Agilent ICP-MS Journal

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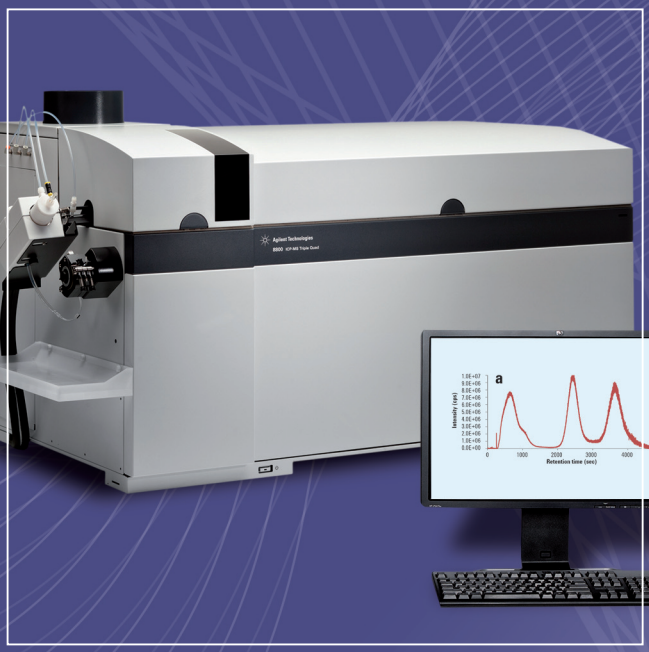

Inside this Issue

The Measure of Confidence

Agilent Technologies

Characterization of Metal Nanoparticles using Centrifugal FFF-ICP-MS

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Introduction

As a result of rapid growth in the production and use of nanomaterial in consumable goods, the release of engineered nanoparticles (ENPs) into the environment is raising concern. Analysts worldwide are researching the ecotoxicity of ENPs to assess their potential negative impact on the health of ecosystems.

The first step to fully understand the environmental effects of ENPs is the development of powerful and sensitive analytical techniques to detect and characterize ENPs in complex environmental matrices. This should be done at environmentally relevant concentrations, namely sub microgram to nanogram per liter.

Bulk characterization techniques, such as dynamic light scattering and electron microscopy are commonly used to size ENPs. However, these techniques exhibit difficulties in analyzing broad and complex mixtures such as environmental samples.

Centrifugal Field-Flow Fractionation (CFFF) is a high resolution mass-based technique that separates and characterizes natural and ENPs dispersed in aqueous and organic media over the size range of 6 nm to 30 µm.

Separation in CFFF is a result of the interaction between a centrifugal field and the sample species. The CFFF channel encircles the centrifuge axis like a belt. The spinning of the channel generates differential acceleration forces at a right angle to the direction of flow. Equilibrium will be achieved when the field-induced and diffusion-induced migrations of sample species are balanced. Smaller sized sample species located closer to the channel center are swept out faster than the larger ones. Particle size (equivalent spherical diameter) can be calculated directly from the elution time using CFFF theory [1].

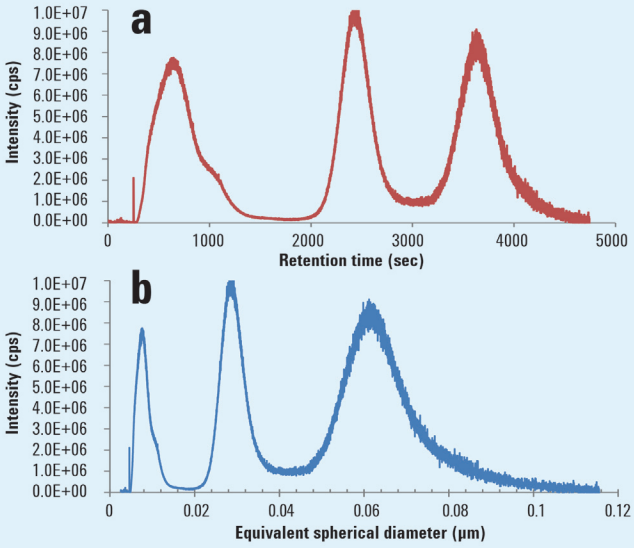


Figure 1. CFFF-ICP-MS analysis of the mixture of 10 nm, 30 nm and 60 nm NIST Gold nanoparticles. **(a)** ^{197}Au intensity (cps) versus retention time (sec), **(b)** ^{197}Au intensity (cps) versus equivalent spherical diameter (µm). The equivalent spherical diameter was calculated from the elution time using CFFF theory.

