, we intend to apply it to research projects important to Nestlé Waters including:
• Monitoring of impurities of added salts in waters e.g. bromine
• Improvement of water processes e.g. iodine
• Low level analysis of mercury

Conclusions

Investment in the 7500ce ORS ICP-MS allowed us to achieve our aim of replacing multiple techniques with a single instrument. The ORS is easy to use and is highly effective at removing interferences eliminating the need for interference correction equations.

Free Upgrade to the New ChemStation Revision B.03.03!

Tomo Yamada, ICP-MS Product Manager,
Agilent Technologies Inc., Japan

Shipment of the latest ICP-MS ChemStation - revision B.03.03, begins August 2006. To encourage users to upgrade to B.03.03, Agilent is offering the software free of charge to all B.0x.0x users.

Why Upgrade?

Revision B.03.03 is faster, easier to use and more powerful than any previous version. With more than 30 new features and enhancements, the latest ICP-MS ChemStation software suite continues to enhance the ease of use and productivity of the 7500 Series ICP-MS. Agilent field staff can also provide more efficient software support to users on the same, and most current ChemStation revision.

New Features of B.03.03

• Faster

New feature in ChemStation B.03.03: The software architecture has been streamlined to eliminate unnecessary delays when switching between tasks, resulting in significantly faster response, especially during manual operation.
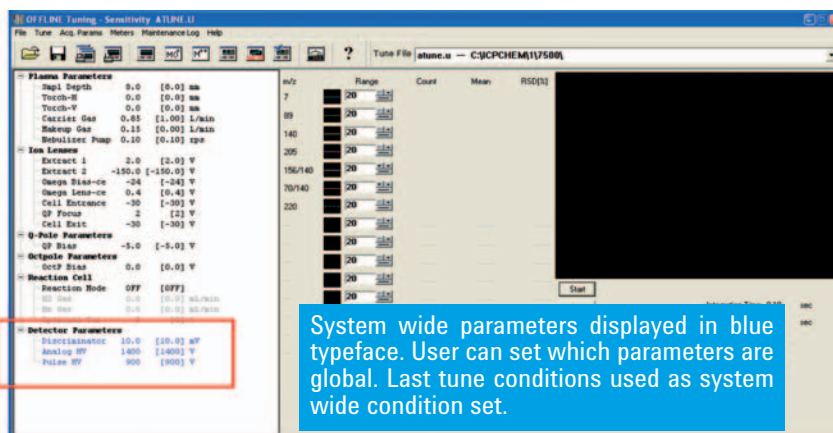
• New Tuning Window

New feature in ChemStation B.03.03: The tune window user interface has been further improved for ease of use. Some of the new features include.

– Comprehensive Multimode Autotune. Now no-gas, He and H_2 mode, as well as detector and P/A factors all can be autotuned with a single click!
– A Multimode tune report can be generated automatically for no gas, He and H_2 modes
– Up to 15 masses or ratios can be viewed simultaneously
– Current set value, original value and slide bar are displayed next to each parameter for faster, simpler manual tuning
– System-wide parameters - user-selectable parameters are applied to ALL tune files (see below)

• System Wide Parameters

New feature in ChemStation B.03.03: Certain parameters like

System wide parameters displayed in blue typeface. User can set which parameters are global. Last tune conditions used as system wide condition set.

Improved ease-of-set-up with System Wide parameters

the EM settings, quadrupole and detector parameters and P/A factors remain constant for all tune modes: these can now be defined as 'System Wide Parameters' which means they are applied to all tune files. This eliminates redundant tuning or the need to copy these values to different tune files resulting in improved speed and reliability.

• Multimode Autotune

New feature in ChemStation B.03.03: Multimode Autotune performs autotuning of all cell modes and P/A factors with a single click of the mouse. This new autotune routine is much faster and more efficient than starting autotune for each gas mode separately. The new Autotune algorithms and target values have been optimized to improve autotune speed and reproducibility.

