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The Measure of Confidence

Agilent Technologies

High Throughput Analysis of Flue Gas Wastewater Samples by ICP-MS

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TestAmerica Laboratories Inc. and
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Introduction

The U.S. Environmental Protection Agency (USEPA) is in the process of revising wastewater effluent guidelines for the steam electric power generating industry. These guidelines will apply to most large-scale thermal power stations in the United States that use coal, oil, gas or nuclear fuel in conjunction with steam turbine generators. Clean Air regulations require that the flue gases from these plants be "scrubbed" to remove SO_2 before release to the atmosphere, and the wastewater from these scrubbers, especially from coal fired plants, typically contains high levels of pollutants. The composition of this flue gas desulfurization (FGD) wastewater varies greatly, but the matrix may include several hundred to several thousand ppm of calcium, magnesium, manganese, sodium, boron, chloride, nitrate, and sulfate.

Measurement of low ppb levels of toxic metals in these wastewater matrices presents a challenge for ICP-MS, due to high levels of dissolved solids and potential interference from matrix-based polyatomic ions. To address this difficult analytical challenge, we developed a new method utilizing the Agilent 7700x ICP-MS, which includes the High Matrix Introduction (HMI) system and reliable interference removal using helium collision mode. The 7700x was operated with the optional ISIS-DS for high sample throughput by discrete sampling.

USEPA Standard Operating Procedure (SOP) development and validation

First, we established that the method performance requirements could be met routinely, including determination of Method Detection Limits (MDL) and Linear Dynamic Range (LDR). We also validated the effectiveness of He mode for removing polyatomic interferences in synthetic high-matrix samples, and confirmed acceptable washout after high matrix samples.

Analytical Sequence	
Warm-up	
Tune instrument	
Perform mass calibration check	
Perform resolution check	
Validate tuning criteria	
Calibration blank	
Calibration standard 1	
Calibration standard 2	
Calibration standard 3	
ICV	
ICB	
Method (Reagent) Blank	
Synthetic FGD Matrix Interference Check	
Laboratory Fortified Synthetic FGD Matrix	
Reporting Limit verification standard	
CCV	
CCB	
10 Samples (which can include all sample types) Must include 1 LCS and 1 MS/MSD pair	
CCV	
CCB	

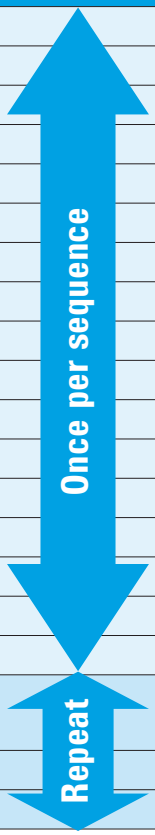

Table 1. Typical FGD analytical sequence including all required quality control. ICV = Initial Calibration Verification, ICB = Initial Calibration Blank, CCV = Continuing Calibration Verification, CCB = Continuing Calibration Blank, LCS = Laboratory Control Sample, MS/MSD = Matrix Spike/Matrix Spike Duplicate

We then applied typical EPA quality control (QC) check criteria to monitor instrument performance in a representative validation sequence that included all EPA mandated calibration and QC samples (Table 1). All required quality control checks were within acceptance limits and, equally importantly, remained within limits for the duration of the 89-sample sequence. Recoveries for the continuing calibration verification checks (CCVs) run periodically after every 10 real samples were well within +/- 15%, as depicted in Figure 1.

The new FGD wastewater method required two new QC samples: a Synthetic FGD Matrix Sample and a Fortified FGD Matrix Sample. These new samples are analogous to the interference check solutions ICS-A and ICS-AB required by EPA method 6020, except the synthetic FGD samples are much higher in total dissolved solids (TDS) than the ICS-A and AB solutions, and contain those matrix elements that are commonly high in actual FGD samples.

A mixed synthetic FGD solution was spiked with all the analyte elements at 40 ppb. Results from the analysis of the synthetic FGD matrix blank and synthetic FGD matrix spike are shown in Table 2.

