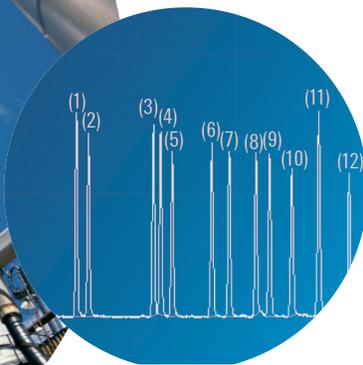


Agilent ICP-MS Journal

May 2010 – Issue 42



Prizes for Papers

Abstracts for Agilent's New Speciation Handbook Due by Sept. 30, 2010. Apple iPads to be Won. See page 8 for details.

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Agilent Technologies

	NIST 1643e	NIST 1643e (10x)	Estuarine Sediment (10x)	River Sediment "A" (10x)	River Sediment "B" (10x)	Soil "A" (10x)	Soil "B" (10x)
9 Be	107.6%	106.6%	95.8%				
23 Na	94.9%	92.9%	96.7%		102.8%	95.0%	91.9%
24 Mg	101.5%	91.7%	101.0%	97.8%	102.2%	99.5%	96.4%
27 Al	103.9%	105.9%	99.6%	100.8%	101.8%	98.0%	96.1%
39 K	99.7%	88.5%	100.5%	99.3%	102.8%	97.8%	95.5%
44 Ca	101.9%	100.1%	97.3%	100.1%	97.7%	97.2%	96.7%
51 V	102.3%	100.0%	97.8%	99.8%	97.3%	99.3%	96.8%
52 Cr	103.5%	102.1%	96.5%	102.7%	101.8%		94.3%
55 Mn	101.4%	98.5%	104.2%	105.9%	104.5%	99.1%	98.5%
56 Fe	104.0%	108.8%	99.2%	101.1%	98.8%	97.8%	96.1%
59 Co	99.0%	96.7%	99.4%	112.4%	98.1%		99.4%
60 Ni	101.8%	100.7%	96.8%	101.2%	96.0%	96.0%	96.8%
63 Cu	100.5%	98.8%	94.8%	98.1%	94.6%	94.6%	100.4%
66 Zn	98.7%	101.8%	94.5%	105.1%	94.4%	96.2%	100.0%
75 As	101.0%	102.1%	99.9%	101.7%	100.0%	100.2%	99.3%
78 Se	94.9%	101.0%	99.2%		93.6%	93.8%	
95 Mo	107.3%	96.5%					
107 Ag	93.1%	91.3%					
111 Cd	99.2%	100.9%		99.6%	97.8%		96.8%
121 Sb	102.2%	99.7%		100.6%	100.0%	101.2%	101.8%
137 Ba	107.9%	99.8%		100.0%	107.9%	107.1%	105.5%
205 Tl	95.5%	94.1%		88.0%	84.0%		
208 Pb	101.3%	104.6%	94.2%	107.4%	104.3%	102.1%	104.8%
232 Th			94.6%	98.4%	93.9%	96.5%	97.3%
238 U				97.1%	91.3%	94.1%	107.7%

Table 2 Accuracy (recovery) for analysis of certified reference waters, soils and sediments. NIST 1643e was analyzed undiluted and diluted, and the excellent agreement between the two sets of results demonstrates the good precision, sensitivity and interference control of the 7700x. Blank cells indicate no certified value.

Conclusions

EPA Method 6020A is applicable to a wide range of elements in samples ranging from clean waters to highly contaminated soils or sludges. Because of this, contract laboratories running Method 6020A may not have detailed information on the composition and concentration of samples analyzed together in a single sequence. The Agilent 7700x ICP-MS is uniquely qualified to perform this difficult application for a number of reasons. All samples, regardless of composition or concentration can be analyzed using a single cell gas mode (He mode), and no prior knowledge of the sample is necessary.

The built-in HMI allows most samples to be analyzed without the need for further dilution after initial sample preparation. Additionally, the HMI significantly improves plasma robustness, which minimizes internal standard failures and extends the number of samples that can be run between calibrations. All of these benefits translate into simpler, faster, more reliable analysis of complex environmental samples.

Further details of this application can be found in Agilent Application Note, 5990-5514EN.