• Pre-emptive Rinse Enhancement

The Pre-emptive Rinse function has been further improved to allow the rinse step to be started at any time during data acquisition and automatically advance to the next rinse
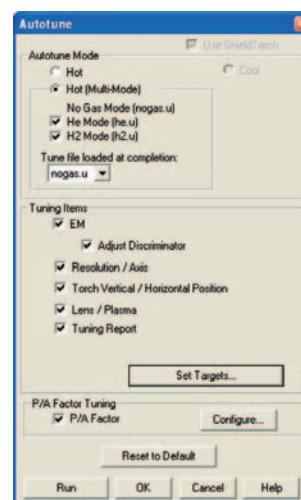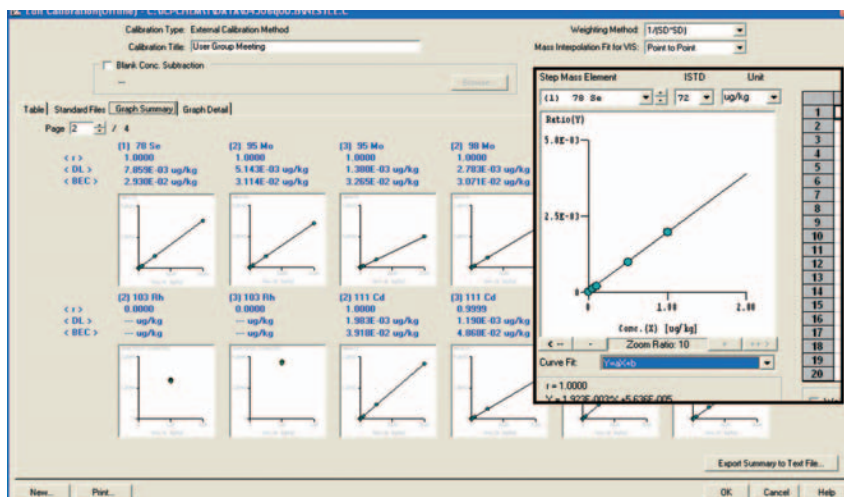

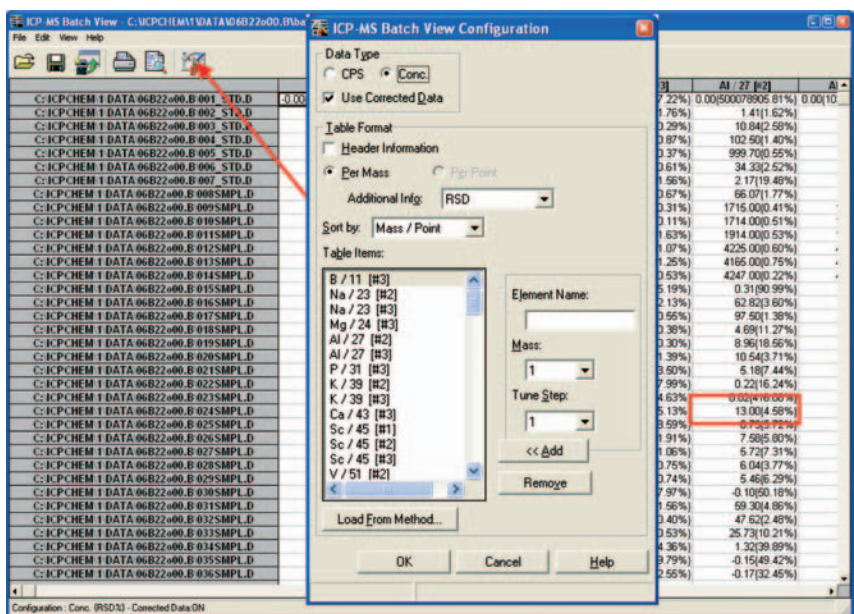**Showing Multimode Autotune and P/A Factor Tuning Window.**

step at the exact end of acquisition - see Journal 27, 5989-5132EN for more details on Pre-emptive Rinse.

• Pre-run Monitor

New feature in ChemStation B.03.03: Pre-run Monitor displays the signal from up to 6 masses

Data Analysis – Graph Summary

Data Batch View

during sample uptake. The user can then manually start data acquisition after visually verifying the sample is being detected and the signal has stabilized. This feature is useful for method development or when manual sample introduction is preferred (e.g. semiconductor or microsample analysis).

• **Data Analysis**
Easy to view calibration data in graph summary format:
– 12 calibration plots can be displayed simultaneously
– Calculated concentration, CPS, internal standard ratio, detector mode & RSD displayed
– Detection limits, BEC's and regression coefficients displayed

The calibration summary data can also be exported to a text file.

