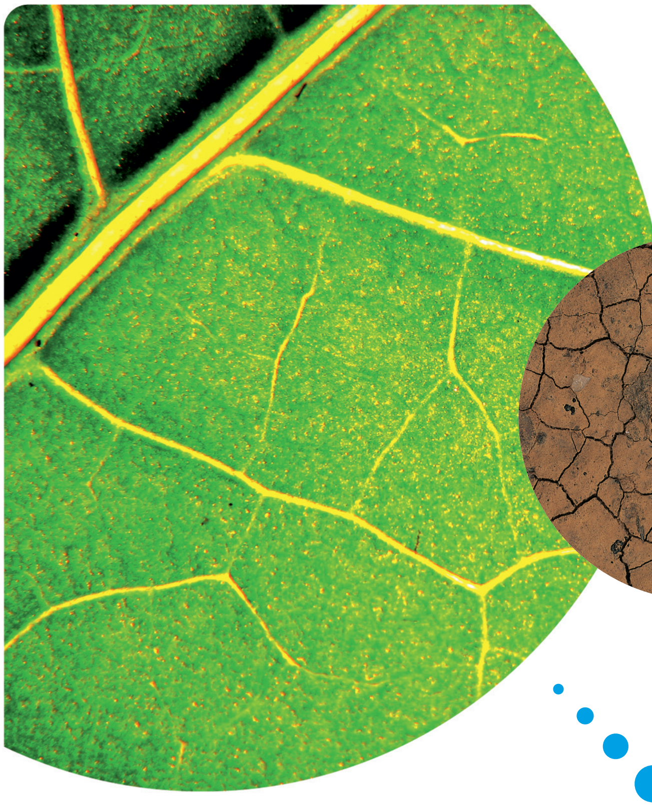
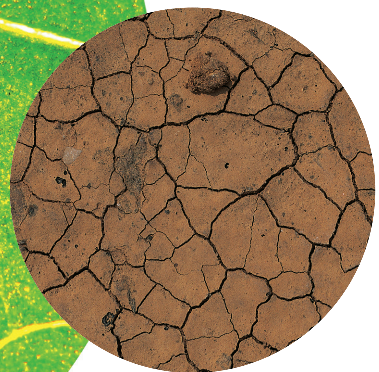

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Agilent Technologies

GC-ICP-MS Helps Solve Biogas Usage Problem

Steven Wilbur
Agilent Technologies, USA

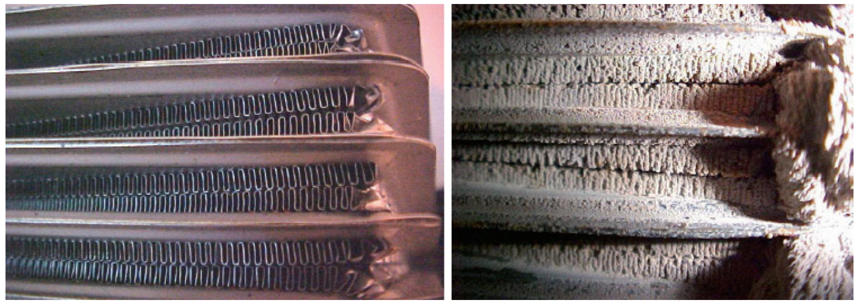


Figure 1. Microturbine component before and after exposure to biogas containing volatile siloxanes [1]

Introduction

Biogas is the term used to describe the mixture of methane, carbon dioxide, nitrogen and other components resulting from the anaerobic fermentation of a variety of bio-degradable materials including animal waste, domestic sewage sludge and municipal landfill waste.

Because of its methane content (40-75%), biogas can be used as a substitute for natural gas and is commonly used at wastewater treatment plants and landfills for heating, electricity generation, and vehicle fuel. However, as a waste byproduct, biogas may also include undesirable components including volatile sulfur and halogen containing compounds, as well as volatile silicon compounds (siloxanes).