For more information on the 7700x visit the Agilent Technologies web site at: www.agilent.com/chem/icpms

Screening for Polybrominated Diphenyl Ethers in Biological Samples by HPLC-ICP-MS

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Introduction

The determination of polybrominated diphenyl ethers (PBDEs), a class of synthetic organic compounds used as flame retardants, is becoming of increasing concern because of their persistence in the environment, bioaccumulation, and potential toxicity. There can exist 209 different PBDE congeners, varying in number and position of bromination but many of them are unstable and tend to debrominate in the environment. The generic structure of a PBDE is given in Figure 1.

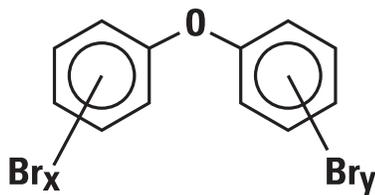


Figure 1. General chemical structure of a polybrominated diphenyl ether

Gas chromatography (GC), used routinely for the analysis of low molecular mass (up to ca. 700) PBDEs, fails for heavier congeners because of the long retention times and on-column degradation. Therefore, HPLC has recently been proposed as an alternative. The separation, carried out by reversed-phase HPLC, requires high contents of organic modifiers for quantitative elution of the PBDEs and reliable and straightforward detection techniques are lacking. ICP-MS is a convenient detector of heteroatom-bearing compounds in HPLC because of its sensitivity and the response being virtually independent of the molecular structure of the compound and readily controlled in different mobile phase conditions. The detection of bromine by ICP MS is, however, negatively affected by two factors: a relatively high 1st ionization potential (11.84 eV) and the presence of common polyatomic interferences.

The goal of this work was the development of an HPLC-ICP-MS method for the rapid screening of the metabolites of decabromodiphenyl ether [1] in rat liver and feces. A new ICP-MS instrument with a fast frequency-matching RF generator was investigated for the high flow rates of organic-rich phases that are necessary for the elution of PBDE compounds in fast HPLC.

Experimental

Instrumentation. An Agilent 7700x ICP-MS equipped with a plasma frequency-matching RF generator and an octopole collision/reaction cell (ORS) was coupled with an Agilent 1200 LC. A reversed phase column (Agilent ZORBAX Eclipse XDB-C18: 4.6 x 50 mm, 1.8 μ m) was used for the separation of PBDEs. A microbore column SB-C18 (Agilent, Zorbax: 150 x 0.5 mm, 5 μ m) and an Agilent 7500ce ICP MS were used in the initial phase of the study.

Reagents, solutions and materials.

Analytical reagent grade chemicals, purchased from Sigma-Aldrich (Saint-Quentin Fallavier, France), and water (18 M Ω cm) obtained via a Milli-Q system (Millipore, Bedford, MA), were used. The PBDE standards were obtained from Wellington Laboratories (Guelph, ON, Canada) with the exception of BDE-209 which was purchased from Sigma-Aldrich.

Sample preparation. Rat liver and feces samples were collected and homogenized, and subsamples of about 1g were taken for analysis. PBDEs were extracted according to the following protocol: each sample aliquot was extracted three times with fresh 5-mL (liver) or 10-mL (feces) portions of acetonitrile and then three more times with similar portions of an acetonitrile:toluene mixture (90:10, v/v). The extracts were combined, evaporated to dryness under N₂ and the residue was re-dissolved in 1.5 mL of toluene.

Procedure. A 10- μ L sample aliquot was chromatographed for 12 min using a gradient of water (A) and acetonitrile (B) according to the following program: 0 - 4 min (70% B), 4 - 8.5 min (90% B), 8.5 - 11.5 min (95% B) and 11.5 - 12 min (70% B) at a flow rate of 1.5 mL/min. The isotopes monitored were ⁷⁹Br and ⁸¹Br. Flow rates of collision gas (helium) and carrier gas (argon) were optimized to obtain the correct ⁷⁹Br/⁸¹Br isotopic ratio and to maximize the sensitivity,

respectively. The optimum values were 2 mL/min for the helium collision gas and 0.65 L/min for the argon carrier gas. The plasma RF power was 1550W. 8% oxygen was added to the argon carrier gas. Spray chamber temperature was maintained at -5°C.

Results and Discussion

Optimization of HPLC-ICP-MS Analysis of PBDEs

The reversed-phase HPLC separations of PBDEs are known to require high concentrations of an organic modifier which cannot be readily tolerated at 1 mL/min by the 7500 Series ICP-MS. Therefore, pre-7700x ICP-MS, a microbore HPLC separation at 50 μ L/min using a dedicated interface was employed. The system allowed a stable detection of bromine but the sensitivity in the organic modifier was one order of magnitude lower than in aqueous solutions and the baseline separation of the pairs of PBDE congeners 85/100 and 207/208 could not be obtained.