• **Batch View**
New feature in ChemStation B.03.03: Multiple data files are tabulated into a database as data is acquired allowing the user to view sample results (cps or concentration) in real time during sequencing, as well as after run completion. Unlike the popular add-in feature Fileview, Batch View is fully integrated into the ChemStation software and updates automatically.

• **Offline Acquisition Editor**
New feature in ChemStation B.03.03: The user can modify another method offline while the current run is running using Offline Acquisition Editor.

How to Upgrade from Older Versions of the 7500 Series ICP-MS ChemStation

For current rev.B.0x.0x users, a free upgrade to B.03.03 can be downloaded from the Agilent ICP-MS website - see instructions below. For 7500 Series users with NT ChemStation software versions (Rev.A), an upgrade to B.03.03 is available to purchase by ordering P/N G3149B.

How to Upgrade to B.03.03

Technical Support

Follow these simple steps to download B.03.03 from the Agilent ICP-MS website:

• Go to **www.agilent.com/chem/icpms**
• Select "Technical Support" from the upper panel on the web page
• Select "Status Bulletins and Patches" under the "Downloads and Utilities" link.
• Click on "ICP-MS ChemStation" (To access this page you will need to enter the 10 digit registration number shown on the "Software Certificate and Registration Packet" supplied with your instrument).
• Select "English version" (or "Japanese version") under the "Updates from Rev.B.0x.0x to Rev.B.03.03" and follow the instructions given.

Minimum PC Hardware Requirements

Some PC's originally supplied with older 7500 mainframes will not meet the requirements shown in Table 1 and a new PC bundle must be ordered with the ICP-MS ChemStation software upgrade.

A new ICP-MS PC hardware upgrade bundle (G3150A #321) is available. This product has been set up for existing ICP-MS ChemStation users, and includes a new PC (with Windows XP O/S), monitor and printer, but not an ICP-MS ChemStation software license (since existing 7500 users already have one).

PC	HP Kayak VL400 7/800 or faster
System Memory	512MB for Windows XP
Hard Disk	10.0 GB or greater
Operating System	Windows XP Professional + Service Pack 2
	Windows 2000 + Service Pack 4
Internet Explorer	Internet Explorer 6 + Service Pack 1
Printer	(English) HP LaserJet 4000/4050/2200
	(Japanese) Canon LBP 430, Brother HL-1240/1440/5040 or
	later models supplied with ChemStation PC
Display resolution	1280 x 1024 pixels
I/O Libraries	ver.M.01.01.04
GPIB	82350A or 82350B, 82341C (for Windows 2000 only)
	(GPIB not needed for LAN model)
Supported Instrument	Agilent 7500 Series only

Table 1. Minimum PC Hardware Requirements

Arsenic Speciation in Urine Becomes Routine

Tetsushi Sakai and Steve Wilbur,
Agilent Technologies

Arsenic exposure may lead to cancer or other adverse effects, but the toxicity is strongly dependent on the species. Of the five As species most commonly found in human urine, the order of toxicity is: As(III) (arsenite) > As(V) (arsenate) > DMA (dimethylarsinic acid) ≥ MMA (monomethyl arsonic acid) >> AB (arsenobetaine). While HPLC-ICP-MS is well accepted as the analytical technique of choice for As speciation in urine, some remaining difficulties have prevented the technique from becoming routine. These are:

- Finding chromatographic conditions that will separate the 5 most important species as well as inorganic chloride in a reasonable time, with good retention time reproducibility, dynamic range and sensitivity.
- Resolving or eliminating the ArCl interference on As which is derived from the high NaCl concentration in urine samples
- Avoiding clogging of the ICP-MS interface from total dissolved solids (TDS) contained in the urine and HPLC buffers.

Optimized Conditions

An Agilent 1100 Series HPLC isocratic pump, with autosampler, thermostatted column compartment, and vacuum degasser was coupled to an Agilent 7500ce ICP-MS system fitted with an Agilent MicroMist glass concentric nebulizer. Typical ICP-MS conditions were used for As analysis, including; forward power: 1550 W, sample flow rate: 1 mL/min, total carrier gas flow: 1.12 L/min. As was monitored at its elemental mass: $m/z = 75$.

