Inside this Issue

2-3  Analysis of Metals in Rock and Mineral Samples Reference Materials by ICP-MS

4  User article: Agilent Partners with RSSL to Create a New Atomic Spectroscopy Center of Excellence in the UK

5  User article: Analysis of Essential and Toxic Metals with Calibration in Synthetic Blood by ICP-MS

6-7  Determination of Cr(III) and Cr(VI) by LC-ICP-MS in Support of the Latest Toy Safety Regulations

7  Agilent Expands Pt Cone Trade-in Credit Program

8  Agilent Celebrates Success of 8800 ICP-QQQ with Shipment of 100th Unit: 8800 Wins 4th Major Industry Award; Agilent Events at 2014 Winter Plasma Conference; Conferences, Meetings, Seminars; Agilent ICP-MS Publications
Analysis of Metals in Rock and Mineral Samples by ICP-MS

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The analytical requirements of the geological survey and mining industries are extreme. Large numbers of rock samples must be crushed, pressed, fused or digested, and analyzed for many elements in a very short time and at low cost per sample. Most laboratories require the use of both ICP-OES and ICP-MS to meet the needs of their clients. But ideally, in the interest of productivity and cost control, a single analysis would be preferred. While ICP-MS is the only technique capable of measuring all of the required elements at trace levels, challenges arise due to the wide range of analyte concentrations, high acid concentration and high total dissolved solids (TDS) of rock digests.

Three key technologies of the Agilent 7700 ICP-MS are designed to improve both performance and speed for the analysis of complex, high matrix samples such as rock and mineral digests, as demonstrated here using the example of mineral certified reference materials (CRMs):

- Discrete sampling using Agilent’s Integrated Sample Introduction System (ISIS-DS). Discrete sampling minimizes exposure of the instrument to the sample by introducing sample only during the actual measurement period; the balance of the analytical cycle time is spent rinsing. Discrete sampling is also fast, since data acquisition is overlapped with the sample uptake and rinse steps for the neighboring samples. The uptake and rinse flows are offline and therefore independent of the requirements of the nebulizer and ICP-MS interface components.
- Aerosol dilution using the Agilent High Matrix Introduction (HMI) system. HMI uses fully automated optimization of plasma conditions, sample depth and aerosol dilution to significantly reduce matrix suppression and improve long term stability when analyzing high matrix samples.
- Helium collision mode (He mode) to reduce interferences and increase upper measurement limit for major elements.

Traditionally, minerals labs have used conventional, non-collision/reaction cell (CRC) technology for interference removal, preferring to rely on mathematical interference correction. The driving force behind this decision has been productivity. CRC modes that use reactive cell gases are not effective for simultaneous measurement of a large number of elements in complex matrices under a single set of cell conditions, and the need for multiple cell modes can add significant measurement time to the analysis. However, in contrast to reaction mode, He mode has the benefit of being universally effective against all polyatomic interferences, so the use of He mode adds only a small amount of additional time compared to no-gas methods. He mode has the added benefits of much better detection limits for interfered elements and higher analytical confidence particularly for variable sample matrices. He mode offers a further benefit of reducing the response for low mass, high concentration elements such as Na, K, Ca, Mg etc. by an order or magnitude or more, thereby effectively raising the upper linear range for these elements into the 1000s of ppm range. In this way, elements that would normally require the use of ICP-OES can be included in the ICP-MS run, significantly reducing the cost of analysis per sample.

While it is possible to use He mode for nearly the entire element list, doing so would increase the run time due to the slightly longer integration times used in He mode. Therefore only those elements that are subject to polyatomic interferences in typical mining samples were analyzed in He mode.

Instrumentation

An Agilent 7700x ICP-MS with standard nickel cones and MicroMist glass concentric nebulizer was used, together with the ISIS-DS for discrete sample introduction. The HMI system was operated in robust mode. He mode was employed to reduce polyatomic interferences, improving detection limits for several elements and completely eliminating the need for mathematical interference correction. A single, consistent He mode cell gas flow rate provides both effective interference removal and extended upper dynamic range for major elements such as Ca and Fe. No analyzer-specific optimization of any kind was required. Instrument conditions are shown in Table 1.