Upon combustion, the sulfur and halogen compounds can form corrosive acids and the siloxanes can form abrasive silicon dioxide (silica). Silicon dioxide is particularly problematic because it accumulates within process equipment, such as boilers, and both reciprocating and turbine engines, causing premature wear and eventual failure. For this reason, levels of volatile siloxanes must be carefully monitored and controlled when biogas is used to fuel expensive machinery.

Analysis of Volatile Siloxanes

Traditionally siloxanes in biogas have been measured using GC/MS with detection limits ranging from 0.02 to 1 ppmv (parts per million by volume) depending on the specific method. However, as engine technology has shifted from fairly robust reciprocating engine usage to cleaner burning microturbine usage (Figure 1), the tolerance to siloxanes has decreased to the point where better analytical sensitivity is required.

GC-ICP-MS was evaluated for sensitivity, ease of use and robustness for siloxanes analysis. While Si analysis can be challenging by ICP-MS, the Agilent GC interface uses a dry plasma for very high temperature and efficient ionization and significantly reduced interferences from oxygen and nitrogen based polyatomics. The use of hydrogen reaction mode on the 7500ce further reduces the N_2 background on Si to insignificant levels, resulting is superior sensitivity for siloxane analysis.

Eight siloxanes, each at approximately 45ppb (µg/L) in methanol, were analyzed using the Agilent 6890/7500ce GC-ICP-MS system. Total run time was less than 10 minutes (Figure 2) and detection limits based on twice the peak-peak signal to noise were < 1 pg per compound. When converted to concentrations in biogas, assuming standard sample collection techniques, the resulting detection limits ranged from change to 0.03 - 0.07 ppbv (parts per billion by volume), which is 100x lower than the most stringent engine manufacturers requirements and more than 500x more sensitive than the lowest reported GC/MS detection limit.

Furthermore, since ICP-MS is capable of compound independent calibration, the unavailability of standards for some compounds is not a problem. Accurate quantification of any volatile Si containing compound can be based on the response of a single standard compound.

The calibration curve shown in Figure 3 was generated using dodecamethylpentasiloxane from 4.5 to 90.45 ppb with excellent linearity ($r^2 = 1.000$). When a standard at 4520 ppb was analyzed against this curve, the calculated concentration was 4244 ppb (94% recovery) indicating that the method was linear up to 50 times higher than the highest calibration point.

Compound	Abbr.	Molecular Formula	Molecular Weight	Boiling Point (°C)
Hexamethyldisiloxane	L2	$C_6 H_{18} O_1 Si_2$	162.38	99
Hexamethylcyclotrisiloxane	D3	$C_6 H_{18} O_3 Si_3$	222.47	134
Octamethyltrisiloxane	L3	$C_8 H_{24} O_2 Si_3$	236.54	153
Octamethylcyclotetrasiloxane	D4	$C_8 H_{24} O_4 Si_4$	296.62	175.8
Decamethyltetrasiloxane	L4	$C_{10} H_{30} O_3 Si_{14}$	310.69	194
Decamethylcylopentasiloxane	D5	$C_{10} H_{30} O_5 Si_5$	370.78	210
Dodecamethylpentasiloxane	L5	$C_{12} H_{36} O_4 Si_5$	384.85	232
Dodecamethylcyclohexasiloxane	D6	$C_{12} H_{36} O_6 Si_6$	444.93	245

Table 1. Characteristics of volatile siloxanes commonly found in biogas [2]