Column Selection
A new column was developed and manufactured by Agilent.
Column   G3288-80000
                (4.6 x 250 mm)
Guard Column   G3154-65002

Mobile Phase
The basic mobile phase consisted of:
- 2 mM phosphate buffer solution (PBS), pH 11.0 adjusted with NaOH
- 0.2 mM EDTA
- 10 mM, CH_3COONa
- 3.0 mM $NaNO_3$
- 1% ethanol

Interference Removal
The new Agilent G3288-80000 column provides the necessary chromatographic resolution to completely separate inorganic chloride from the arsenic species under isocratic conditions, thereby eliminating the ArCl interference on As.

As a result, this method is suitable for use with the non-ORS 7500a ICP-MS as well.

Analysis of Urine Samples

The new methodology was applied to the analysis of NIES CRM No.18 urine, using a 5 µL injection of the undiluted sample (Figure 1A). The results agree well with the certified values (AB 66.0 µg/L, DMA 31.0 µg/L). Repeated injections (n = 15) of a 1/10 diluted human urine sample spiked at 5 µg/L demonstrates good long term stability and robustness of the method (Figure 1B).

Conclusions

A new HPLC-ICP-MS method capable of separating all 5 important arsenic compounds in human urine within 12 minutes has been developed through careful, systematic optimization of all parameters, including the development and manufacture of a new column. The method is robust enough for the analysis of undiluted urine with limits of detection of 0.1 µg/L or less for the individual As species.

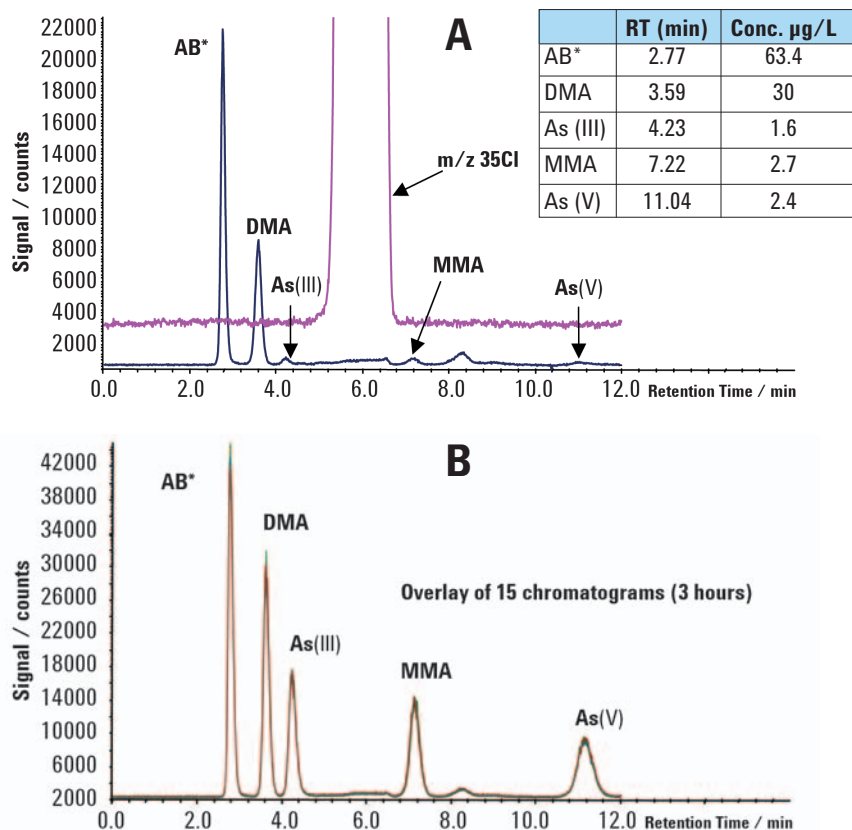|	RT (min)	Conc. µg/L
AB*	2.77	63.4
DMA	3.59	30
As (III)	4.23	1.6
MMA	7.22	2.7
As (V)	11.04	2.4

Figure 1. (A) Undiluted 5 µL injection of NIES CRM No.18 urine standard. (B) Reproducibility of 15 x 1/10 human urine samples (spiked 5 µg/L)
*Arsenobetaine, while well separated from the four anionic species, elutes with the void volume and may co-elute with other neutral or cationic species if present.

www.agilent.com/chem/icpms

New Inert kit and PFA nebulizer

Tomo Yamada, Agilent Technologies Inc., Japan

After extensive development and testing, Agilent has introduced a new inert sample introduction kit and a new design PFA concentric nebulizer for the 7500 Series.