Method Validation

Six mineral CRMs (Table 2) were digested in quadruplicate and analyzed repeatedly under varying
conditions in order to evaluate and optimize the various components of the method. The method performance was verified as follows: A single initial calibration was performed, and a calibration check (CCV) and blank check (CCB) were automatically performed after every 20 samples. In total, 365 analyses were completed in 8 hours 49 minutes at an average time per sample of 87 seconds. Figures of merit including detection limits, recovery of certified values, long term stability, and washout of "sticky" elements such as Hg and Au were calculated. Full details can be found in Reference 1.

Table 2. Geological reference materials. The OREAS materials were purchased from Ore Research and Exploration, North Victoria, Australia. The ore grade and mid-range multi-element CRMs were provided by ALS Minerals, Vancouver Canada.

Results and Discussion

Table 3 includes acquisition method details and figures of merit including linearity and method detection limits (3σ, 10 replicates of a standard at near the estimated DL) calculated for the solutions as measured and in the original rock samples. Most elements were acquired in no-gas mode, i.e. with the cell unpressurized. He mode was used for the major elements Ca and Fe, and those elements (Ti, V, Cr, Ni, Cu, As and Se) which would normally require mathematical correction to correct for polyatomic interferences. Figure 1 shows example calibration curves for Se and Au.

Table 3. Analyte elements and isotopes, internal standards, cell mode, calibration linearity and method detection limits. "On instrument" detection limits are in the solutions as measured, "in sample" detection limits are corrected for initial sample weight and final volume and reflect the actual concentration in the undigested rock samples.

Conclusions

The Agilent 7700 ICP-MS with ISIS-DS can provide a single analytical technique which meets the extreme requirements of the geological survey and mining industries.

Reference

For a full account of the suitability of the 7700 Series ICP-MS for this application, including a full data set, see Agilent White Paper: Investigations into the use of helium collision mode and aerosol dilution for ultra-trace analysis of metals in mineral reference materials, publication number 5991-2811EN.

The publication is freely available from agilent.com/chem/icpms.
Agilent Partners with RSSL to Create a New Atomic Spectroscopy Center of Excellence

Alan Cross, Raimund Wahlen

RSSL, one of the UK’s foremost contract laboratories, recently unveiled the latest stage of its expansion with the opening of its new metals laboratory, and signing of a laboratory partnership agreement with Agilent.

The new laboratory is extremely well equipped, meaning that RSSL will be able to provide a better service in routine metals testing for a wide range of customers mainly from the food, drink and pharmaceutical industries. RSSL’s customer base also includes manufacturers and suppliers in the healthcare, personal hygiene and packaging sectors, and given its reputation for investigative work and problem solving, customers from other industries often call on RSSL’s analytical expertise to help with specific issues.

As a multi-disciplinary laboratory, RSSL can select from a range of techniques to address key commercial questions. This might mean providing analysis that helps manufacturers understand the factors that determine product performance, or that define the key characteristics of a product. It also means addressing issues of product safety, authenticity and contamination.

In the metals laboratory, the focus is largely on product safety, making sure that trace metal levels don’t exceed permitted limits, but there is also work in assessing and affirming levels of desirable elements in fortified foods and food supplements.

**Regulated Metals Analyses**

Within the pharmaceutical sector, metals are of concern due to their presence in mined excipients (TiO₂), biological tissues, production equipment (reactors, pipes etc) and their use as catalysts. Strict rules apply over the legal limits for metal contamination in pharmaceuticals, and the challenge is to find the best, most accurate, reliable and cost-effective methods of analysis. RSSL’s investment is geared up to the proposed implementation of General Chapters <232> and <233> of the US Pharmacopoeia, and the existing European Pharmacopoeia Chapters 2.4.20 and 5.20, which deal with the analysis of elemental impurities using modern spectroscopic methods.