The field also permits separation of nanoparticles based on their composition, coating thickness, and coating material. This unique feature could be very useful for analyzing environmental samples which are usually complex in composition.

ICP-MS is a sensitive multi-element analytical technique with an exceptionally low detection limit (parts per trillion) for natural and ENPs. ICP-MS can be utilized as an online detector coupled directly to a CFFF instrument. The hyphenated system provides multi element-based size and elemental ratio distributions, providing a comprehensive elemental characterization technique for ENPs.

In this study, separation and characterization of gold nanoparticles (NPs), as well as a mixture of gold and silver NPs with similar size distributions (different density) is presented.

Experimental

Materials

Three gold NPs standards (10 nm, 30 nm and 60 nm) at nominal concentration of 50 ppm were purchased from National Institute of Standards and Technology (NIST), Gaithersburg, MD, U.S.A. Silver and gold NP standards with similar size distributions (nominal mean diameter of 20 nm) and nominal concentrations of 56 ppm (Au NPs) and 3 ppm (Ag NPs) were purchased from BBInternational, Cardiff, UK.

Two mixtures were prepared using the commercial NP standards: (1) A 1:1:1 ratio mixture of three Au NP standards (10 nm, 30 nm and 60 nm) and (2) A 1:9 ratio mixture of 20 nm Au and 20 nm Ag NP standards.

Instrumentation

A CF2000 system (CFFF), Postnova Analytics GmbH, Landsberg, Germany was interfaced directly to a 7700x ICP-MS to monitor ^{197}Au and ^{107}Ag intensities during the separation. The operating parameters are given in Table 1.

Table 1. CFFF-ICP-MS operating conditions

CFFF	
Instrument	CF2000
Initial field	4500 rpm
Final field	100 rpm
t_1	10 min
Channel flow rate	0.5 mL/min
Channel thickness	231 µm
Relaxation time	2.5 min
Carrier	0.05% NovaChem*
Injection volume	5 & 20 µL

ICP-MS	
Instrument	7700x
Nebulizer	Micromist
Neb gas flow	1.02 L/min
Make up gas flow	0.1 L/min
Sample depth	7 mm
RF power	1550 W
Dwell time	0.1 sec
Isotopes monitored	^{107}Ag, ^{109}Ag, ^{197}Au

*Ionic and non-ioninc surfactant mixture available from Postnova Analytics

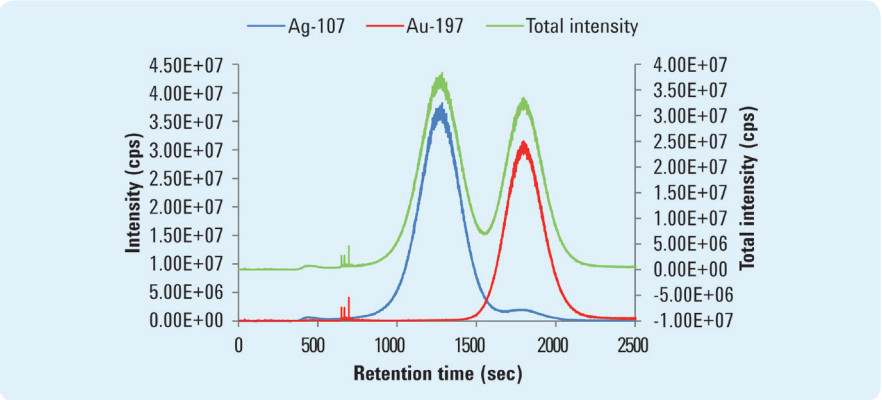


Figure 2. ^{197}Au and ^{107}Ag intensities (cps) versus retention time (sec) for a mixture of 20 nm silver and 20 nm gold nanoparticles obtained by the hyphenated CFFF-ICP-MS system.

Results and Discussion

Mixture of Au NPs standards

Figure 1a illustrates the ^{197}Au intensity (cps) plotted against the elution time (sec) of the mixture of the NIST standards obtained from the CFFF-ICP-MS hyphenated system. The plot shows a baseline separation between 10 nm (570 sec) and 30 nm (2386 sec) and almost a baseline separation between 30 nm and 60 nm (3616 sec) Au NPs. The Au 10 nm standard exhibits a small shoulder eluting at 1220 sec which could be due to aggregated NPs.