New Agilent Inert Kit

The new inert kit (G3285A) is all-PFA and features an o-ring free end cap, push-fit torch connector and demountable torch. The inert kit has been carefully designed to fit perfectly on the 7500 Series mainframes. An exhaustive testing and design program has resulted in excellent long term stability and elimination of droplet formation in the connecting tube – the weak point of any inert sample introduction system. Both platinum and sapphire injectors are available with different internal diameters (i.d.) to suit every application (Table 1). An optional 2nd gas port at the torch connector allows for the addition of oxygen for organic solvent analysis. The new inert kit (#101 with sapphire injector) will be included as part of the accessory kit shipped as standard with the Agilent 7500cs from September.

New PFA Concentric Nebulizer

In addition to this new inert kit, a completely new-design PFA concentric nebulizer has also been introduced. It produces a highly reliable and reproducible aerosol and can be used with the inert kit and also the

Part number	Description
G3285A #101	Inert kit - Sapphire injector (i.d. 2.5mm)
G3285A #102	Inert kit – Platinum injector (i.d. 2.5mm)
G3285A #103	Inert kit - Sapphire injector (i.d. 1.5mm) with O_2 port
G3285A #104	Inert kit – Platinum injector (i.d. 1.5mm) with O_2 port
G3285-80000	PFA Concentric Nebulizer (200 uL/min.)
G3285-80001	PFA Concentric Nebulizer (200 uL/min) with I-AS probe

Table 1. Ordering information
Note: The inert kits do not include a nebulizer – choose G3285-80000 or G3285-80001 above

standard quartz spray chamber. The nominal uptake rate is 200 uL/min and is consistent from nebulizer to nebulizer. Samples can be pumped or free aspirated. A version with an integrated probe for the Agilent integrated auto-sampler (I-AS) is also available. All new inert kit and nebulizer options are available on the Agilent price list from August 1st, 2006.

Use of Collision Cells for EPA Method 200.8 for Drinking Water

Steve Wilbur, Agilent Technologies Inc., USA

As a leading manufacturer of collision/reaction cell (CRC) ICP-MS systems used in the environmental testing industry, we would like to help clarify the intent and ramifications of the recent EPA Office of Water memo (July 14, 2006) stating that the use of enabled CRC technology is currently not permissible for **drinking water compliance monitoring** using EPA method 200.8.

This memo is the result of the rapid increase in the use of CRC-ICP-MS in recent years without the corresponding development of appropriate quality assurance protocols to insure that the data generated is equivalent to, or better than, that using mathematical interference correction equations.

Since the approach to CRC technology varies significantly with the various ICP-MS manufacturers, devising a simple, universal set of QA/QC protocols is challenging. However, Agilent had been actively supporting EPA's efforts to validate a collision cell enabled version of method 200.8 with appropriate quality assurance criteria to insure equivalent or better results when compared with mathematical correction equations.

Technology Not in Question

EPA, in general, supports the use of CRC-ICP-MS and calls it a major technological advance. Their main concern is in minimizing what they perceive as a requirement for

significant operator intervention in achieving and verifying optimum CRC performance. While Agilent ICP-MS systems are simple to tune and operate in CRC mode, we support EPA's contention that this needs to be validated. We believe that a performance-based approach using interference check standards similar to those required by EPA-6020 will meet the requirements, and we have provided data and guidance to support this.

Furthermore, Agilent is supporting the efforts of the American Council of Independent Laboratories (ACIL) to work with the National Environmental Laboratory Accreditation Council (NELAC) and EPA to validate the use of collision cell technology for all applications of Method 200.8.

In the meantime, please be aware that, as issued, this memo applies only to **drinking waters** for regulatory compliance, and **not to any other uses for method 200.8.** Since most drinking waters are relatively free of complex matrix, the impact on data quality will be smaller than for other matrices.

The upside is that, through this memo, the EPA Office of Water has finally, formally declared their intent to develop a modified method for drinking water compliance monitoring using CRC technology.

In Summary

Agilent Technologies still recommends the 7500ce for environmental applications at this time. We fully expect the EPA to approve the use of CRC-ICP-MS for drinking waters and other applications in due course.

Please feel free to contact me directly with questions or comments. **steven.wilbur@agilent.com**

New! Guide to Upgrade Products for 7500 Series ICP-MS

See at a glance which upgrades are available for the 7500 Series ICP-MS. The 14-page upgrade guide details the options available to users of the Agilent 7500 Series ICP-MS who require additional functionality from their instrument.