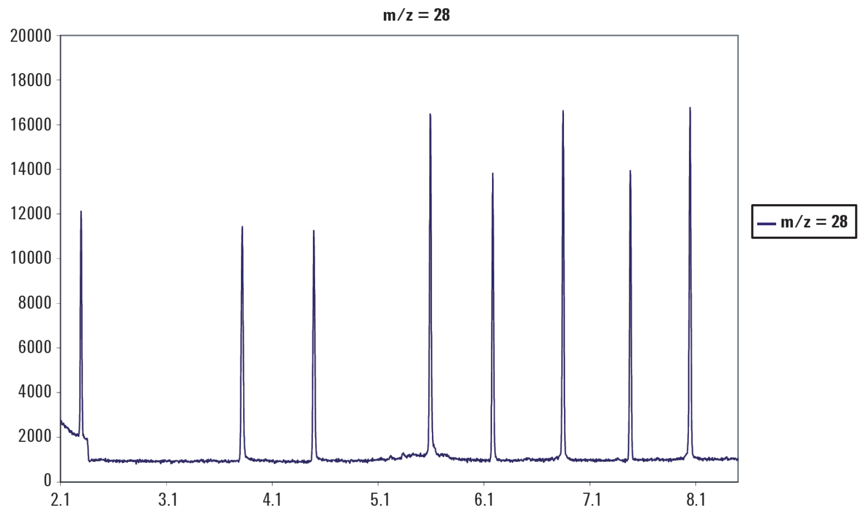


Figure 2. Chromatogram of eight siloxanes at approximately 45 ppb (µg/L) each in methanol analyzed using GC-ICP-MS

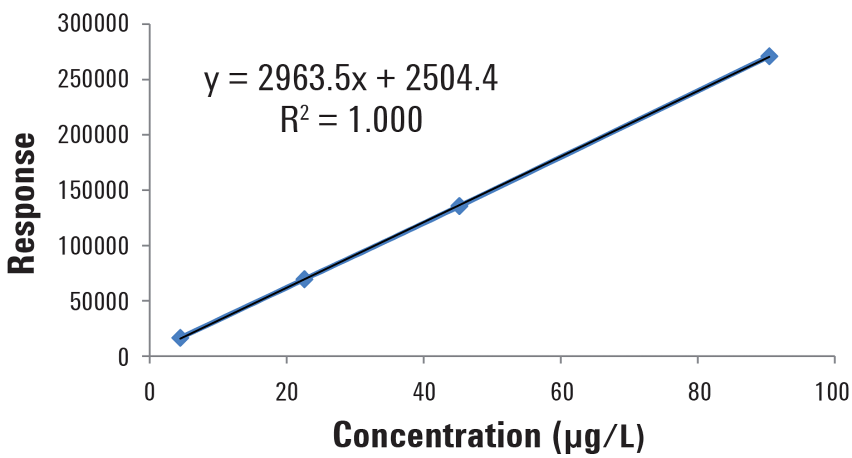


Figure 3. Calibration plot of dodecamethylpentasiloxane from 4.5 to 90.45 ppb

Conclusions

Volatile siloxanes pose increasingly significant problems for biogas use at wastewater treatment plants and landfills. As a result, process equipment manufacturers are imposing stricter limits on acceptable concentrations of Si in biogas. In some cases, these limits cannot be reliably measured using the currently used methodologies. GC-ICP-MS can easily achieve the desired detection limits, with excellent linearity, reproducibility and ease of use.

Acknowledgements and References

1. Courtesy Jeffery Pierce, SCS Engineers
2. Wheless, E. and Pierce J., "Siloxanes in Landfill and Digester Gas Update"

www.scsengineers.com/Papers/Pierce_2004Siloxanes_Update_Paper.pdf

Rinse Solution for Boron Analysis and Boron Isotope Ratios

Claire Wright, CSIRO Land and Water, Center for Environmental Contamination Research Urrbrae, South Australia

Fred Fryer
Agilent Technologies, South Asia

Glenn Woods
Agilent Technologies, UK

Introduction

Boron is an essential micronutrient required by plants for growth, reproduction and survival.