In a second attempt, ultra-high performance HPLC using 1.8 μ m beads was examined in order to improve the separation efficiency. Our optimization efforts have resulted in the baseline separation of all the PBDEs investigated except the pair of PBDE congeners 207/208 which have the same molecular mass and vary only slightly in structure.

This satisfactory separation could, however, be obtained using a 4.6 mm column at flow-rates of 1.5 mL/min and using a mobile phase containing more than 70% of acetonitrile during most of the duration of the run. However, under these conditions, the plasma of the 7500 ICP-MS could not be sustained. Therefore, the ability of the new 7700x ICP-MS (equipped with the fast frequency-matching RF generator) to tolerate such solutions was of great interest. Using a standard sample introduction system (Meinhard nebulizer) and double-pass Scott spray chamber cooled down to -5°C, acetonitrile could be aspirated directly into the plasma of the 7700x at 1.5 mL/min without affecting its stability. A chromatogram of the mixture of PBDE standards obtained under these conditions is shown in Figure 2.

Analytical Figures of Merit

The effect of the acetonitrile concentration on the sensitivity was examined by comparing the slopes of the calibration curves obtained for a Flow Injection Analysis (FIA)

ICP-MS analysis of NaBr solution using the mobile phases containing 0, 35, 70, 80 and 95% v/v acetonitrile. The limits of detection calculated as blank + 3 σ were: 4, 16, 18, 18 and 16 ng/mL, respectively. It can be seen that although the organic modifier reduced the sensitivity by a factor of 4, this decrease happened between 0 and 35% fraction of acetonitrile. Consequently, the sensitivity remained constant at acetonitrile concentrations exceeding 35% which largely facilitated quantification.

As all the investigated compounds elute at acetonitrile concentrations above 35%, no trend in the decrease of the detection limits was observed. They were on the level of 20 ng/mL (as Br) and similar for all of the compounds, taking into account the uncertainty about the exact concentration of the compound in the purchased standards.

Quantification of the PBDEs in Biological Samples

The method was applied to probing for the metabolite products of decabromodiphenyl ether (bis(pentabromophenyl) ether, BDE-209) and the quantification of the residual compound. A typical HPLC-ICP-MS chromatogram of the liver sample is shown in Figure 3. It shows the absence of metabolites of decabromodiphenyl ether, the latter being the only compound present. It could be quantified by the method of standard addition (3-levels). The concentrations determined (3 independent measurements) were 7.9 ± 0.2 and 14.1 ± 1.1 mg/mL (as Br) for the extracts of liver and feces (chromatogram not shown), respectively. The precision for three independent measurements was 6.8% and 6.9% for liver and feces samples respectively.

Conclusions

The use of the 7700x ICP-MS equipped with a fast frequency-matching RF generator was demonstrated to allow the introduction of an HPLC mobile phase containing up to 95% acetonitrile at a high flow rate (1.5 mL/min). This development opens up new opportunities for HPLC-ICP-MS applications. In fact this performance was the key feature that enabled the development of our method for the screening for metabolites of decabromodiphenyl ether (bis(pentabromophenyl) ether) in a rat metabolic study. The HPLC-ICP-MS

