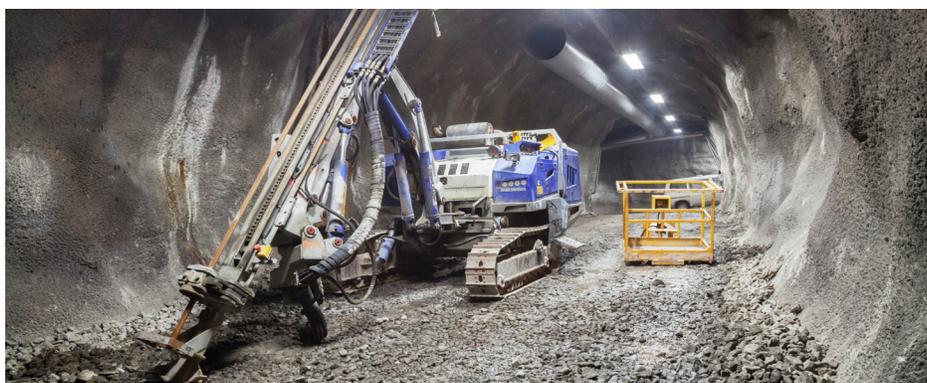**Agilent**

Trusted Answers

Ultra-Trace ICP-MS Analysis of Metals in Mineral Reference Materials

Measuring trace levels and higher concentrations of elements in acid digested geological samples.

Authors

Tetsushi Sakai
Agilent Technologies, Japan

Steve Wilbur
Agilent Technologies, Inc., USA

Introduction

The analytical requirements of the geological survey and mining industries are demanding in terms of high number of samples, number of elements, time/cost constraints and the difficult matrices. Depending on the range of elements and concentrations, some samples are analyzed twice, with higher concentration elements measured by ICP-OES (ICP-optical emission spectroscopy), and trace elements measured using ICP-MS. For such samples, a single analysis would improve productivity and lower cost per sample. While ICP-MS is the only technique capable of measuring all of the required elements at trace levels, the wide range of analyte concentrations, high acid concentration and high total dissolved solids (TDS) of rock digests are challenging for the technique.

The Agilent 7900 ICP-MS includes three key technologies designed to improve performance and speed for the analysis of complex, high matrix samples including:

1. 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; with the balance of the analytical cycle time spent rinsing. Discrete sampling is also fast, since data acquisition is overlapped with the sample uptake and rinse times, the flows of which are not dependent on limitations of the nebulizer or ICP-MS interface components.

2. Aerosol dilution using the Agilent Ultra High Matrix Introduction (UHMI) system. UHMI uses optimized plasma conditions, sample depth and aerosol dilution to significantly reduce matrix effects and improve long term stability when analyzing high matrix samples. UHMI system extends the aerosol dilution range up to a factor of 100, tolerating TDS levels of up to 25% (10 times higher than the previous generation HMI), a matrix level 100 times above the accepted limit for conventional ICP-MS systems [1].

3. The 4th generation Octopole Reaction System (ORS^4), operating in helium collision mode (He mode), is able to reduce interferences and increase dynamic range. Traditionally, minerals labs have not employed the use of 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 relying on reactive 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. Alternatively, He mode has the benefit over reaction mode of being universally effective against all polyatomic interferences. Therefore, the use of He mode as the only gas mode adds only a small amount of additional time compared to no-gas methods, with the added benefits of much better detection limits for interfered elements and higher analytical confidence.

He mode has the additional 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 requirement for slightly longer integration times when using He mode. Therefore only those elements that are subject to polyatomic interferences in typical mining samples were analyzed in He mode, including high energy He mode.

Experimental

Standards and samples

Standards were prepared from stock solutions into 3% HCl/2% HNO$_3$ diluted in ultrapure water. Standard elements are listed in Table 3. All calibration elements were present in each calibration level at the following concentrations; Hg and Au (0, 0.1, 1, 5, 10 ppb), Ca, Ti and Fe (0, 10, 100, 500, 1000, 5000 ppb), remaining elements (0, 1, 10, 50, 100, 500 ppb).