The bioavailable or labile pool of boron (the exchangeable fraction) in soil can be estimated using isotope dilution mass spectrometry (IDMS) by measuring the distribution of an added stable boron isotope (^{10}B) between a soil solution and solid phase over a period of time. Stable boron isotopes are chosen since radioactive boron isotopes have a half life of < 1 second. IDMS quantification of boron requires accurate measurement of both boron isotopes at mass 10 and 11 with enriched ^{10}B added in an unnatural abundance. Interference on either isotope must be eliminated or corrected for. Mass bias, which is stable for a given instrument, can be compensated for by reference to a standard of known mass ratio. However, bias in the determination of $^{11}B/^{10}B$ ratio can also come from a background signal of natural boron retained from a previous sample (poor washout of the sample), or elevation of the ^{11}B signal due to ^{12}C. The carbon signal can vary by a large amount since the carbon level in soil samples can vary significantly, and the rinsing solutions used may contain carbon. Retention of boron (memory effect) largely comes from the sample introduction area of the ICP-MS i.e. uptake tubing, spraychamber, nebulizer glassware, torch and the plasma/sample interface. Uptake peristaltic pump tubing can be avoided by using a self aspirating or direct injection method but these systems are either manual or require additional hardware. The use of specialized nebulizers such as direct injection nebulizers and PFA micro concentric nebulizers have been shown to reduce boron carryover [1] but such nebulizers can be difficult or costly to obtain and use.

One of the aims of this work was to establish a routine, reliable and rugged method for ICP-MS measurement of boron isotopes that utilizes the standard sample introduction system.

Boron Memory Effects

Various rinse solutions were investigated (Table 1) using the 7500ce ICP-MS. Operating parameters are given in Table 2. A 10 minute rinse time was used to establish the baseline signal of boron for each rinse solution. Boron standards (10 ug/L and 100 ug/L) in 2% HNO_3 (representative of the expected boron levels in a digested soil sample) were then introduced for 10 minutes followed by a rinse cycle. ^{10}B was monitored using time resolved analysis (TRA).

Solution 1	Nitric acid – same as the sample digest chemistry
Solution 2	*Mannitol in water – 0.25% mannitol
Solution 3	*Mannitol in ammonia – 0.25% mannitol in 0.1M NH_4OH
Solution 4	Ammonia – 0.1M NH_4OH
Solution 5	Agilent rinse solution.

Table 1. Commonly reported rinse solutions used to minimize boron retention

*Boron readily complexes with polysaccharides and alcohols and so mannitol ($C_6H_8(OH)_6$ has been frequently reported for stabilizing and transporting boron through the formation of a stable complex.

Rinse Solutions Results

The starting baseline was high for nitric acid (Rinse solution 1) and mannitol (Rinse solution 2), and > 15 minutes was needed to achieve baseline after sample introduction. Similarly the boron sample signal took >5 minutes to stabilize. Overall, these methods would take > 25 minutes per sample.

Sample uptake rate	0.25 rps
Peristaltic Pump Tubing	Solva™ – 0.89mm id (orange/orange)
Nebulizer	Glass Expansion v-spray
Nebulizer gas flow	0.5 L/min
Make-up gas flow	0.7 L/min
Spraychamber	Quartz Scott type
Spraychamber temperature	2°C
Sample depth	8 mm
RF Power	1550W
Interface cones	Ni

Table 2. 7500ce ICP-MS operating parameters

Alkaline mannitol (Rinse solution 3) showed the highest background and was unusable, compared to either ammonia or mannitol alone. It is hypothesized that the ammonia/mannitol rinse cleans the glass of boron accumulated over many years of analysis, scavenging boron from the glass surface. Therefore, while this should have been the best solution, background from existing contamination (even in high purity, boron-free silica) made it unusable. However, the stabilization time was <3 minutes and the washout time was <5 minutes indicating that with clean glassware, this solution should work well. Agilent rinse solution (Rinse solution 5) - a combination of ammonia, EDTA, Triton X100 and H_2O_2 provided the lowest boron background (<5000 cps) with fast stabilizing and washout times (<3 minutes to original baseline) – see Figure 1.