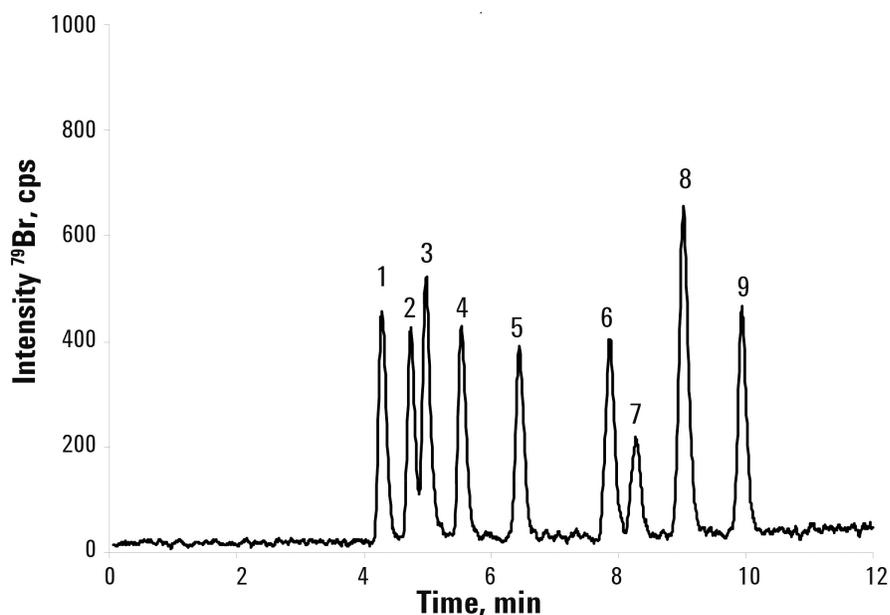


Figure 2 HPLC-ICP-MS chromatogram of the PBDE standards; 1 - BDE 47, 2 - BDE 85, 3 - BDE 100, 4 - BDE 138, 5 - BDE 155, 6 - BDE 201, 7 - BDE 206, 8 - BDE 207 and 208, 9 - BDE 209, at 0.25 mg/mL each

method offers the accuracy of HPLC with radioactivity detection and is an alternative to other methods for screening PBDE metabolites in biological samples.

Acknowledgements

The authors would like to thank Anne Riu, Laurent Debrauwer, and Daniel Zalko from INRA, UMR 1089, Toulouse, France for donating the samples.

Reference

1. http://en.wikipedia.org/wiki/Decabromodiphenyl_ether#cite_ref-EU2002_2-2

Further Reading

The full version of the article is available in JAAS; 2010, DOI: 10.1039/C000686F Reproduced by permission of The Royal Society of Chemistry (RSC), www.rsc.org/jaas

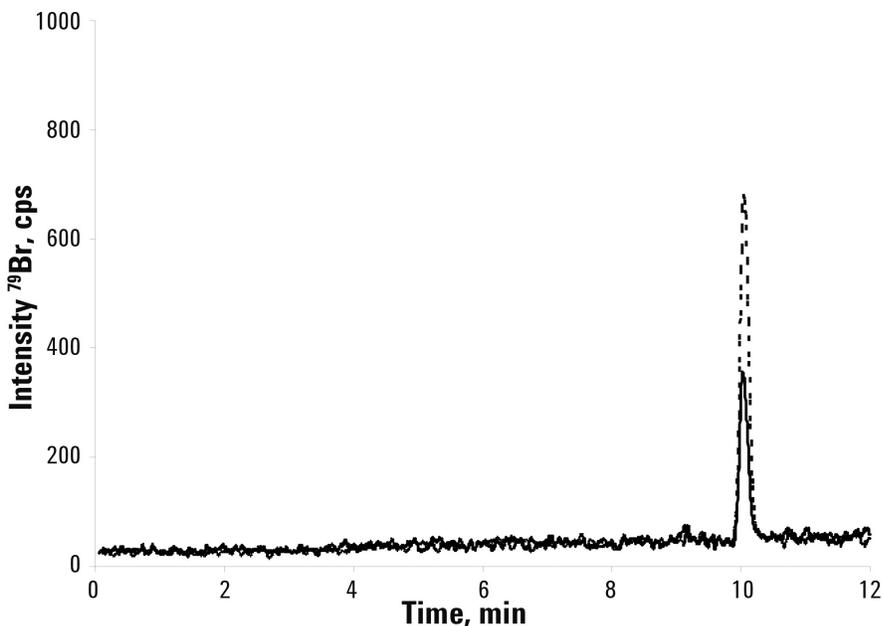


Figure 3. HPLC-ICP MS chromatograms of liver samples. Solid line: sample; dashed line: sample spiked with 0.25 mg/mL of bis(pentabromophenyl) ether.

New Agilent GC-ICP-MS Interface Kit for 7700 Series ICP-MS

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ICP-MS Product Marketing, Agilent Technologies, Japan

Agilent's new GC-ICP-MS interface kit (G3158C) connects the 7700 Series ICP-MS with the 7890A GC (Figure 1), and provides superior GC-ICP-MS performance in the analysis of volatile organic and organometallic compounds.