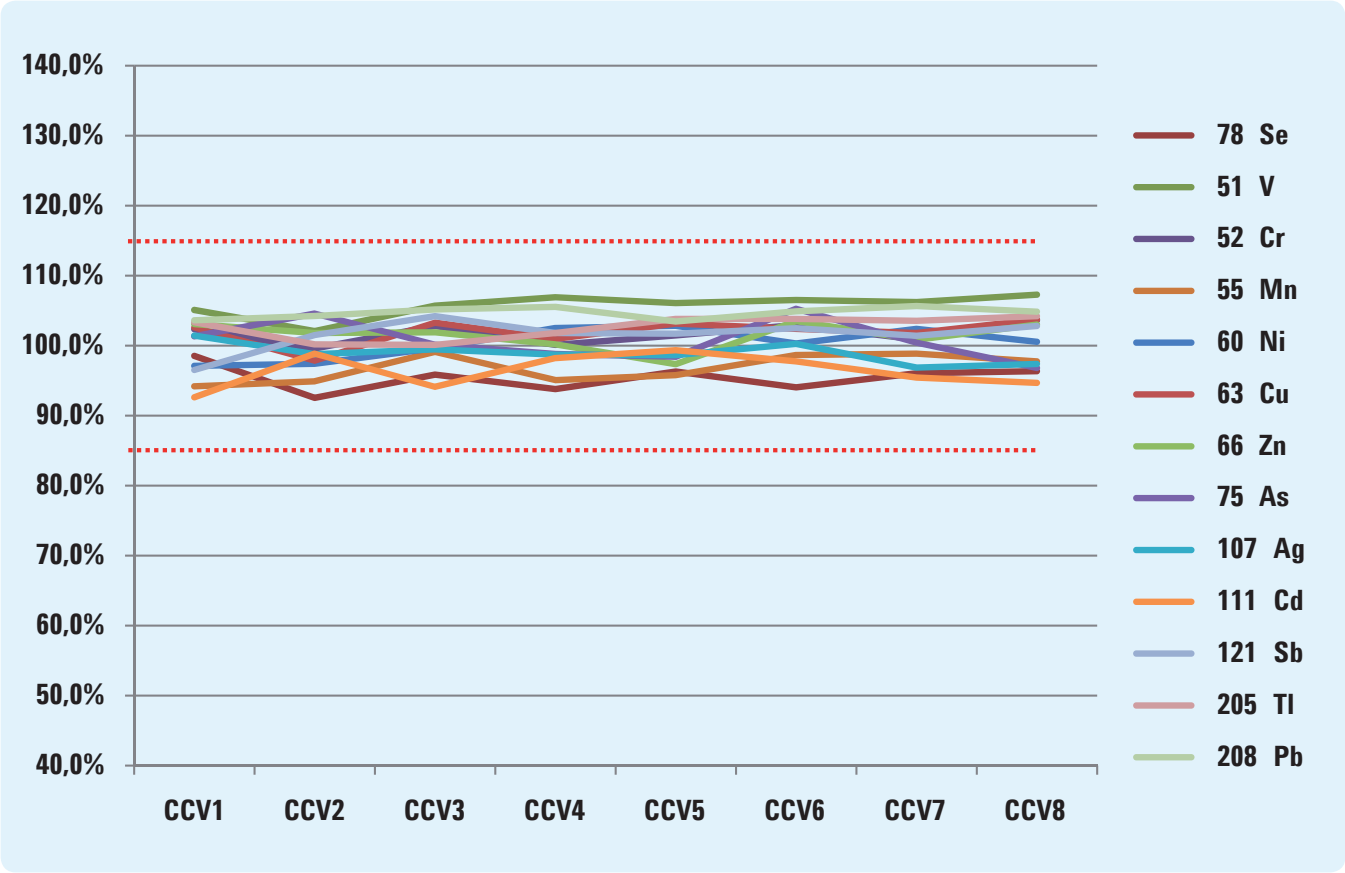

Figure 1 CCV recoveries over a sequence of 89 analyses, including real FGD samples, all required QC samples, and synthetic FGD matrix samples. Control limits (85-115%) are indicated in red.