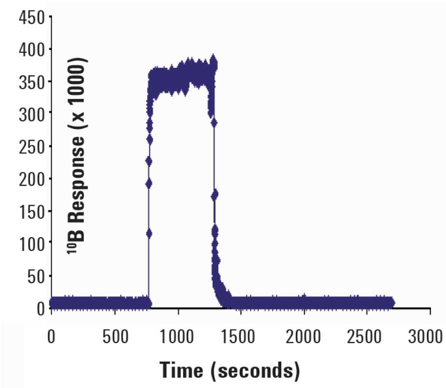


Figure 1: Response of ^{10}B using the Agilent rinse solution

Carbon Effect on ^{11}B Determinations

A further aim of the study was to investigate the effect of carbon interference on the analysis of boron. A solution of 1000 mg/L sucrose in solution with 10 ug/L boron, beryllium and lithium was analyzed by the 7500ce. As Figure 2 indicates, there was no overlap of mass 12 (C) on mass 11 (B).

The effect of varying carbon levels on different boron concentrations was undertaken by analyzing NIST CRM 951 boric acid (^{11}B = 80.1% abundance, ^{10}B = 19.9% abundance) in varying sucrose concentrations (1000 mg/L sucrose = 421 ppm C). The results presented in Table 2 show that there is no effect from carbon on 11:10 B ratio even at the lowest boron concentration.

Boron ug/L	Sucrose mg/L	11/10B
10	0	4.4 ± 0.02
10	10	4.4 ± 0.07
10	100	4.3 ± 0.04
10	500	4.4 ± 0.03
10	1000	4.4 ± 0.02
100	0	4.4 ± 0.004
100	10	4.4 ± 0.03
100	100	4.4 ± 0.02
100	500	4.4 ± 0.02
100	1000	4.4 ± 0.01

Table 2. Carbon effect on boron isotope ratios

Conclusions

An alkaline rinse solution containing EDTA, hydrogen peroxide and a surfactant was selected as the most efficient washout procedure for the removal of memory effects on boron determinations by ICP-MS. The low stable baseline allowed for lower quantification limits for boron (< 1 µg/L) and the sample stabilisation times < 4 min) and wash-out times after sample analysis (< 3 min) were fairly rapid.

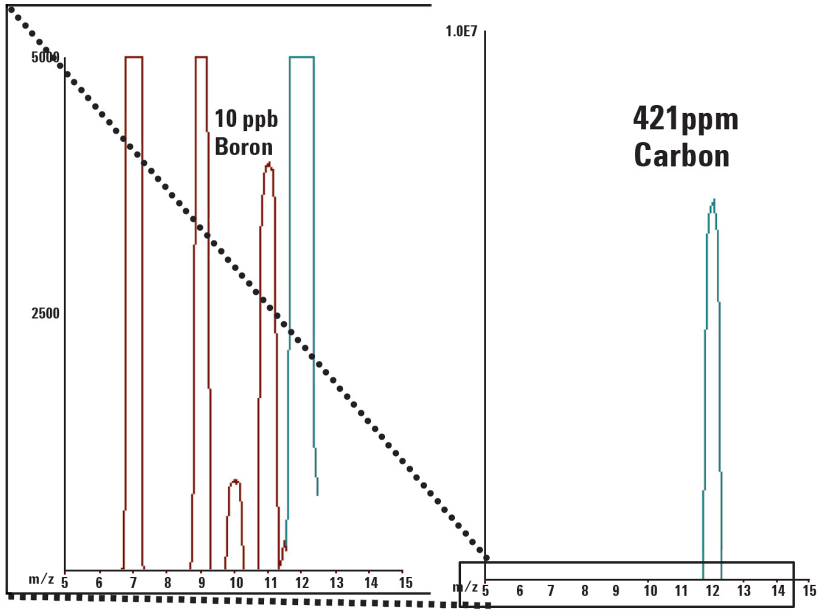


Figure 2: Expanded mass axis scale showing the signal from mass 7 to 12 amu. Note: No overlap of carbon peak (m/z 12) on boron (m/z 11).