In the case of food and drink, the basic principles of EU legislation on contaminants in food are contained in Regulation 315/93/EEC. Regulation EC 1881/2006 lays down maximum levels for certain contaminants in foodstuff, including lead, cadmium, mercury and inorganic tin. These metals can be present in foodstuffs as a result of their natural background levels in the environment, from human activities such as farming, industry or car exhausts, or from contamination during food processing and storage. On the other hand, certain trace metals are vital for human nutrition, and are often used in fortification of foods and in dietary supplements, so it is important to be able to give consumers accurate information about the content of these metals in the foods they purchase.

**Full Range of Atomic Spectroscopy Instrumentation**

The new Agilent instruments have been added to enhance RSSL’s current capabilities, and to address upcoming commercial challenges. The new instrumentation includes an Agilent 7700x ICP-MS, a 720 ICP-OES, a 240FS AAS, a 240Z GFAAS and a 4100 MP-AES. These five complementary technologies give RSSL options to quantify trace metal contamination in all kinds of matrices, with accuracy and efficiency not possible by wet-chemistry methods.

As a long time user of Agilent’s products, RSSL was always in favor of equipping the new lab with familiar and trusted technology, and the partnership arrangement was a suitable way to further strengthen this relationship. “From Agilent’s perspective, the new Atomic Spectroscopy lab at RSSL adds significant capabilities to the existing network of partner sites and the Centre of Excellence in Cheadle”, explains Rai Wahlen, Agilent Atomic Product Specialist. He added: “RSSL will also develop new techniques and applications for Agilent, benefiting from Agilent’s support and expertise, and both companies and their respective customers will benefit from this arrangement by being able to respond to the changing requirements of the latest regulations and market trends much more quickly.”

Given the wide customer base that RSSL works with, the partnership gives Agilent some insight into a wide range of ‘real-life’ commercial issues, on which to plan and test new developments, albeit that RSSL’s confidentiality agreements with customers inevitably mean specific ‘case data’ is withheld. As an established demonstration site for Agilent equipment, it also gives Agilent a vibrant, busy and relevant environment in which potential new customers can see its equipment in action.

“We see the arrangement working well for all parties,” says Alan Cross, Metals Scientist at RSSL. “There is potential for us to develop new methods for Agilent’s customers. Quite often, it is only when customers see the technology in use and are able to receive an explanation of the results from us, that they realise how beneficial all of these techniques might be in addressing the product development or product trouble-shooting issues that are holding back their business.”
Analysis of Essential and Toxic Metals with Calibration in Synthetic Blood by ICP-MS

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Introduction
The accurate determination of some metals in complex matrices like blood or urine can still be challenging by collision/reaction cell (CRC-)ICP-MS. Isotope dilution mass spectrometry (IDMS) is considered the most accurate method for total blood metals analyses, but it is relatively expensive, and cannot be applied easily to mono-isotopic metals such as Mn or As. Alternatively, the use of internal standards (ISTDs) can compensate for matrix effects by correcting the analyte response proportionally to measured changes in the ISTD response. However, unlike IDMS, differences in the chemical compositions of the calibration standards and blood solutions can still lead to analytical errors due to differences in ionization behavior of the ISTD in different matrices. In this work, we demonstrate that by matching the ionic strength of the calibration standards with that of the blood samples (matrix matching), the bias in the internal standard technique can be virtually eliminated resulting in improved accuracy and precision.

Our method uses a basic aqueous solution (containing n-butanol, NH₄OH, H₂EDTA and Triton X-100, spiked with ISTDs) which is a well-established and reliable diluent for blood samples. In addition, the calibration standards are prepared in the same solution with the addition of NaCl and CaCl₂ for matrix matching. The use of this synthetic matrix (SM) is much simpler and more reliable than the more common use of whole blood for the purpose of matrix matching.