Figure 1b depicts the ^{197}Au intensity (cps) of the mixture plotted against particle diameter calculated from elution time using the CFFF theory [1]. The plot shows three peaks representing the three standards centered at 7.4 nm, 29.2 nm and 59.5 nm. The small shoulder on the 10 nm standard peak is measured to be 12 nm in diameter.

Mixture of Au and Ag NPs

Figure 2 shows the element-based fractrograms (individual and total intensities versus retention time) of the mixture of 20 nm silver and 20 nm gold NPs obtained from the CFFF-ICP-MS. The total elemental intensity (^{107}Ag + ^{197}Au) shows a bimodal distribution for the mixture with the two populations separated by almost 9 minutes. The first population eluting at 1220 sec retention time is due to the Ag NPs. The second population is mainly composed of the Au NPs and a small Ag component. Separate batch ICP-MS analyses of the original standards were performed and the results confirmed that the Ag component in the Au NPs was due to the impurity in the original suspension.

Figure 3 shows the ^{107}Ag (a) and ^{197}Au (b) intensities plotted against the equivalent spherical diameter. The diameter axes in both graphs were converted directly from the retention time using the CFFF theory [1] and $\Delta\rho$ (the difference in density between the particle and carrier solution) values of 9.5 g/mL and 18.3 g/mL for the Ag and Au NPs respectively. The Ag NPs exhibited a size distribution with a main peak centred at 16.2 nm. Whereas the Au nanoparticles had a peak centred at 20.4 nm.

Resolution

The analysis data of the NIST mixture suggested a resolution (Rs =$\Delta t/4\sigma$ [2]) of 2.6 between 10 nm and 30 nm particles, and 1.3 between 30 nm and 60 nm particles. The resolution for the 20 nm silver and 20 nm gold mixture was calculated as 1.0 which corresponded to a 27% difference in particle mass. The minimum mass resolution was estimated as 13% for the set of run conditions used in these experiments.

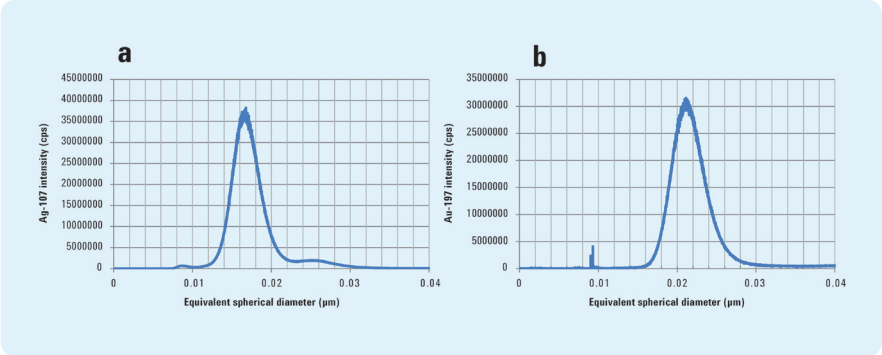


Figure 3. Intensity versus equivalent spherical diameter for (a) nanosilver and (b) nanogold, in a mixture of 20 nm silver NPs and 20 nm gold NPs.

Conclusions

Hyphenated CFFF-ICP-MS was utilized successfully for the high resolution and high precision separation and characterization of metal nanoparticles. Direct size measurement was possible using CFFF theory, without the need for calibration. The data suggests that the methodology is capable of separating metal nanoparticles (different type and size) with a minimum mass resolution of 13%. This unique feature could be exploited by researchers and industries who are seeking a powerful and sensitive analytical technique for the characterization of complex and polydisperse multi-element samples.

The method also detected a low level impurity in one of the commercial standards. This demonstrates the usefulness of the methodology in quality control of reference and standard materials.