Potential ^{12}C interference on ^{11}B signal was shown not to be apparent.

Eliminating both memory and carbon interference effects, should allow simple, accurate boron quantification by isotope dilution ICP-MS.

References

1. Ana Cláudia S. Bellato; Amauri A. Menegário; Maria Fernanda Giné, Boron isotope dilution in cellular fractions of coffee leaves evaluated by ICP-MS with direct injection nebulization, J. Braz. Chem. Soc. vol.14 no.2 São Paulo Mar./Apr. 2003.

More Information

For more details on the Agilent rinse solution (rinse solution 5), please visit the Agilent ICP-MS User Forum.

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.

- Go to **www.agilent.com/icp/ms**
- Look for the User Forum link under Additional Information
- Once in the ICP-MS User Forum, click on Agilent ICP-MS User Resources.
- Open file: "Rinsing Protocol for Rapid Measurement of 'Sticky' Analytes by 7500 Series ICP-MS"

How to Download ICP-MS ChemStation Software Updates

Tomo Yamada
ICP-MS Product Manager,
Tokyo Analytical Division,
Agilent Technologies

Make sure you are getting the most from your 7500 Series ChemStation software by updating to the latest software revisions for both Windows 2000 and XP operating systems.

To check which Product number and Revision you are using, click on "**Help**" menu and select "**About**" in the ChemStation software.

Updating to the latest revision is important – it eliminates any minor faults that have been identified and fixed in earlier versions, and enables Agilent field staff to support you more efficiently.

For current rev.B.0x.0x users, a free upgrade to B.03.04 (for Windows 2000 users) or B.03.06 (for Windows XP users) can be downloaded from the Agilent ICP-MS website - see instructions below.

1. Visit **www.agilent.com/chem/icpms**

2. Select "**ICP-MS Software**" located in the center column of the page.

3. Select "**ICP-MS ChemStation Updates & Downloads**".
(To access this page, you will first need log in to the Agilent site, or register if you haven't done so previously, and then enter the 10 digit registration number shown on the "Software Certificate & Registration Packet" supplied with your instrument).

4. Click on "**ICP-MS ChemStation**".

5. To download the relevant patch file for your ChemStation version, click on the applicable ChemStation update.

A list of updates available on-line is given in Table 1.

For 7500 Series users with older, NT ChemStation software versions (Rev.A), an upgrade to B.03.06 (O/S not included) is available to purchase by ordering P/N G3149B.

Please note that some PCs originally supplied with older 7500 mainframes will not meet the requirements for B.03.06 – see **Pre-install Notice** on the website. Should a new PC be required, a new ICP-MS PC hardware upgrade bundle (G3150A opt.321) is available.

ChemStation Product No.	Update from	Update to	Operating System / Interface	Features
G1834B	B.01.00 – B.03.05	B.03.06	**Windows XP SP2** / LAN	All B.03.04 features plus • Support OpenLAB ECM Integration • Semiquant factors for Helium mode • Control CETAC EXR-8 Autosampler
G1834B	B.01.00 – B.03.03	B.03.04	**Windows 2000 SP4** / LAN or GP-IB	• New Tuning Window • System Wide Parameters • Autotune for three Gas Mode • Pre-Run Monitor • Batch View • Offline Acquisition Editor • Coexistence with Agilent LC/GC ChemStation (English) • Pre-emptive rinse support • 15 channels available in Sensitivity Tune • New Calibration editor screen • File archive and extraction tool • Self-diagnostics
G1834A	A.01.00 - A.02.01	A.02.02	**Windows NT4 SP6a** / GP-IB	• Multi tune (for easier ORS operation)

Table 1: Agilent 7500 ICP-MS ChemStation upgrades available on-line for Windows XP, 2000 and NT operating systems.