The new GC-ICP-MS interface has been enhanced to include:

- Much simpler, quicker connection and removal from the ICP-MS
- More robust and reproducible torch mounting, for improved long term stability
- A stable, self-centering torch injector that simplifies installation and setup and insures optimum performance
- Fully inert, Sulfinert® steel lined transfer line and injector that can be heated to 300°C from the GC oven to the plasma with no cool spots
- Convenient docking station to hold and protect the interface when not in use (Figure 2)



Figure 2. Docking station for GC-ICP-MS interface kit located on the right hand side of the GC

In addition to these reliability and ease of use enhancements, the new interface maintains the advantages of its predecessor including:

- High temperature, dry plasma that delivers superior sensitivity for high ionization potential elements such as Hg, As and Se and the halogens.



Figure 1. New GC-ICP-MS interface kit (G3158C) connected to an Agilent 7700 Series ICP-MS

- Freedom from background interferences on sulfur and phosphorus enabling trace measurement at elemental masses
- Uniform high temperature maintained all the way to the tip of the ICP injector, preventing peak tailing and loss of high boiling analytes due to condensation in the injector

a mixed organotin standard. GC and ICP-MS operating conditions are summarized in Table 1. The analysis was completed in less than 12 minutes with a detection limit for tributyl tin (TBT) of 5.9 ppt (Figure 3). This data demonstrates that the GC-ICP-MS is capable of rapid and sensitive detection of organotin. The new interface has also been proven for more difficult applications such as S speciation in fuels and the separation of polybrominated diphenyl ether (PBDE) flame retardants.

Organotin Analysis

The analytical performance of the new interface was evaluated by analyzing

GC operating parameters	
Injection	1 µL
Column	HP-5 (30 m x 0.32 mm i.d. x 0.25 µm film thickness)
Oven program	70°C (1 min), 30°C /min > 190°C (0 min), 15°C /min > 270°C (4 mins)
Carrier gas	He at 2 mL/min (constant flow)
Inlet temp	290°C
Transfer line temp	250°C
ICP injector temp	250°C
ICP-MS operating parameters	
RF power	1200W
Sample depth	8 mm
Carrier gas	0.80 L/min
Aux gas	1.50 L/min

Table 1. Method parameters for the separation of organotins using GC-ICP-MS

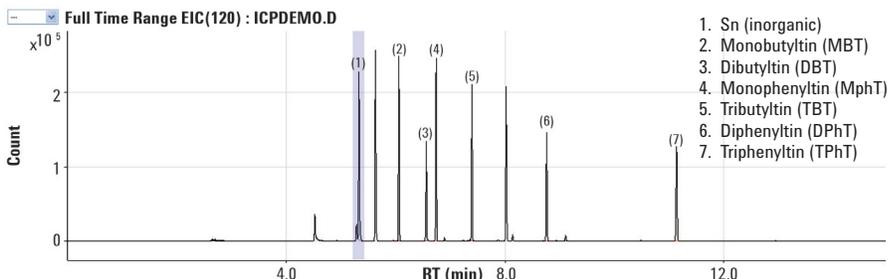


Figure 3. Chromatogram of a 1 µL injection of a 10 ppb mixed organotin standard

High Temperature Simulated Distillation by GC-ICP-MS

A preview of things to come

Steve Wilbur

ICP-MS Applications Specialist,
Agilent Technologies

Simulated distillation or SimDis is a technique widely used in the petroleum refining industry to quickly determine the yield distribution (boiling point vs. amount) of crude feed stocks, intermediates and products. With the ability to simultaneously measure elements other than carbon, GC-ICP-MS can provide critical information about feedstock quality, such as, the distribution and concentration of sulfur species. However, there are significant technical challenges to be overcome. The transfer line from the outlet of the GC column to the ICP-MS must be able to quantitatively convey compounds whose boiling points can exceed 600°C (> 1000°F) into the ICP plasma. This requires both extraordinary temperature control and inertness. In addition, the ICP-MS must be able to control common interferences, particularly on sulfur.