Samples consisted of the 6 milled geological Certified Reference Materials (CRMs) listed in Table 2. First, 20 mL 75% aquaregia (HCl:HNO$_3$:H$_2$O = 9:3:4) was added to 2 g of each CRM in PFA digestion bottles. After standing for 15-30 minutes, the bottles were placed on a hotplate and heated at 160-210 °C for 60 to 90 minutes. After cooling for about 15 mins, the samples were mixed, transferred to 50 mL polypropylene autosampler tubes, brought to 50 g total weight using deionized water and allowed to settle. The clear supernatant was analyzed directly without filtration. Each sample was prepared in 4 replicates. Two preparation blanks were prepared for each batch. Butanol (1%) was added via the online internal standard solution containing 100 μg/L Rh and Ir to all standards, samples and blanks. The addition of organic carbon has been shown to improve the detection limits for several critical elements including As, Se and Te. In addition, the butanol provides a low mass internal standard (carbon) which is normally unavailable in this analysis because the most common low mass internal standard, 6Li, may be present in mineral samples.

Table 1. Six geological reference materials (RM) were used. The OREAS materials were purchased from Ore Research and Exploration, Bayswater North, Victoria, Australia. The ore grade and mid-range multi-element CRMs were provided by ALS Minerals, Vancouver, BC, Canada.

Material	Description
OREAS 24b	Granodiorite lithogeochem/Blank
OREAS 501	Au-Cu-Mo-S ore RM
OREAS 502	Au-Cu-Mo-S ore RM
OREAS 902	Cu ore RM
OGGeo08	Ore grade multi-element CRM
MRGeo08	Mid-range multi-element CRM

Instrumentation

An Agilent 7900 ICP-MS with standard nickel cones, MicroMist glass concentric nebulizer, and UHMI system was used for all measurements. The Agilent 7900 was equipped with the Agilent Integrated Sample Introduction System (ISIS) configured for discrete sampling (DS). The UHMI system was operated in robust mode. The ORS[4] was operated in He mode to reduce polyatomic interferences, improving detection limits for several elements and completely eliminating the need for mathematical interference correction. It also extends the upper dynamic range for low mass elements such as Ca and Fe by reducing their response through ion scattering in the cell. Instrument conditions are shown in Tables 2a and 2b.

Table 2a. Instrument conditions used for all analyses.

Parameter	Setting
ICP-MS	
RF power (W)	1600
Sampling depth (mm)	10
Carrier gas flow (L/min)	0.80
Dilution gas flow (L/min)	0.25
Nebulizer pump (rps)	0.5
Spraychamber temp (°C)	2
Extract 1 (V)	-2
ISIS	
Load time (s)	5
Load speed (%)	40
Stabilization time (s)	8
Rinse time (s)	10
Rinse speed (%)	60
Acquisition	
Points per peak	1
Replicates	3
Sweeps/replicate	10
Total acquisition time (s)	49

Table 2b. Instrument conditions that differed for the different collision cell modes.

Parameter	No gas mode	He mode
ICP-MS		
Helium flow (mL/min)	0	4.3/10
Energy discrimination (V)	5	5/7

Results and discussion

Table 3 shows figures of merit including calibration linearity over the stated ranges as well as method detection limits (3σ, 10 replicates of a standard at near the estimated DL) for both the on-instrument solutions as well as the original rock samples. Some 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 that would normally require mathematical correction to control polyatomic interferences (Ti, V, Cr, Ni, Cu, As and Se).

Table 3. Analyte elements and isotopes, internal standards, cell mode, integration time and method detection limits (MDL).