New, Easier to Align Torch for 7500 Series ICP-MS

Paul McMahon
Technical Marketing Engineer, Tokyo Analytical Division, Agilent Technologies

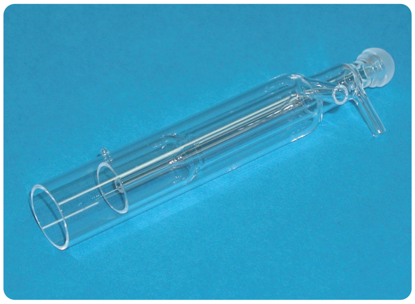


Figure 1. New Standard Torch, 2.5 mm, 2 projections, HMI compatible, (Agilent product number: G3270-67002)

Agilent has modified the design of the standard quartz torch for the 7500 Series ICP-MS for more precise, all round alignment.

Agilent's standard torch and stand already allow precise alignment in the x- and y-axis. However, the addition of an extra projection that fits to a hole in the new torch stand provides reproducible alignment in the z-axis as well. The new standard torch is also compatible with the High Matrix Introduction (HMI) accessory.

The new torch stand (Agilent product number: G3270-60501) is available by contacting your Agilent representative. Note: the new torch can be used without upgrading the torch stand.

The new 2.5 mm internal diameter torch (Agilent product number: G3270-67002) is backward compatible with all Agilent 7500 Series models and replaces G1833-65423, which is no longer available.

To order the new torch, please visit the on-line Agilent Store at:

- **www.agilent.com/chem/store**
- Click on "7500 Series Supplies" under "ICP Mass Spectrometry"
- Look for item G3270-67002 in "Torch Supplies"

or

- Enter the torch product number, G3270-67002, in the "Search Store" facility

Reduce Pump Noise with Quiet Cover for 7500 ICP-MS

Tomo Yamada
ICP-MS Product Manager, Tokyo Analytical Division, Agilent Technologies

If you want to reduce the acoustic noise generated by the vacuum pump of your 7500 ICP-MS, Agilent has a solution in the form of the "Quiet Cover II" (Figure 1).

Figure 1. Quiet Cover II installed on a 7500 ICP-MS

The new cover (product number: G3199B) is compatible with a range of BOC Edwards pumps including the E2M18 used with Agilent 7500 ICP-MS.

The Quiet Cover offers:

- Reduced pump noise: sound absorbing cabinet with resistant foam insulation
- Easy movement with locking castors
- Easy access: no tools necessary to remove sectioned cover
- Easy to maintain: built in "Lift and Tilt" lever raises end of pump to drain oil
- Stable temperature: two integrated fans maintain temperature inside cover

For More Information visit:
www.agilent.com/chem/quietcoverII

User Testimonials: 7500 Series Carries On following Lab Power Loss

In separate incidents in labs in the US and UK, the 7500 Series has proved resilient to power fluctuations – helping users to remain productive when other instrumentation failed.

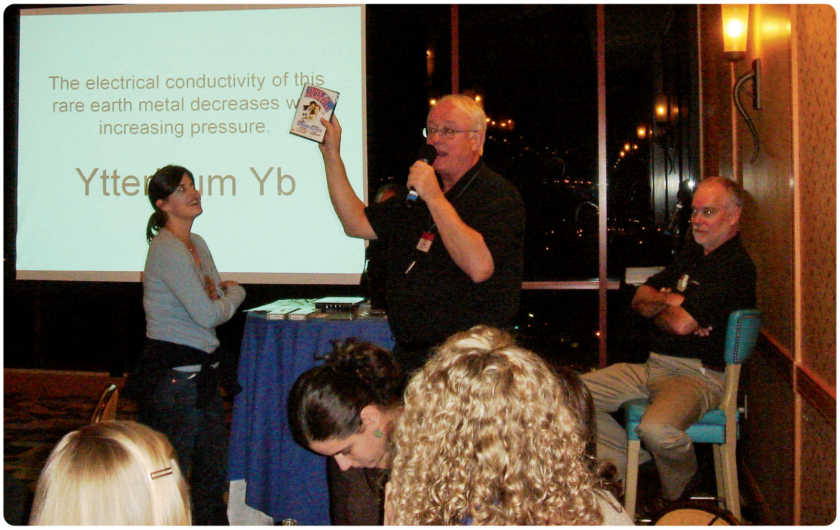
As Ernie Walton of TestAmerica in Savannah, USA explained: "We were running the Agilent 7500c when there was a brownout (reduction in voltage) in the lab, the lights dimmed and some instruments and computers shutdown but the Agilent 7500c just kept on going!" Although brownouts are uncommon in the lab, the 7500's robustness enabled TestAmerica to carry on their ICP-MS analyses uninterrupted.