References

1. Giddings J.C. Science 1993 (260), 1456-1465
2. Giddings J.C., Unified Separation Science, Wiley and Sons, New York, 1991

More Information

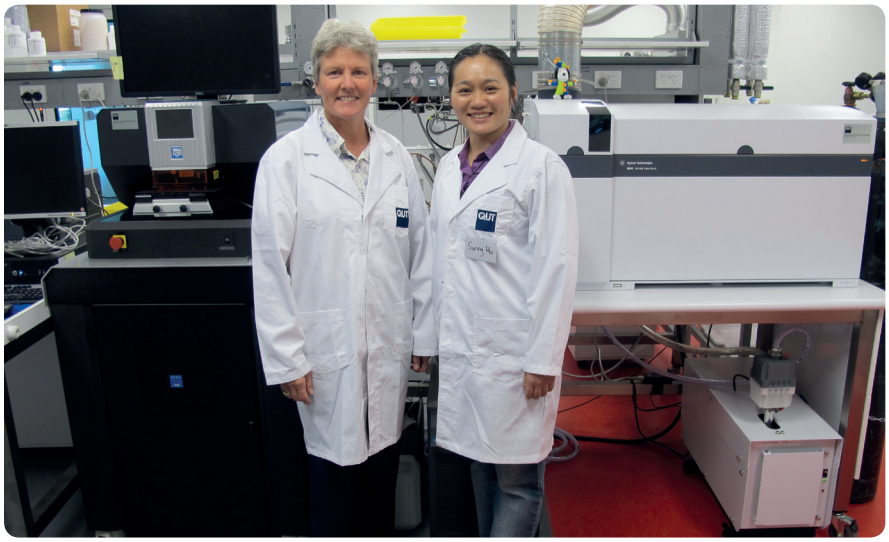
Find out more about Field-Flow Fractionation at: **www.postnova.com**

Two 8800 ICP-QQQs Support Multiple Research Goals at Queensland University of Technology

Australia's Prime Minister recently opened a cutting-edge science and engineering teaching and research facility at Queensland University of Technology (QUT) in Brisbane; a center that has been designed to inspire the public, students and staff alike.

The new Science and Engineering Centre (pictured above) combines state-of-the art research labs, and work/meeting space with a high-tech public area known as "The Cube", that stretches over two floors. The Cube features one of the world's largest touch and display systems and provides visitors with an opportunity to experiment with live science, making it an ideal destination for families and groups of school children. There is also a dedicated "science on view" exposition space within the Cube, where researchers are encouraged to share their work both internally and externally, as well as public spaces within the Science and Engineering Centre as shown in the photo below.

Breaking down barriers – Agilent ICP-MS clearly on view from one of the many public spaces within QUT



Research Officers Dr Charlotte Allen and Dr Sunny Hu with one of the Centre's two 8800 ICP-QQQs; this 8800 is coupled to a New Wave laser ablation system

The Science and Engineering Centre also houses the **Institute for Future Environments (IFE)** – a new institute established to support interdisciplinary R&D research to problem-solve issues such as global food security and managing scarce natural resources.

Within the IFE, the Central Analytical Facility has been set up to provide analytical support to the science and technology faculties across the university. Research Officer Dr Charlotte Allen (pictured) manages the analytical lab, and together with Dr Sunny Hu (pictured), is responsible for the set up and operation of the two Agilent 8800 Triple Quad ICP-MS that have recently been installed.

Prior to the availability of triple quad ICP-MS, QUT had considered purchasing a high resolution ICP-MS and a single quadrupole ICP-MS. The timing coincided with the introduction of the 8800, and Executive Director Prof. Ian Mackinnon was quick to realize the great potential of the technique for the Institute's workload in terms of analytical capability, flexibility, and relative ease of operation and maintenance compared to hi-res ICP-MS. Consequently QUT was among the first labs in Asia to place an order for an 8800 and the first lab in the world to place an order for two instruments.

One of the 8800s will be dedicated to environmental work and includes an ASX 520 autosampler and Integrated Sample Introduction System (ISIS) with the potential for HPLC-speciation; this unit will be managed by Dr Hu. The ICP-MS in the photo is coupled to a New Wave laser ablation system for the direct study of solid samples and this system will be overseen by Dr Allen. QUT also operate an Agilent OES for general solutions analysis as well as a 7500ce ICP-MS that supports undergraduate teaching.

At the time the 8800s were ordered, the IFE was in process of being established and staffed. Dr Allen, who was selected to run the analytical lab based on her previous extensive experience with LA coupled to an Agilent ICP-MS for geological studies, is tasked with developing the analytical service provision of her well-equipped lab to help achieve the University's research goals across multiple applications such as mining, minerals, geology, materials, and life sciences. With such a variety of potential applications, QUT required the instrument capability of their ICP-MS to be as flexible as possible.