Mass /Analyte	FGD Matrix Check Solution	Fortified FGD Recovery (%)	Carryover Check	CCV (ppb)	CCB (ppb)
51 V	-0.187	102.2%	-0.068	48.885	0.101
52 Cr	12.699*	96.6%	0.015	48.851	0.117
55 Mn	-0.101	94.3%	-0.328	48.435	0.100
–60 Ni	0.247	88.4%	-0.009	48.535	0.154
63 Cu	0.094	91.6%	0.096	47.316	0.115
66 Zn	3.181	86.1%	-0.302	49.804	0.100
75 As	0.107	110.0%	-0.043	48.205	0.009
78 Se	0.538	120.2%	-0.144	49.605	0.186
107 Ag	0.145	94.3%	0.010	47.632	0.003
111 Cd	0.039	98.9%	-0.017	48.695	0.017
121 Sb	0.181	98.4%	0.015	50.806	0.031
205 Tl	0.021	90.3%	0.000	48.108	0.008
208 Pb	0.436	92.1%	0.003	48.381	0.008

Table 2. Analysis of mixed matrix FGD interference check sample and spiked FGD matrix solution. CCV expected value = 50 ppb. *Cr contaminant verified by secondary isotope

Conclusions

The newly developed SOP meets all USEPA requirements for the analysis of highly contaminated and extremely high-matrix FGD wastewater samples. The combined advantages of the HMI system with helium collision mode and discrete sampling allow the 7700x ICP-MS to quickly and reliably analyze long sequences of FGD samples for both major and trace elements. The highly robust conditions – as evidenced by both internal standard recoveries and excellent long-term stability – allow the samples to be analyzed with minimal dilution, resulting in the best possible method detection limits, even for elements that typically suffer from polyatomic interferences.

More Information

Agilent application note: Analysis of Flue Gas Desulfurization Wastewaters by ICP-MS, 5990-8114EN

Application of Compound Independent Calibration to Arsenic Speciation

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Introduction

Liquid Chromatography (LC) coupled to ICP-MS has gained increasing popularity for speciation studies during the last 15 years. ICP-MS offers sensitivity in the ng/L range for most elements, including Sn, Se, As, Hg, etc. However ICP-MS cannot determine the compound form (or species) of the element directly and therefore a separation technique has to be employed. LC (or ion chromatography (IC)) allows the use of column chemistries to separate the species and "identify" the individual forms of the elements based upon their retention times. With well-developed separation chemistry that is reliable and reproducible, LC-ICP-MS is an elegant and simple solution to the problem of species identification.

Provided the chemistry is stable, the only real limitation to routine analysis is calibration of the species of interest. Standards for some species might not be commercially available (or obtainable in a pure enough form for use as calibration standards) or are prohibitively expensive for routine use – for example arsenobetaine can be as expensive as €200 for 50 mg.

Column	G3288-80000 (4.6 × 250 mm) G3154-65002 (Guard Column)
Flow rate	1.0 mL/min
Injection volume	5 µL
RF power	1550 W
Sampling depth	9.0 mm
Spray chamber temp	2 °C
Carrier gas	1.04 L/min
Makeup gas (to purge mobile phase)	0.3 L/min
Nebulizer	MicroMist

Table 1. LC-ICP-MS operating conditions

Figure 1. MassHunter Workstation instrument control and Data Analysis

An alternative would be to use the ICP-MS's capability for Compound Independent Calibration (CIC) using the heteroatom – in this case arsenic. Within the plasma all compounds are essentially converted to their component atoms before ionization; therefore the compound's response is based solely upon the As signal and calibration for As should be independent of the species.

Here we compare data obtained using Compound Independent Calibration (CIC) to that obtained using traditional Compound Specific Calibration (CSC).