Results and Discussion
As one of the reference laboratories for the Wisconsin State Laboratory of Hygiene (WSHL) Filter Paper Blood Lead Proficiency Testing Program (FPPTP), we analyze pooled whole blood specimens that WSLH will eventually use to prepare proficiency testing samples for filter paper blood lead spots. During the FPPTP June 2011 event, eleven of the sample solutions were analyzed twice; first with calibration standards that did not contain the SM (Figure 1(a)) and second with calibration standards in the SM (Figure 2(b)). Both sets of sample results were calculated using 5 different ISTDs.

When the SM calibration is used, near perfect agreement (slopes, intercepts and correlation coefficients) is observed between WSHL Pb means and measured results, using either ¹⁰³Rh, ¹⁸⁵Re, ¹⁹³Ir or ²⁰⁵Tl as the ISTD. Only a slight bias was observed when ⁷²Ge was used as the ISTD. Without the SM, the different ISTDs produced much more variation in the comparative plots.

Conclusions
Our study demonstrates that under matrix matched conditions a number of ISTDs are acceptable for a given analyte, regardless of first ionization potential or atomic mass. This approach eliminates the need for the use of multiple ISTDs to correct instrument run instabilities, and may potentially offer a universal technique to improve the accuracy of ICP-MS results for metal analyses in complex matrices.

Reference
For a full account of this application, see Agilent application note: 5991-2991EN

Disclaimer: Results and conclusions in this report are those of the authors and do not necessarily represent the views of the California Department of Public Health.
Determination of Cr(III) and Cr(VI) by LC-ICP-MS in Support of the Latest Toy Safety Regulations

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Chromium (Cr) has various oxidation states but normally exists as either trivalent Cr, Cr(III), or hexavalent Cr, Cr(VI). While Cr(III) is an essential trace nutrient for human health, Cr(VI) is well-known as a toxic substance. Cr(VI) is recognized as a human carcinogen and so the maximum contamination level of Cr(VI) is strictly regulated. For example, the European Union (EU) prohibits the use of Cr(VI) in electronic equipment under the Restriction of Hazardous Substances Directive (RoHS).

Similarly, the EU Toy Safety Directive (2009/48/EC) seeks to ensure the safety of children by minimizing their exposure to potentially hazardous or toxic toy products. The European Standard on the safety of toys (EN71) supports the requirements of EU Directive 2009/48/EC, and Part 3 of the Standard (EN71-3) covers the migration of certain elements from various categories of toy products, based on the assumption that toys may be chewed, sucked or swallowed. The most recent (2012) revision of EN71-3 came into force on 20 July 2013; since then all toys sold in the EU must comply with the revised Standard.

Toy materials and parts of toys are divided into three categories: Category I: Dry, brittle, powder-like or pliable materials; Category II: Liquid or sticky materials; Category III: Coatings and scraped-off materials. EN71-3 specifies migration limits for 17 elements: Aluminum, antimony, arsenic, barium, boron, cadmium, chromium, cobalt, copper, lead, manganese, mercury, nickel, selenium, strontium, tin (and organotin compounds), and zinc. Cr has separate migration limits for Cr(III) and Cr(VI) as detailed in Reference 1. Toy materials in Category II (liquid products that may be most easily swallowed) must meet the lowest limit of 5 ppb for Cr(VI). The sample preparation method specified in EN71-3 applies a total dilution factor of 500x. This means that the limit for Cr(VI) in the samples as measured is 10 ppt, so this application needs a very sensitive method for Cr species.

Experimental

The Agilent 7700x ICP-MS was connected to an Agilent 1260 Bioinert LC. Helium (He) mode was used to remove spectral interferences such as $^{40}\text{Ar}^{12}\text{C}$, $^{34}\text{S}^{16}\text{O}$, $^{37}\text{Cl}^{16}\text{O}$ and $^{35}\text{Cl}^{16}\text{O}$ that would interfere with the low level measurements of the Cr isotopes. He mode enables the 7700 to achieve the required low DL for the Cr species, and also allows independent optimization of the chromatographic method without having to compromise the chromatography to ensure that the Cr species peaks are resolved from peaks formed from carbon, sulfur and/or chlorine compounds. To measure the two Cr species, cationic Cr(III), which exists as [Cr(H2O)6]3+ in solution, is converted to the anion [Cr(EDTA)-]3 by chelation with EDTA. The two Cr species can then be effectively separated using an anion exchange column. Integrated method setup and sequence control of the combined LC-ICP-MS system was carried out from the ICP-MS MassHunter software. Full details of the method can be found in Reference 1.