Element	Isotope	Internal Standard	Cell mode	Integration time (s)	MDL (µg/L) on instrument[1]	MDL (µg/kg) in sample[2]
Li	7	[13]C	No gas	0.1	0.072	1.8
Be	9	[13]C	No gas	0.3	0.039	1.0
B	11	[13]C	No gas	0.1	0.796	20
Ca	44	[13]C	He	0.1	83.6	2089
Sc	45	[103]Rh	He	0.3	0.221	6
Ti	47	[103]Rh	He	0.1	2.0	51
V	51	[103]Rh	He	0.1	0.421	11
Cr	52	[103]Rh	He	0.1	0.481	12
Mn	55	[103]Rh	He	0.1	0.171	4
Fe	56	[103]Rh	He	0.1	1.0	26
Co	59	[103]Rh	He	0.1	0.054	1.3
Ni	60	[103]Rh	He	0.1	0.7	18
Cu	65	[103]Rh	He	0.1	0.484	12
Zn	66	[103]Rh	He	0.1	0.569	14
Ga	71	[103]Rh	No gas	0.1	0.159	4
Ge	74	[103]Rh	No gas	0.3	0.211	5
As	75	[103]Rh	He	0.3	0.073	2
Se	80	[103]Rh	He	1.0	0.264	7
Rb	85	[103]Rh	He	0.1	0.218	5
Sr	88	[103]Rh	He	0.1	0.076	1.9
Y	89	[103]Rh	He	0.2	0.018	0.5
Zr	90	[103]Rh	He	0.2	0.122	3.0
Nb	93	[103]Rh	He	0.3	0.006	0.1
Mo	95	[103]Rh	He	0.3	0.059	1
Ag	107	[103]Rh	He	0.3	0.033	0.8
Cd	111	[103]Rh	He	0.5	0.017	0.4
In	115	[103]Rh	He	0.3	0.012	0.3
Sn	118	[103]Rh	He	0.3	0.110	3
Sb	121	[103]Rh	He	0.3	0.106	3
Te	126	[103]Rh	He	0.5	0.093	2.3
Cs	133	[103]Rh	He	0.3	0.013	0.3
Ba	137	[103]Rh	He	0.1	0.085	2.1
La	139	[103]Rh	He	0.1	0.027	0.7
Ce	140	[103]Rh	He	0.1	0.018	0.4
Hf	178	[103]Rh	He	0.3	0.011	0.3
Ta	181	[193]Ir	He	1.0	0.001	0.04
W	182	[193]Ir	He	0.3	0.021	0.5
Re	185	[193]Ir	He	0.5	0.003	0.1
Au	197	[193]Ir	He	0.5	0.024	0.6
Hg	201	[193]Ir	He	0.5	0.050	1.3
Tl	205	[193]Ir	No gas	0.1	0.010	0
Pb	208	[193]Ir	No gas	0.1	0.063	1.6
Bi	209	[193]Ir	No gas	0.1	0.038	0.9
Th	232	[193]Ir	No gas	0.1	0.007	0.2
U	238	[193]Ir	No gas	0.1	0.010	0.3

1. *"On instrument" detection limits are in the solutions as measured.*

2. *"In sample" detection limits are corrected for initial sample weight and final volume and reflect the actual concentration in the undigested rock samples*

Internal standard recoveries

Three internal standard elements were chosen to match the analyte mass as closely as possible from among elements that are not commonly present in acid digests of geological samples. They were ^{13}C, [103]Rh and [193]Ir as indicated in Table 3. Internal standard recoveries relative to the initial calibration blank for the entire 6 hour sequence of rock digests are shown in Figure 1. Internal standard behavior across the mass range was very consistent and well within typical specifications used by the industry.

Figure 1. Internal standard recoveries over a 6 hour sequence of 240 analyses of rock digests.

Continuing Calibration Verification recoveries and precision

Calibration stability was checked after each 20 regular samples via the analysis of a continuing calibration verification (CCV) standard and a blank check (CCB). The CCV contained the trace elements at 100 ppb and Hg & Au at 10 ppb. CCV recoveries for a selection of analytes across the mass range which were measured periodically during the entire sequence are plotted in Figure 2. All CCV recoveries were within ± 20% of the prepared concentration.