A .pdf file of the **Upgrade Products for Agilent 7500 Series ICP-MS Instruments, 5989-5172EN** can be downloaded from the external Agilent website at:
www.agilent.com/chem/icpms

Recorded e-Seminars

If you missed the recent ICP-MS e-seminar by Prof. Joe Caruso, University of Cincinnati, or would like to review the presentation again, you can now do so on-line at:
www.agilent.com/chem/eseminars-icpms

Choose from the following titles:
- A Metallomics Approach for Analysis of Biological and Environmental Compounds via ICP-MS*
- Applying Reaction Cell ICP-MS to Routine Multielement Analysis
- Environmental Analysis: A Comparison of Cell and Non-cell ICP-MS
- Developments in Speciation Measurement with ICP-MS as a Detector
- Semiconductor Applications of Octopole Reaction Cell ICP-MS
- Reaction Cell ICP-MS for Environmental Metals Analysis

*Turn off pop-up blocker

Trade Shows and Conferences

6th The 16th Annual V.M. Goldschmidt Conference 2006, 27 August - 1 September 2006 Melbourne , Australia. **www.goldschmidt2006.org**

JAIMA SHOW 2006, 30 August - 1 September 2006, Makuhari Messe, Japan

Asia-Pacific Winter Conference on Plasma Spectrochemistry
November 27 - December 2, 2006
Bangkok, Thailand
www-unix.oit.umass.edu/˜wc2006/

2007 European Winter Plasma Conference, February 18-23, 2007, Taormina, Sicily, Italy
www.uc.edu/plasmachem/taormina.htm

Welcoming New Agilent ICP-MS Users

A very warm welcome to all companies and institutions that have recently added an Agilent ICP-MS to their analytical facilities. Remember to join the Agilent web-based ICP-MS User Forum – the place where you can exchange information relating to your 7500.

To access the Forum, you will simply need to log-in to the Agilent web site, or register if you haven't already, and enter your instrument's serial number on your first visit only.

Look for the link to the ICP-MS User Forum from:
www.agilent.com/chem/icpms

Winter Plasma Conference 2007

Join the Agilent ICP-MS team at the 2007 European Winter Plasma Conference, February 18-23, 2007, in Taormina, Sicily, Italy. Agilent are again sponsoring the European Plasma Award for Spectrochemistry – a prize presented to for either a single outstanding piece of work or for continued important contributions to the field of plasma spectrochemical development.

Agilent ICP-MS User Meeting – the finer details for the Agilent ICP-MS User Meeting to be held at the WPC are yet to be finalized - see the Agilent ICP-MS web site or the next issue of the ICP-MS Journal for more information. If you are planning on attending the WPC, check out the array of education short courses at introductory and advanced levels on the conference web site at: **www.uc.edu/plasmachem/taormina.htm**

JAAS Top 10

A recent paper by Prof. Joe Caruso's group at the University of Cincinnati, featuring the 7500ce, was one of the most accessed JAAS articles in May 2006: **Reversed Phase Ion-pairing HPLC-ICP-MS for Analysis of Organophosphorus Chemical Warfare Agent Degradation Products,** Douglas D. Richardson, Baki B. M. Sadi and Joseph A. Caruso, J. Anal. At. Spectrom., 2006, **21**, 396

Agilent ICP-MS Publications

To view and download these latest publications, go to www.agilent.com/chem/icpms and look under "Library Information"

- Upgrade Products for Agilent 7500 Series ICP-MS Instruments, 5989-5172EN
- The Analysis of Carbonate Associated Sulfur by 7500ce ORS-ICP-MS, 5989-5318EN
- Determination of Ceruloplasmin in Human Serum by Immunoaffinity Chromatography and Size Exclusion Chromatography-ICP-MS, 5989-5304EN
- Ultra-Trace Analysis of Beryllium in Water and Industrial Hygiene Samples by ICP-MS, 5989-5438EN
- Ultra-Trace Analysis of Organophosphorus Chemical Warfare Agent Degradation Products by HPLC-ICP-MS, 5989-5346EN
- Achieving Optimum Throughput in ICP-MS Analysis of Environmental Samples with the Agilent 7500ce ICP-MS, 5989-5001EN

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