Results and Discussion

Figure 1 shows overlaid chromatograms of the calibration standards and an inset of the Cr(VI) calibration plot. The chromatograms correspond to the calibration standards containing 5 ppt, 10 ppt, 20 ppt, 50 ppt and 100 ppt Cr(VI) and 10 times higher concentrations of Cr(III). The Cr species were completely resolved at retention times of 0.85 and 1.67 min. for Cr(III) and Cr(VI), respectively.

A summary of the method validation and analysis results of three toy materials is given in Table 1.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Cr(III) (μg/kg)</th>
<th>Cr(VI) (μg/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample 1</td>
<td>98.0 ± 4.2</td>
<td>111.2</td>
</tr>
<tr>
<td>Sample 2</td>
<td>97.2</td>
<td>98.1</td>
</tr>
<tr>
<td>Sample 3</td>
<td>102.7</td>
<td>96.2</td>
</tr>
</tbody>
</table>

Table 1: Summary of the method and analysis results

DL and MDL

Figure 2 shows overlaid chromatograms of 10 replicate analyses of the level 1 (lowest level) calibration standard: 50 ppt Cr(III) and 5 ppt Cr(VI). From the S/N of the chromatogram, Detection Limits (DLs) in solution were determined to be 3.1 and 2.0 ppt for Cr(III) and Cr(VI), respectively. Peak-to-peak noise was measured over the range shown in the figure, and DLs were calculated as the concentration giving S/N = 3. The DLs achieved are sufficiently...
To meet the requirements of EN71-3 for category 2 toy material, which has the lowest migration limit, Method Detection limits (MDLs) in the original sample material were also calculated from the 10 chromatograms. The MDLs were defined as concentration equivalent to 3σ of the quantified values of 10 analyses, (see Table 1).

Conclusions
A method has been developed using an Agilent 7700x ICP-MS connected to an Agilent 1260 Bio inert LC for the speciation of Cr (separation and determination of Cr(III) and Cr(VI)) in toy material, to comply with the new limits specified in EN71-3:2012. The European Standard EN71-3 supports the goals of the EU Toy Safety Directive 2009/48/EC, and requires the accurate determination of Cr(VI) at 10 ppt in the measured solution following sample preparation. The new LC-ICP-MS method was validated at single digit ppt DLs for both Cr species, meeting the performance required for the application.

Reference
1. Agilent application note: LC-ICP-MS method for the determination of trivalent and hexavalent chromium in toy materials to meet European regulation EN71-3:2012 Migration of certain elements, 5991-2878EN

The publication is freely available from agilent.com/chem/icpms.

Figure 2. 10 replicate chromatograms of level 1 standard: 50 ppt Cr(III) and 5 ppt Cr(VI)

Figure 1: Used platinum interface cones supplied by Agilent, Spectron or Glass Expansion can be returned for a trade-in credit.

Agilent Expands Pt Cone Trade-in Credit Program

Eric Vanclay
Supplies Product Manager, Agilent Technologies

Agilent has made two further enhancements to the platinum cone trade-in program:
1. Agilent ICP-MS users who purchase replacement platinum (Pt) interface cones from Agilent can now receive a trade-in credit for the return of used platinum cones originally purchased from Spectron or Glass Expansion.

2. Agilent is also now accepting used platinum torch shields for credit, as part of this program.

Agilent’s trade-in credit program:
• Delivers significant cost savings to your laboratory as the net purchase price for replacement platinum cones is reduced
• Helps to reduce environmental impact by reducing waste
• Conserves highly valuable platinum supplies.