Experimental

An Agilent 7700x ICP-MS was coupled to an Agilent 1260 HPLC fitted with an Agilent arsenic speciation column and guard column as described by Sakai et al [1]. The mobile phase consisted of 2.0 mM PBS/0.2 mM EDTA/10 mM CH_3COONa/3.0 mM $NaNO_3$/1% EtOH, pH 11.00 adjusted with NaOH and Ar purged throughout the run. This configuration allows the direct injection of undiluted urine. Instrumental conditions are given in Table 1. Both the HPLC and ICP-MS were fully controlled by the MassHunter Workstation software (Figure 1).

Results and Discussion

In order to test the robustness of the method over a typical analytical run, twelve patient urine samples were injected directly along with calibration standards. Analysis of the samples and standards was repeated three times giving a total run time of over 13 hours.

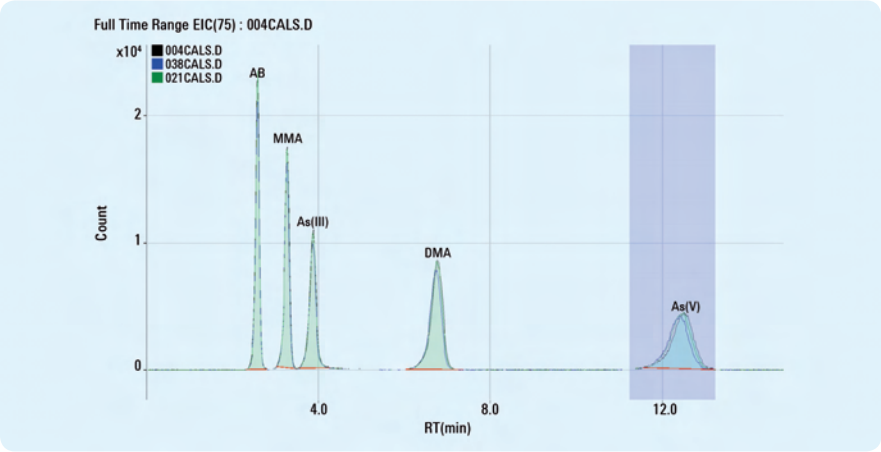

Figure 2. Overlaid chromatograms (50 µg/L standard) over a 13h run of undiluted urine (highlight displays As(V) integration window)

	AB		MMA		As(III)		DMA		As(V)
Sample	**CSC**	**CIC**	**CSC**	**CIC**	**CSC**	**CIC**	**CSC**	**CIC**	**CSC**
Patient 1	49.41	48.72	3.69	3.32	0.36	0.32	0.53	0.61	0.42
Patient 2	514.55	507.33	6.82	6.13			0.67	0.77	0.92
Patient 3	10.33	10.19	7.60	6.83	0.66	0.59	0.90	1.04	0.75
Patient 4	21.85	21.55	1.54	1.38					0.66
Patient 5	21.63	21.32	1.49	1.34					1.01
Patient A	1.26	1.24	200.62	180.34	4.21	3.76	21.99	25.42	5.27
Patient B	63.36	62.47	33.22	29.86	0.60	0.54	1.95	2.25	1.11
Patient C	158.89	156.66	20.33	18.27	0.39	0.35	0.68	0.79	1.71
Patient D	63.07	62.18	5.95	5.35	0.35	0.31	0.62	0.71	0.74
Patient E	981.72	967.95	25.61	23.02	0.96	0.86	2.13	2.46	1.23
Patient F	3.54	3.49	8.43	7.58			0.83	0.96	2.76
Patient G	43.18	42.58	46.11	41.45			2.38	2.75	3.53
CIC/CSC	0.986		0.899		0.891		1.16		1.00

Table 2. Comparison of CSC and CIC data in µg/L for arsenobetaine (AB), monomethylarsonic acid (MMA), arsenite As(III), and dimethylarsinic acid (DMA). All peaks calibrated using arsenate (As(V))

Repeatability for a 50 µg/L standard is displayed in Figure 2. A standard was used in order to display any signal drift or retention time shift for all 5 species after multiple injections of undiluted urine (x36) and standard solutions (x12).

The samples were quantitated using CSC and recalculated using CIC based upon the most readily available inorganic arsenic standard – As(V). Data are presented in Table 2. The ratio of CIC/CSC displays the good agreement between the two calibration strategies.