Figure 2. CCV recoveries and precision (%RSD, n=13) for trace elements (all 100 ppb apart from 10 ppb for Hg and Au) over the 6 hour sequence.

Recoveries of CRM analyte elements

As an additional measure on long-term quantitative stability, recoveries of OGGeo08 and MRGeo08 CRM analyte elements were monitored over the sequence. The recoveries for the majority of elements are very close to certified values documenting excellent accuracy and interference removal (Table 4). The precision over the 37 replicate analyses of the sample during the 6 hour sequence was also good for the majority of elements (Table 4). Excellent accuracy and precision are evident for elements at low ppb concentrations up to 100s or 1000s of ppm.

Table 4. Mean concentration determinations, % recovery and measurement precision (%RSD, n=37) for all certified elements in OGGeo08 and MRGeo08 CRMs.

Isotope	OGGeo 08				MRGeo 08			
	Mean (µg/L)	RSD%	Certified values (µg/L)	Recovery %	Mean (µg/L)	RSD%	Certified values (µg/L)	Recovery %
[7]Li	989.1	3.8	1328	74.5	1110.2	7.4	1348	82.4
[9]Be	28.7	3.7	30	95.8	32.2	4.0	32	100.6
[44]Ca	384213.8	4.1	367700	104.5	467241.9	3.5	448000	104.3
[45]Sc	212.9	2.5	272	78.3	261.2	2.2	320	81.6
[47]Ti	110314.9	2.2	129440	85.2	143301.0	2.0	157960	90.7
[51]V	2872.9	2.4	3308	86.8	3803.9	1.9	4160	91.4
[52]Cr	2615.5	2.5	3360	77.8	3038.0	2.8	3760	80.8
[55]Mn	12869.7	2.7	16640	77.3	14500.1	2.5	17920	80.9
[56]Fe	1705500.1	2.3	2143960	79.5	1265282.6	2.3	1504680	84.1
[59]Co	3323.4	3.0	4000	83.1	681.2	1.8	780	87.3
[60]Ni	303528.9	2.1	338560	89.7	25968.6	2.1	27480	94.5
[65]Cu	295759.1	2.1	342200	86.4	23770.8	1.9	25920	91.7
[66]Zn	227420.3	2.3	284120	80.0	26826.8	2.1	31240	85.9
[71]Ga	294.8	2.8	360	81.9	345.8	2.1	404	85.6
[74]Ge	9.9	3.2	13.2	75.2	8.5	3.6	8.4	101.5
[75]As	4087.7	2.3	4840	84.5	1191.0	1.9	1288	92.5
[80]Se	372.8	2.5	440	84.7	35.8	2.8	48	74.5
[85]Rb	4278.5	2.3	5240	81.7	5325.0	1.8	5880	90.6
[88]Sr	2643.8	3.4	2752	96.1	3350.1	2.6	3360	99.7
[89]Y	608.2	2.9	708	85.9	753.7	2.1	844	89.3
[90]Zr	881.0	2.5	940	93.7	900.4	1.7	904	99.6
[95]Mo	34602.2	2.2	37400	92.5	572.6	1.6	584	98.0
[107]Ag	705.9	2.1	808.0	87.4	165.0	1.8	174.0	94.8
[111]Cd	703.8	2.2	776.0	90.7	82.0	1.8	90.0	91.1
[115]In	54.4	2.2	59.6	91.3	6.5	2.1	6.5	99.4
[118]Sn	477.5	2.4	552	86.5	128.6	2.0	140	91.9
[121]Sb	996.5	3.4	720.0	138.4	163.9	2.7	120.0	136.6
[126]Te	6.3	9.0	5.8	107.9	1.0	15.9	0.8	130.0
[133]Cs	361.0	5.3	388	93.0	434.3	4.9	440	98.7
[137]Ba	2273.3	4.7	3240	70.2	17644.9	4.0	17320	101.9
[139]La	1155.1	4.2	1192	96.9	1452.8	4.0	1428	101.7
[140]Ce	1707.1	3.5	2520	67.7	2107.0	3.2	3000	70.2
[178]Hf	36.1	4.4	32.8	110.1	34.8	4.3	30.8	113.1
[182]W	117.7	2.7	123.6	95.3	114.2	2.0	108.0	105.7
[185]Re	53.6	3.3	57.600	93.1	0.4	6.2	0.360	98.6
[197]Au	2.4	2.0	-	-	0.1	8.1	-	-
[201]Hg	17.3	2.3	19.29	89.6	2.4	5.1	-	-
[205]Tl	49.1	2.0	-	-	29.3	2.4	-	-
[208]Pb	261431.9	1.9	278920	93.7	39637.1	2.3	41600	95.3
[209]Bi	366.0	2.2	440	83.2	25.6	2.4	29	88.3
[232]Th	609.3	2.6	704	86.6	830.6	2.6	868	95.7
[238]U	175.7	2.6	200	87.8	207.3	2.8	220	94.2