Dr Teresa Jeffries, ICP-MS Facility Manager at the National History Museum, London, UK, was equally impressed with the 7500's endurance as she explains: "We had a power failure last night. I had a visitor here running the instrument at the time. The user was of course rather shocked as everything shut off around him, and really worried that this morning he would come in to find chaos. However I have to say I was astonished this morning to find the Agilent 7500cs had got itself pumped down again. It fired up as normal and has required absolutely no retuning or anything".

The 7500 Series' efficient recovery after power loss is due to its design criteria and build quality. All Agilent ICP-MS are manufactured in accordance with a strict quality regulation program which includes environmental testing for shock, vibration, electrostatic discharge and unusual power line conditions. In addition, an auto-recovery function allows the 7500 to automatically return to stand-by mode (vacuum ready) following an interruption in the power supply – minimizing downtime for users.

Winter Plasma Conference 2008

Don Potter
Worldwide ICP-MS Marketing Manager,
Tokyo Analytical Division, Agilent Technologies



Elemental Bingo master, Chris Scanlon, in action at Agilent's ICP-MS user meeting

The 15th Winter Plasma Conference was held on Jan 7-12th in Temecula, California, USA and was well attended by plasma spectrochemists from around the world. This year's conference featured especially strong sessions on metallomics and proteomics confirming that there is a great deal of research activity in these areas.

As ever Agilent held an ICP-MS User Meeting which was very well attended with over 180 users joining us in the conference hotel on Tuesday evening. This year, our regular master of ceremonies, Chris Scanlon brought us something different – Elemental Bingo! A great time was had by all.

Here's looking forward to the next Winter Conferences in Tsukuba, Japan, Nov 16-21, 2008 and Graz, Austria, Feb 17-20, 2009.

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 new ICP-MS. You will also find a host of resources in the Forum designed to help you get the most from your 7500.

To access the Forum, you will simply need to log-in to the Agilent web site, or register if you haven't done so previously, 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**

4500 Series Reaches EOS

The Agilent 4500 Series ICP-MS has reached its End of Support (EOS). For more information on transitioning to the 7500 Series, contact your Agilent support sales representative or visit: **www.agilent.com/chem/icpms**

Trade Shows and Conferences

Pittcon 2008
March 1–7, 2008, New Orleans, LA, USA
www.pittcon.org

Agilent ICP-MS Publications

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

- Application: Direct Elemental Analysis of Biodiesel by 7500ce ICP-MS with ORS, 5989-7649EN
- Success Story: Sanofi-aventis, A high throughput assay for oxaliplatin in clinical samples, 5989-7077EN

Front page photo:
Agilent's Dr. Junichi Takahashi (left), senior applications specialist in the Semiconductor Marketing Group based in Tokyo, Japan, receiving an award from the Japan Society for Analytical Chemistry in recognition of his 30 year contribution to the development of trace elemental analysis by atomic spectroscopy.

Agilent ICP-MS Journal Editor
Karen Morton for Agilent Technologies
e-mail: editor@agilent.com

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