Early project work and specific requests for analytical support requiring the use of the ICP-QQQ include:

- The study of small insects to understand how metals affect the hardness of their exoskeleton.
- Growth of bone and teeth around surgical implant sites.
- Precise work on rare earth element patterns in precambrian rocks to provide an insight into how the earth accreted as a planet.

QUT has also recently been awarded funding from the Australian Research Council (ARC) Discovery Grants to investigate novel, multi-technique dating of continental sedimentary rocks in order to examine the effects of a high sediment flux from an enigmatic, major mountain-building event on a distant continental margin. ICP-QQQ will be used to date minerals in the sand that contain U that has decayed to Pb so that the age of crystallization of these sand grains can be determined. The aim of the research is to expand understanding of the range of tectonic influences (formation of mountains and basins) between continental interiors and margins; these processes have direct influence on onshore resource potential.

When asked which applications she was most excited about investigating, Dr Allen explained that it was early days at QUT for her and her team of operators, as the 8800s had literally just been installed. Adding "I just want to get these babies off the ground and see what they can do!" Allen envisages that once her colleagues across the different faculties at the university become aware of the capabilities of the 8800s with LC and LA, then requests for support with their research projects will come flooding in and will, without doubt, be many and varied. She is also hoping to find some time to pursue her own research interests.

QUT Played Host to the Agilent Australian ICP-MS User Group Meeting

Australia's ICP-MS user base took the opportunity to check out the facilities at QUT's Institute for Future Environments at the recent Agilent User Group meeting held in April.

Further Information

Find out more at the Queensland University of Technology web site: **www.qut.edu.au**

Expansion of Agilent's ICP-MS Pt Cone Trade-in Credit Program

Eric Vanclay
Supplies Product Manager,
Agilent Technologies

Figure 1: Used platinum cones can be returned for a trade-in credit and recycling.

Agilent is continuing to expand the geographies where we offer the trade-in credit program on used platinum cones for our ICP-MS users. Our latest additions cover Australia, Korea and South East Asia. The program was first introduced in May 2012 and already covers North America, Western Europe, and Japan. Using this program, you receive a trade-in credit against return of used platinum cones when purchasing replacements.

Agilent's trade-in credit program:

- Delivers significant cost savings to your laboratory
- Helps to reduce environmental impact
- Conserves highly valuable platinum supplies by allowing Agilent to recycle the platinum in the cones.

How does the program work?

When you need to replace a platinum sampling or skimmer cone, ask your order processor about this program. They will send you return instructions together with an Environmental Health and Safety (EHS) form. All you need to do is clean the cones and follow the simple instructions to return the used cones to Agilent. Once Agilent has confirmed the type and quantity of the cones received, a credit will be applied directly to your account.

Agilent platinum sampling and skimmer cones for the 8800/7700/7500 Series ICP-MS qualify for the trade-in credit. The value of the credit is based on the market value for platinum, and will be adjusted as platinum prices fluctuate.

Let Agilent's platinum cone trade-in credit program work for you!

Learn more about how Agilent's trade-in credit on used Agilent platinum cones for the 8800/7700/7500 ICP-MS can help you save money!

www.agilent.com/chem/PtCone

Reflections on 2013 European Winter Conference on Atomic Spectroscopy

Once again, the European Winter Conference on Plasma Spectrochemistry (EWPC) that took place in Krakow, Poland, from February 10-15, proved to be the premier conference in the atomic spectroscopy calendar and a truly international event. Over 360 spectroscopists, plus a large number of representatives from instrument and related companies, travelled from 33 different countries located across Europe, Africa, the Americas, and Asia.

Together with its sister events that are held in the US and Asia, the WPC attracts many users of atomic spectroscopy instrumentation, as well as the most preeminent research groups from industry and academia, who are influential and recognized not only in the broader research and academic markets, but also in applied markets.

Under the "Expanding the Horizons of Atomic Spectroscopy" theme, Agilent's atomic spectroscopy group hosted a series of successful events, reinforcing our leadership position as investors and innovators in the field of spectroscopy:

Interactive Panel List discussion at Agilent Lunch & Learn Symposium

Led by Ryszard Lobinksi from the CNRS in Pau, France, panel members, all early adopters of ICP-QQQ or MP-AES plus Prof. Jakubowski (this year's Plasma Prize winner), discussed the benefits of ICP-QQQ vs other techniques in terms of applications, ease of use and benefits of new technologies for routine/research labs. A similar discussion also took place about MP-AES. The panel shared their expectations for future technological developments and the event finished with a question-and-answer session where the 110 attendees were invited to field questions and share their ideas.