Optimizing the washout protocol

Several typical analyte elements such as gold are critical at very trace levels, and are difficult to rinse out. A rinse solution composed of 3% HCl/2% HNO_3 + 20 mM thiourea was used in the autosampler flow-through rinse port, as well as for the discrete sampling carrier solution. Figure 3 shows a summary of percent carryover in ten blanks after the high calibration standard for all analyte elements. "Sticky" elements Sb, W, Au, Hg, Pb and Bi washed down to 0.1% or less by blank 2.
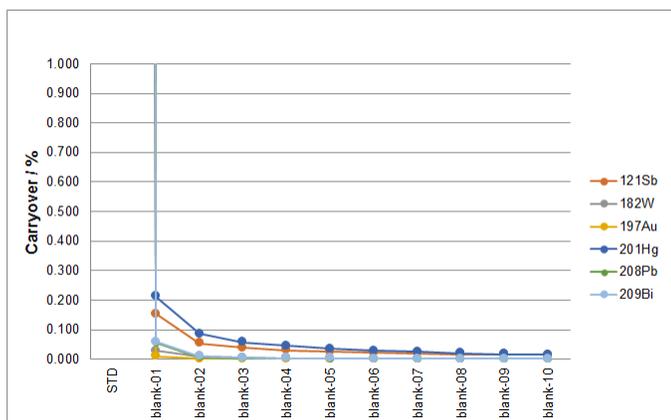
Figure 3. Carryover performance for "sticky" elements in the first blank after the high calibration standard.

Conclusions

In this study, 48 elements (3 internal standards and 45 analytes), were analyzed by ICP-MS in 90 sec per sample, with excellent stability over more than 6 hours.

UHMI and ISIS-DS provided unsurpassed matrix tolerance and minimal drift for long sequences of high TDS rock digests.

Using helium mode increased analytical confidence and lowered detection limits, while adding only a minimal amount of additional measurement time. Additionally, the use of He mode extended the dynamic range for low mass, high concentration elements into the 1000s of ppm range, allowing the analysis of these samples in a single measurement.

The analysis was simple and reliable, with detection limits in the low ppb range for the original ore samples. Excellent accuracy was demonstrated by the analysis of a range of mineral certified reference materials.

This study proved that the Agilent 7900 ICP-MS with UHMI and ISIS-DS was able to analyze acid digested geological samples, which have previously proven challenging for the technique. The instrument was used to determine both trace levels of some elements and higher concentrations of others in each geological sample, removing the need for a separate analysis by another technique. This will improve productivity and reduce the cost of analysis per sample.

References

1. Performance of the Agilent 7900 ICP-MS with UHMI for high salt matrix analysis, Agilent publication 2014, 5991-4257EN