How does the program work?
Agilent, Spectron and Glass Expansion platinum sampling and skimmer cones and platinum torch shields for the 7700/8800 and older 7500 Series ICP-MS are accepted. The value of the credit is based on the market value for platinum, and will be adjusted as platinum prices fluctuate.

This program covers North America, Western Europe, Australia, SE Asia, South Korea & Japan.

Learn more about saving money with Agilent’s trade-in credit program at agilent.com/chem/PtCone
Agilent Celebrates Success of 8800 with Shipment of 100th Unit

Team effort: Staff at Agilent’s Tokyo Analytical Division mark shipment of the 100th 8800 ICP-MS.

The 100th Agilent 8800 Triple Quadrupole ICP-MS was shipped from Agilent’s Hachioji site in Tokyo, Japan on August 7, 2013—less than 18 months from its release in April 2012.

As the 8800 team celebrated the shipment, factory manager Mitsuki Goto said: “We are extremely proud of having shipped 100 units—all trouble free! I think that is a real achievement which is down to excellent collaboration and communication between the development and factory-based teams.”

“We are proud that the 8800 has been so well accepted by so many customers so quickly,” commented Naoki Sugiyama, 8800 product manager. “As expected, 8800’s can be found in many high-tech companies like semiconductor and materials; but also many other industries such as environmental, food and life sciences have invested in the 8800 as it offers unique research and analysis capabilities.”

8800 Wins 4th Major Industry Award

The 8800 Triple Quadrupole ICP-MS was named as an R&D 100 Award winner in July 2013. These prestigious awards recognize the 100 most technologically significant products introduced into the marketplace over the past year. Other awards presented to the 8800 include SelectScience’s Scientists’ Choice Award, Instrument Business Outlook 2012 Product of the Show, and Chinese Analytical Industry ACCSI-Award.

This information is subject to change without notice.

Agilent Events at 2014 Winter Plasma Conference

Join us at the 2014 Winter Plasma Conference, January 6-11, in Amelia Island, Florida, US. We will again be holding several customer events including lunch seminars on our latest technology and a special customer evening event. For more information on the conference, please visit: http://icpinformation.org For more information on what Agilent will be doing at the show, please contact your local product specialist.

Conferences. Meetings. Seminars.

• RAFA 2013, Nov 5-8, Prague, Czech Republic, rafa2013.eu/
• AAPS Annual Meeting, Nov 10-14, San Antonio, TX, US, aaps.org/annualmeeting/
• EAS, Nov 18-20, Somerset, NJ, US, eas.org
• ISTERH, Nov 18-22, Tokyo, Japan, isterh2013.com/information/index.html
• ISRANALYTICA, Jan 8-9, Tel Aviv, Israel, bioforumconf.com/isranalytica14

Agilent ICP-MS Publications

• Title: Agilent 8800 ICP-QQQ Application Handbook
  Pub No.: 5991-2802EN
  The new 8800 ICP-QQQ Application Handbook features over 25 applications in semiconductor, environmental, materials, nuclear, life sciences and more.

  Printed copies are available on request although quantities are limited. Find out more at: agilent.com/chem/icpqqq-soar

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

• Application note: Analysis of selenoproteins in rat serum by Triple Quadrupole ICP-MS, 5991-2750EN
• Application note: Analysis of inorganic impurities in lubricating oils by ICP-MS, 5991-3263EN
• Application note: Analysis of trace metallic impurities in hydrocarbon fuels by ICP-MS, 5991-3264EN
• Application note: Determination of essential and toxic metals in blood by ICP-MS with calibration in synthetic matrix, 5991-2991EN
• Application note: Single particle analysis using the 7700x ICP-MS, 5991-2929EN
• Application note: Using ICP-MS and Mass Profiler Professional to determine the effect of storage temperature and packaging type on the trace metal composition of wine, 5991-2570EN
• Application note: LC-ICP-MS method for the determination of trivalent and hexavalent chromium in toy materials to meet European regulation EN71-3:2012 Migration limit, 5991-2878EN
• White paper: Investigations into the use of helium collision mode and aerosol dilution for analysis of metals in mineral reference materials, 5991-2811EN

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