Conclusions

A direct data comparison demonstrates the feasibility of CIC as an alternative to compound specific calibration (CSC); a calibration regime using two or more of the readily available (or cheaper) As species combined with CIC would undoubtedly yield even closer agreement. The benefit of CIC can also be extended to unexpected/unknown peaks e.g. arsenosugars.

Reference

1. T. Sakai, S. Wilbur, "Routine Analysis of Toxic Arsenic Species in Urine Using HPLC with ICP-MS" Agilent application note, 5989-5505EN

Agilent 1260 HPLC and Agilent 7700x ICP-MS used for speciation work

Acknowledgement

The authors would like to give special thanks to Leeds NHS Teaching Hospital, UK for providing the patient samples.

Evolution of the PFA Micro-concentric Nebulizer

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www.savillex.com

Introduction

The nebulizer is one of the most critical components of an ICP-MS, influencing the sensitivity, stability, matrix tolerance, washout, and oxide level of the system. Nebulizer choice will also depend on the need to run HF containing samples, and to handle micro-volume samples. In addition, improvements in ICP-MS robustness and interference removal (delivered by Agilent's HMI and ORS) have resulted in users running more challenging samples than ever before. In recent years, the use of PFA micro-concentric pneumatic nebulizers (PFA nebulizers) has grown rapidly in ICP-MS, due to their greater efficiency, inertness and applicability to micro-volume samples. Initially focused on semiconductor applications, PFA nebulizers are now being used in other areas such as for isotope ratios in geological samples, and for low-volume clinical samples. Since these nebulizers have essentially zero dead volume (the uptake tube is also the capillary, so no connector is required) they have begun to be used in ultra high throughput applications, where even a few seconds saved in washout time is valuable. Working in co-operation with Agilent, Savillex has designed a PFA nebulizer with some unique features that give it excellent performance in routine use.

Design Considerations

The critical design area of a PFA nebulizer is between the end of the capillary (inside the nebulizer body) and the orifice at the tip. With conventional glass concentric nebulizers, liquid sample exits the capillary at the nebulizer tip, where the flow of carrier gas shears the liquid in a process called prefilming, creating a thin film of liquid. The gas flow then converts the liquid into a finely-divided aerosol by the venturi effect. With PFA nebulizers, the capillary terminates behind the nebulizer tip, and so prefilming takes place inside the nebulizer body [1]. The more efficient gas-liquid interaction results in a smaller mean droplet size (~9 um) with a narrower size distribution, so transport to the plasma and drying and decomposition are more efficient than with glass concentric, V-groove, cross flow and parallel path nebulizers [2]. In designing the Savillex C-Flow PFA nebulizer, special attention was paid to the positioning of the capillary inside the nebulizer tip, to optimize performance, reproducibility and sample uptake rate.

C-Flow Design

The C-Flow is unique among PFA nebulizers in that the capillary is physically supported all the way to the inside of the nebulizer tip. The capillary is also positioned centrally within the body, making it a true concentric PFA nebulizer. This is achieved by use of an inner support which fits precisely inside the body (Figure 1).

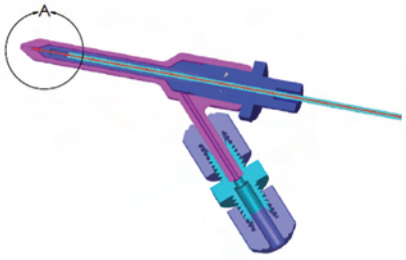

Figure 1. C-Flow drawing showing inner support

Argon carrier gas flows around the support, forming an annular gas stream around the end of the capillary. The capillary protrudes into space behind the tip (Figure 2). As sample liquid exits the capillary, the annular gas stream shears the liquid, causing prefilming to occur around the complete inner circumference of the tip. Liquid/gas interaction and energy transfer is optimized, resulting in a very fine and consistent aerosol.