Both of these requirements can only be met using a transfer line and ICP injector which are uniformly heated all the way to the plasma, combined with the use of dry plasma. The newly enhanced Agilent GC-ICP-MS interface meets these requirements by virtue of the following unique features:

- Both the transfer line and ICP injector are independently heated and controlled by the GC
- The entire transfer line and ICP injector are lined with highly inert Sulfinert® stainless steel
- Argon makeup gas which helps convey the GC effluent to the ICP is preheated in the GC oven to the temperature of the currently eluting compounds
- The high flow rate of heated argon through the transfer line minimizes the time spent between the GC and ICP torch to < 100 milliseconds, significantly reducing the opportunity for interaction between the eluting compounds and the transfer line

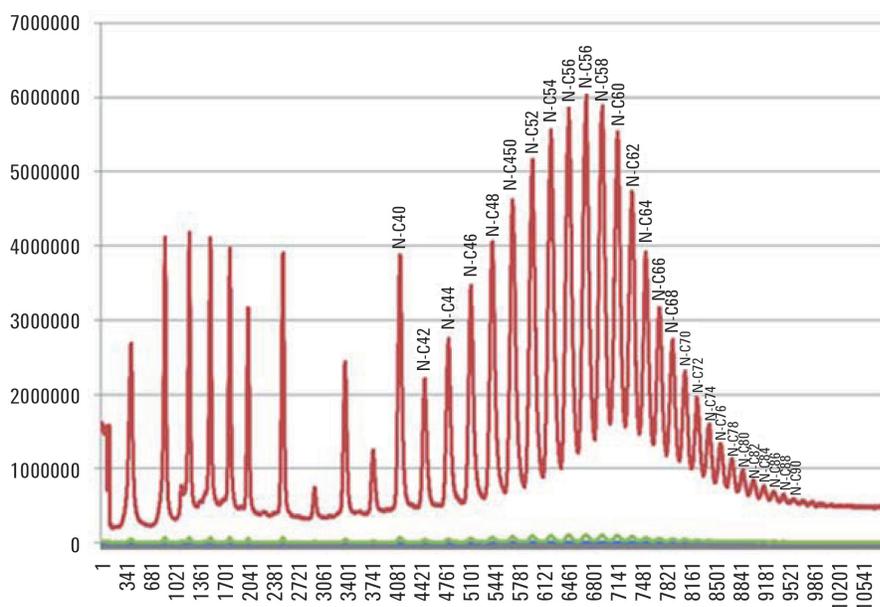


Figure 1. Boiling point reference standard showing marker hydrocarbons

Figure 1 shows the extracted ion chromatograms for carbon (^{12}C in red, ^{13}C in green) of a hydrocarbon standard up through C_{90} . The discrete peaks in the extracted ion chromatograms for this boiling point reference standard from carbon number C_{40} – C_{90} are labeled.

Figure 2 shows a chromatogram of NIST 2724B sulfur in diesel standard to illustrate the capabilities of this newly configured system, for monitoring both carbon and sulfur with a single detector.

The hydrocarbon components are plotted as ^{13}C in blue and the sulfur containing components as ^{32}S in red. It is not possible to measure ^{32}S simultaneously with other elements using a wet plasma due to the intense interference from O_2^+ .

Only the Agilent GC interface provides the high temperature, inertness and the dry plasma conditions required for these difficult applications.

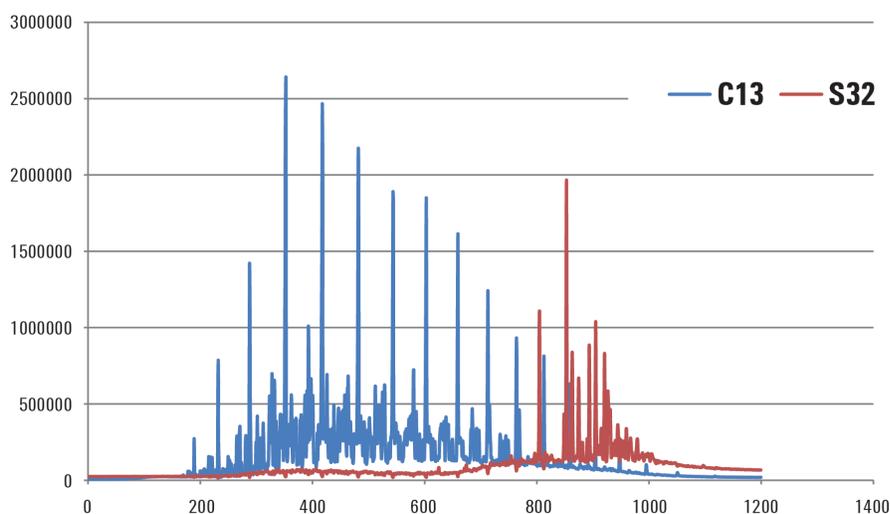


Figure 1. Carbon and sulfur extracted ion chromatograms for NIST 2724B sulfur in diesel

Agilent Celebrates the 4000th ICP-MS Shipment

Tomo Yamada
ICP-MS Product Manager,
Agilent Technologies, Tokyo, Japan



Agilent 4500, 7500 and 7700 Series ICP-MS: more than 4000 ICP-MS units have been manufactured and shipped from Agilent's Tokyo Analytical Division in Japan.