Agilent's User Evening Event

With more than 125 attendees at the Agilent Evening Event, there was a warm and friendly atmosphere which served as an excellent opportunity for customers to network and share their experiences.

Poster Presenters Prefer Agilent ICP-MS 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 213 posters presented at the WPC showed that a quadrupole ICP-MS instrument was used in 115 presentations (54%) with an Agilent ICP-MS system cited in 60 posters. Ignoring posters that were presented by representatives from the instrument companies, 53% cited Agilent systems showing, once again, that more presenters use Agilent ICP-MS than any other manufacturer's system (Figure 1).

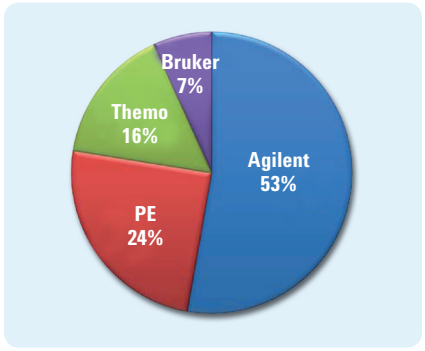
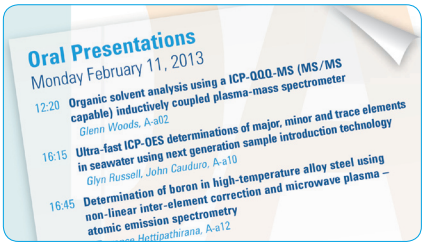


Figure 1. Posters citing ICP-QMS by manufacturer, excluding papers by instrument company representatives.

Agilent personnel presented 23 posters and 3 oral presentations at the WPC.



You can request a copy of some of the posters from: **www.agilent.com/chem/wpc**, see page 8 for a list of titles.

Proud Plasma Prize Winner 2013

Agilent has sponsored the prestigious **European Award for Plasma Spectrochemistry** at each European WPC since its inception in 2002. This year, Agilent's ICP-MS Marketing Manager, Ken Suzuki (pictured), presented the 6th Award to Professor Norbert Jakubowski from the Federal Institute for Materials Research and Testing (BAM, Berlin, Germany).

The award includes an expenses paid 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 Hosts Inaugural ICP-MS Users' Group Meetings in Vietnam

The first ever ICP-MS Users' Group Meetings to be held by Agilent in Vietnam took place in Hanoi on 29 January and in Ho Chi Minh City on 31 January 2013. A total of 50 customers attended these half-day events that were opened by Agilent's District Manager, Mr. Gordon Tai. Gordon also took this opportunity to introduce Agilent and our regional support infrastructure. This was followed by an update on Agilent Technologies' latest Atomic and Molecular Spectroscopic Portfolio by Mr. Steven Pang, Agilent's Spectroscopy Business Manager for Singapore and the regional distributor organization.

There were two customer presentations: Mr. Nguyên Quang Trung from the Institute of Environment, Hanoi, shared his experience using his 7700x; while in Ho Chi Minh City, Mr. Trân Chí Dung of the Centre for Analytical Services and Experimentation shared some aspects of his speciation work on As, Cr, and Hg using the Agilent 1260 LC coupled to an Agilent 7700x.

Agilent's Senior Applications Chemist from Japan's Field Organization, Mr. Katsuo Mizobuchi, presented field application data in a well-received talk describing how the latest Agilent 8800 ICP-QQQ has transformed ICP-MS technology and performance.

A customer interaction activity, *Mass Hunting* saw participants actually "hunting" around the seminar room looking for clues and solutions to solve a series of tasks designed to help them understand our 7700 and 8800 systems better. The first team in each city to complete all the tasks correctly won a special prize provided by Agilent's Tokyo Analytical Division (TAD).

Agilent Technologies Vietnam plans to make the User Group meeting a regular event to support our customers in one of the fastest growing areas of use of ICP-MS technologies.

Participants at the ICP-MS User Group meeting held in Hanoi on 29 January 2013

Excellent turn out at the ICP-MS User Group meeting held in Ho Chi Minh City on 31 January 2013

SelectScience Readers Vote Agilent 8800 ICP-QQQ Best New Spectroscopy Product of 2012

The 8800 Triple Quadrupole ICP-MS was named Best New Spectroscopy Product in the 2012 Scientists' Choice Awards. Introduced early last year, the 8800 ICP-QQQ remains the only instrument of its kind, providing superior performance, sensitivity and flexibility compared with existing quadrupole ICP-MS technology, and delivering consistent and reliable results even when sample composition is complex or variable.