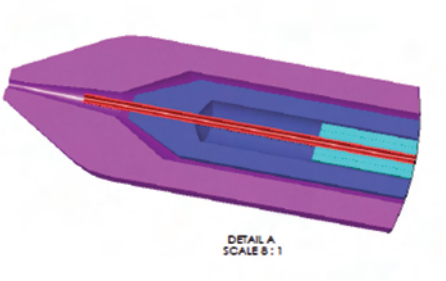

Figure 2. Close up of C-Flow tip, showing the capillary (red) protruding into the space behind the orifice.

The tip design provides several key benefits:

- High sensitivity due to efficient gas/liquid energy transfer and fine aerosol
- Better reproducibility from nebulizer to nebulizer – free aspiration rate spec is +/- 15%
- Aerosol direction is co-axial to the nebulizer –typically +/- 2 degrees
- Reliable, reproducible performance even at 50uL/min flow rates

One limitation of concentric nebulizers is the potential for blockages due to particulates in the sample. The C-Flow uses a slightly larger inner diameter (ID) capillary than is typical for PFA nebulizers, and has a uniform capillary ID all the way to the tip, which significantly reduces the likelihood of blockage.

Typical applications of the C-Flow 50 are in semiconductor: high Si matrix (1000 ppm Si) and phosphoric acid analysis, where reduced sample loading on the plasma is beneficial. The C-Flow 200 is more widely applicable. Both nebulizers can be free aspirated or pumped. All C-Flow nebulizers ordered from Agilent are pre-cleaned by aspirating HNO_3/HF for 8 hours.

Ordering Information

The C-Flow 50 will join the C-Flow 200 on the Agilent price list from July 1, 2011.

Agilent part numbers:
C-Flow 50: G3285-80002
C-Flow 50 w/I-AS Probe: G3285-80003
C-Flow 200: G3285-80000
C-Flow 200 w/I-AS Probe: G3285-80001

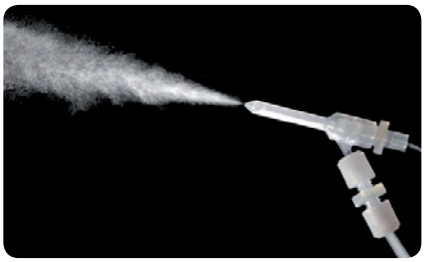

Figure 3. C-Flow 200 showing aerosol formation

References

1. J.L. Todolí, J.M. Mermet, Spectrochimica Acta Part B 61 (2006) 239–283.
2. Liquid Sample Introduction in ICP Spectrometry. A Practical Guide. J.L. Todolí and J.M. Mermet, Elsevier. ISBN: 978-0-444-53142-1

Agilent GC-ICP-MS Expert Users Meet in Germany

The scope of GC-ICP-MS applications has developed beyond Sn and Hg speciation to include a diverse range of fascinating topics. The specialized expertise acquired from this diversity is often not widely shared across differing applications. In order to promote the sharing of best practices and encourage open dialog between expert users of GC-ICP-MS, Agilent invited speakers from around Europe and North America to a full day of presentations, discussions, and laboratory demonstrations at the Waldbronn Center of Excellence in Germany. The following users discussed topics as diverse as high temperature simulated distillation in the refining industry, food safety, species specific isotope dilution, and inter-laboratory comparisons of new methods, among others:

- Dr. D. Lück – BAM
- Dr. Christian Wolf – Merck
- Dr. Jens Sloth – DTU
- Dr. Christelle Bonnemason – UT2A
- Dr. Jenny Ellis – Chevron
- Dr. Jorge Ruiz-Encinar – University of Oviedo
- Nicole Fellner, Peter Planitz, Steve Wilbur and Ed McCurdy all of Agilent Technologies

The meeting helped to increase the valuable interaction between Agilent and our GC-ICP-MS users, with open discussions centering around the design of the new interface hardware and software, and the latest GC options that can be used to further enhance the capabilities of the GC-ICP-MS coupling. Everyone learned a lot, made some useful contacts and enjoyed some warm hospitality in an informal setting.