Since the introduction of the 4500 Series ICP-MS in 1994, Agilent's Tokyo Analytical Division (TAD) has shipped over four thousand 4500 Series, 7500 Series and 7700 Series systems to customers located in more than 80 countries across all major continents. We'd like to thank you - our users - for your continued support, feedback and collaboration that allows us to stay at the forefront of ICP-MS development.



Agilent's Tokyo based ICP-MS team gathered to acknowledge another landmark event: the shipment of the final 7500 ICP-MS from TAD. Agilent has now shifted full production to the 7700 Series ICP-MS.

2011 European Plasma Prize
European Award for
Plasma Spectrochemistry
Submission deadline 9 July 2010.
Find out more at
www.agilent.com/plasmaprize or
www.winterplasmazaragoza2011.es

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Call For Papers for Agilent's Speciation Handbook – Prizes to be Won

Submit a half page abstract of documented hyphenated ICP-MS applications by 30 Sept, 2010 for a chance to win an Apple iPad (Government employees may not be eligible). For more information or to submit an abstract, contact Steve Wilbur: steven.wilbur@agilent.com

Conferences. Meetings. Seminars.

Forum Labo and Biotech
June 1-4, 2010, Paris, France
www.forumlabo.com

15th Biennial National Atomic Spectroscopy Symposium
7th July 2010, Cambridge, UK
www.rsc.org

5th Nordic Conference on Plasma Spectrochemistry
June 6-9, 2010, Loen, Norway
www.nordicplasma.com

SEGH 2010
June 27- July 2, 2010, Galway, Ireland
www.nuigalway.ie/segh2010

Agilent ICP-MS Publications

To view and download the latest ICP-MS literature, go to www.agilent.com/chem/icpms and look under “Library Information”

- **Application Note:** Simple, Reliable Analysis of High Matrix Samples According to US-EPA Method 6020A using the Agilent 7700x ICP-MS, 5990-5514EN
- **Application Note:** Maximizing Productivity in High Matrix Samples using the Agilent 7700x ICP-MS with ISIS Discrete Sampling, 5990-5437EN
- **Application Note:** Sensitive, High-Throughput Analysis of Lead in Whole Blood using the Agilent 7500cx ICP-MS with ISIS-DS, 5990-5416EN
- **Tech Feature:** New Agilent GC-ICP-MS Interface - Fully Heated Interface for the 7890 GC & 7700 ICP-MS Allows Routine Analysis of High Boiling-Point Compounds, 5990-5798EN
- **Tech Feature:** Maximizing ICP-MS Productivity for High Matrix Samples Using the 7700x with ISIS Discrete Sampling, 5990-5631EN
- **Tech Feature:** Pharmaceutical Analysis by ICP-MS: New USP test for elemental impurities to provide better indication of potentially toxic contaminants, 5990-5427EN

The following **Scientific Posters** are also freely available online. Go to the **Poster** section of the **ICP-MS Literature Library** or use the **Search** facility to search by title.

- New Design of Ion Lens and Collision/Reaction Cell for ICP-MS: He Mode on the ORS³ for Effective Interference Removal in a Range of Complex Matrices
- Introducing the New Agilent 7700 Series ICP-MS; Improved Performance for Speciated Analysis
- Meeting Current and Future Regulatory Requirements for Trace Metals in Drinking Water Using Simplified Helium Collision Mode ICP-MS
- Improving Collision Cell Efficiency for the Separation of Challenging Polyatomic Interferences
- Trace Level Analysis of V, As and Se Using He Cell Gas via Kinetic Energy Discrimination and Collisional Dissociation in Acidic Matrices
- Performance Evaluation of Helium Mode ICP-MS for High-matrix Sample Types in a High-throughput European Laboratory
- Strategies for Increasing Effective Plasma Temperature and Improving Matrix Decomposition in ICP-MS
- Combining Discrete Sampling with Helium Collision Mode for High Throughput ICP-MS Analysis of High Matrix Samples

Front page photo: Kazumi Nakano, ICP-MS Applications Engineer based in Tokyo, Japan and Fred Fryer, ICP-MS Applications Chemist for Australia and New Zealand

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