SelectScience, an independent, member-based online publication serving scientists and industry professionals, presented the award to Agilent representatives at the Pittcon Conference and Expo in Philadelphia. The annual Scientists' Choice Awards give SelectScience members the opportunity to vote for their favorite products and services.

"Every year, the Scientists' Choice Awards celebrate the new laboratory products and equipment making a real and meaningful difference in the work of scientists who serve a variety of industries," said Kerry Parker, editor and general manager of SelectScience.

"We are very pleased to learn that scientists from all over the world are experiencing the benefits of this revolutionary new ICP-MS instrument," said Philip Binns, Agilent vice president for spectroscopy products. "The 8800 provides improved performance and flexibility in a variety of important applications, including semiconductor manufacturing, advanced materials, clinical and life sciences, and a wide range of research and routine applications where problematic interferences can hamper the capabilities of conventional ICP-MS technologies."

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Summary of Agilent Posters Presented at Winter Plasma Conference

- Application of MS/MS reaction cell in the newly developed ICP-QQQ for the determination of S, P, Si and Cl in the organic solvents
- Effect of storage temperature and packaging type on the trace metal analysis of wine
- Ultra-trace analysis of Au and PGMs in geological samples using ICP-MS with mixed gases
- Uranium measurement in urine with Agilent 7700 ICP-MS
- Determination of trace rare earth elements in high purity rare earth compounds by ICP-QQQ
- Simultaneous determination of trace elements in high purity steel by ICP-QQQ
- Removal of titanium based interferences on nickel, copper and zinc by ICP-QQQ
- Determination of trace metallic impurities such as P and Ti in high purity Si by ICP-QQQ
- Triple Quad ICP-MS/MS: illuminating the challenges in clinical analyses
- Silicon determination in diesel and biodiesel by MP-AES
- Cognac analysis using the Agilent 4100 MP-AES
- Determination of Cr, Ni, Pb and V in ethanol fuel by MP-AES
- Vegetable oil analysis for biodiesel production using the Agilent 4100 MP-AES
- Determination of main metals and contaminating elements in various high performance passivates by MP-AES
- Advances in liquid sample introduction in ICP-OES: a new efficient prototype for reduced sample consumption
- Determination of palladium content in Valacyclovir Hydrochloride using ICP-OES with AGM-1 (Auxiliary Gas Module)
- Bioimaging of rice tissue using LA-ICP-MS
- Lead isotope analysis: removal of ^{204}Hg isobaric interference from ^{204}Pb using ICP-QQQ
- Trace-level speciated analysis of Cr(III) and Cr(VI) using LC-ICP-MS

Request a copy of the posters at: **www.agilent.com/chem/wpc**

Conferences. Meetings. Seminars.

- **CIM Convention**, May 5-8, Toronto, Ontario, Canada, **www.cim.org/toronto2013**
- **Canadian Society for Chemistry Conference**, May 26-30, Quebec, Canada, **www.csc2013.ca**
- **ASMS**, June 9-14, Minneapolis, USA, **www.asms.org**
- **XXXVIII Colloquium Spectroscopicum Internationale**, June 16–20, Tromsø, Norway, **www.csi2013.net**
- **ICASS & Spectr'Atom Conference**, June 25-28, Mont Tremblant, Quebec, Canada, **www.csass.org/ICASS.html**
- **Metallomics 2013**, July 8-11, Oviedo, Spain, **www.metallomics2013.com**
- **Goldschmidt 2013**, August 25-30, Florence, Italy, **http://goldschmidt.info/2013**

Agilent ICP-MS Publications

To view and download the latest ICP-MS literature, please follow the links from **www.agilent.com/chem/atomicspec**

- **Application note:** Sulfur, phosphorus, silicon and chlorine analysis in NMP using the Agilent 8800 Triple Quadrupole ICP-MS, 5991-2303EN
- **Application note:** Accurate determination of sulfur in biodiesel using Isotope Dilution-Triple Quadrupole ICP-MS, 5991-2337EN
- **Advertorial:** Low-Level Analysis of Inorganic Arsenic in Apple Juice by LC-ICP-MS, 5991-2049EN

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