Atomic Spectroscopy Column

Researchers at Major Conference on Atomic Spectroscopy Prefer Agilent Instrumentation

Over 500 spectroscopists travelled from more than 30 countries to Zaragoza, Spain, from Jan 30 - Feb 4 2011, for the Winter Conference on Plasma Spectrochemistry (WPC). The WPC is the premier conference event in the atomic plasma spectroscopy calendar and attracts the most preeminent research groups from industry and academia. Under the "Clearly Better Together" theme, Agilent's atomic spectroscopy group hosted a series of successful events:

- "Meet with Spectroscopy Experts over Lunch" seminar – 155 attendees
- Agilent's ICP User Evening Event – over 190 attendees
- Participation by Steve Wilbur in a round table discussion on Analytical Control Laboratories

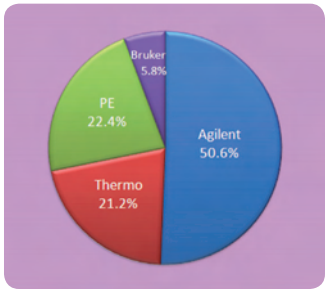

Figure 1. Percentage of quad-ICP-MS posters by manufacturer

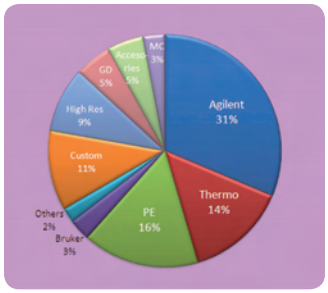

Figure 2. Agilent contribution (ICP-MS plus ICP-OES) compared to total atomic spectroscopy posters (all techniques) from all vendors

Philip Binns of Agilent presents the 5th Plasma Award to joint winners Prof. Sanz-Medel (center) and Prof. Vanhaecke (right)

Poster Presenters Prefer Agilent Systems

While Agilent ICP-MS systems are widely used in routine labs around the world, their performance and flexibility mean they are also the most widely used quadrupole ICP-MS in research. An analysis of the 329 posters presented at the WPC showed that a quadrupole ICP-MS instrument was used in 156 presentations (47%) with an Agilent ICP-MS system cited in 79 posters. With the total number of posters citing quad-ICP-MS up compared to the WPC in Graz (124), in 2009, the study shows once again that more presenters use Agilent than any other ICP-MS (Figure 1).

As a gauge for current market trends in research labs' use of instrumentation in the field of plasma spectrochemistry, we plotted the number of posters using various instruments including quad ICP-MS & ICP-OES by manufacturer, Glow Discharge (GD), Multi-collector (MC) and High Resolution ICP-MS. Figure 2 shows that Agilent atomic spectroscopy instrumentation was cited in 31% of all atomic spectroscopy posters, more than any other vendor, giving a useful indication of the preferred tools used to develop future applications.

Joint Winners of Plasma Award 2011

Agilent has sponsored the prestigious European Award for Plasma Spectrochemistry at each European WPC since its inception in 2002. This year, Agilent's Philip Binns (pictured) presented the 5th Award to joint winners: Prof. Vanhaecke, University of Ghent and Prof. Sanz-Medel, University of Oviedo. The award consists of a EUR5000 cash prize plus a trip to Japan to present a symposium or Agilent event. Sponsorship of the prize underlines Agilent's commitment to promoting high quality research and innovation in this field, as well as supporting this important conference and its organization.

Agilent Australia Celebrates 100 ICP-MS Installations

The 100th ICP-MS sold by Agilent Australia is up and running in the Department of Environment and Research Management in Queensland.

From Darwin to Hobart and Perth to Dunedin, through plane crashes and earthquakes, Agilent 4500, 7500 and 7700 ICP-MS systems have delivered results for a diverse range of applications – many highly complex and/or demanding often requiring extreme sample throughput.

- **Agilent 4500** – the first 4500 was sold to the University of Auckland in 1996 to research cis-platin anti cancer drugs by HPLC-ICP-MS and the last 4500 with ISIS and a T-mode interface was sold in 1999 to Sydney Water for water analysis.
- **Agilent 7500** – 73% of 7500 units sold between 2000 and 2009 were equipped with an ORS collision cell. The first 7500 went to the ANU Research School of Earth Sciences for laser ablation studies and the last to Intertek Minerals in Perth to provide low level quantification in various leach or digest solutions in support of mining and mineral exploration.
- **Agilent 7700** – the University of Tasmania, CODES, purchased the first 7700 for laser ablation-ICP-MS analysis with many more units installed and on order.

Loyal User Base: 7700 user Cameron Scadding, Managing Director of TSW Analytical, Perth, presented at a recent Agilent ICP-MS User meeting. According to Scadding: "Out of all of the meetings/conferences that I attend I consider your meeting to be one of the most beneficial."

And finally ... special thanks go to the Uni of Tasmania, Macquarie Uni and Ecowise in Melbourne who have invested in one of each generation of Agilent ICP-MS!

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Apple iPads Go To Best Speciation Handbook Contributions

Many excellent submissions were received following Agilent's invitation to contribute to the Second Edition of the Agilent Handbook of Hyphenated ICP-MS, and i-Pads were awarded to the authors of the papers judged to be the best in each of 4 categories. The winners in each category were:

Category 1 LC(IC)-ICP-MS Applications

Antimony Speciation in Natural Waters by HPLC-ICP-MS
Pierre Tremblay, François Bossanyi and Jean-Pierre Blouin, Centre d'Expertise en Analyse Environnementale du Québec, Québec, Canada

Category 2 GC-ICP-MS Applications

Determination of Organotin Compounds in Urine Samples Using GC-ICP-MS
Jean Dumont and Fabienne Séby, Ultra-Traces Analyses Aquitaine, Pau, France
Nadine Frery and Stéphanie Vandentorren, Institut de veille sanitaire, Saint Maurice, France

Category 3 ICP-Multi-MS Applications

Fractionation and Identification of Arseno Fatty Acids from Cod-liver Oil by the Parallel use of HPLC Online with ICP-MS and ES-MS
Kenneth O Amayo, Andrea Raab and Jörg Feldmann, Trace Element Speciation Laboratory, University of Aberdeen, Scotland, UK

Category 4 Other Hyphenated ICP-MS Applications

Quantitative Characterization of Gold Nanoparticles by Field-Flow Fractionation Coupled On-line with Light Scattering Detection and ICP-MS
Bjørn Schmidt, Katrin Loeschner, Jens J. Sloth, and Erik H. Larsen, National Food Institute, Technical University of Denmark Mørkhøj Bygade 19, DK-2860 Søborg, Denmark

Congratulations to the winners! And thanks to everyone who submitted a manuscript. The First Edition of the Speciation Handbook has been immensely popular, and the Second Edition also promises to provide a really useful overview of the various techniques used for elemental speciation and their applications.

Conferences. Meetings. Seminars.

2011 Agilent Atomic Spectroscopy Seminar Tour
12 May - 19 July, US and Canada
Space is limited. So register today at:
www.agilent.com/chem/AtomicSeminar

Analytical Symposia
in Singapore, Malaysia and Thailand
Learn more
www.agilent.com/chem/agilent-experience

METALLOMICS 2011: 3rd International Symposium on Metallomics
15 - 18 June 2011,
Münster, Germany
www.metallomics2011.org

TEF-4: International IUPAC Symposium for Trace Elements in Food
19 - 22 June 2011,
King's College in Aberdeen, Scotland
www.abdn.ac.uk/tef-4

Agilent ICP-MS Publications

To view and download the latest ICP-MS literature, go to **www.agilent.com/chem/icpms** and look under **"Literature Library"**

- **Application Note:** Direct measurement of metallic impurities in 20% ammonium hydroxide by Agilent 7700s ICP-MS, 5990-7914EN
- **Application Note:** Direct analysis of trace metallic impurities of high purity hydrochloric acid by Agilent 7700s ICP-MS, 5990-7354EN
- **Advertorial:** 7700 Series ICP-MS Data Evaluation Using Agilent Mass Profiler Professional, 5990-7577EN

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