Investigations into the use of helium collision mode and aerosol dilution for ultra-trace analysis of metals in mineral reference materials

White Paper

Mining

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Introduction

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 a very large number of elements in a very short time and at low cost per sample. Typically, samples are analyzed at least twice, depending on the range of elements and concentrations, with higher concentration elements being measured by ICP-OES (ICP-optical emission spectroscopy), and trace elements measured using ICP-MS. Alternatively, x-ray fluorescence spectroscopy can be used with prepared solid samples when trace detection limits are not required. Dedicated mercury analyzers, or graphite furnace AA instruments may also be employed for specific elements. 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, the wide range of analyte concentrations, high acid concentration and high total dissolved solids (TDS) of rock digests are challenging.

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In this work, several novel approaches to the ICP-MS analysis of mineral samples were combined and evaluated with the goal of measuring all relevant elements at typical concentrations in a single analytical run.

Three key technologies designed to improve the performance and speed of the Agilent 7700 ICP-MS when analyzing complex, high matrix samples were applied to the analysis of mineral certified reference materials (CRMs). They are:

- 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.

- Aerosol dilution using the Agilent High Matrix Introduction (HMI) system. The proprietary HMI technology uses optimized plasma conditions, sample depth and aerosol dilution to significantly reduce matrix effects and improve long term stability when analyzing high matrix samples.

- Helium collision mode (He mode) 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.

Experimental

Six mineral CRMs were digested in quadruplicate and analyzed repeatedly under varying conditions in order to evaluate and optimize the various components of the method. He mode parameters, internal standard selection, addition of butanol to increase the response of arsenic and selenium, and addition of thiourea to the rinse and carrier solutions to aid washout were all evaluated. The details of the optimized method are described below. The method performance was tested 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 resulting in an average time per analysis 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.

Instrumentation

An Agilent 7700x ICP-MS with standard nickel cones, MicroMist glass concentric nebulizer, and equipped with the Agilent Integrated Sample Introduction System (ISIS-DS) for discrete sample introduction was used. The HMI system was operated in robust mode. Helium collision 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 low mass elements such as Ca and Fe by reducing their response through ion scattering in the cell. Instrument conditions are shown in Table 1.

Table 1. Instrument conditions used for all analyses. Note that conditions are nearly identical in no-gas and helium modes.

Parameter	No gas mode	Helium mode
ICP-MS		
RF power (W)	1600	
Sample depth (mm)	10	
Carrier gas flow (L/min)	0.6	
Dilution gas flow (L/min)	0.55	
Nebulizer pump (rps)	0.5	
Spraychamber temp (°C)	2	
Extract 1 (V)	0	
Helium flow (mL/min)	0	4
Energy discrimination (V)	5	3.5
ISIS		
Load time (s)	10	
Load speed (rps)	0.5	
Stabilization time (s)	18	
Rinse time (s)	10	
Rinse speed (rps)	0.5	
Acquisition		
Points per peak	1	
Replicates	3	
Sweeps/replicate	10	
Integration time (s)	0.1 (most elements)	0.3 (most elements)
Total acquisition time (s)	43	

Standards and Samples

Standards were prepared from stock solutions diluted into 3% HCl/2% HNO$_3$ in ultrapure water. Standard elements are listed in Table 3. All calibration elements were present in each calibration level at the following concentrations; Hg (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 6 milled geological certified reference materials (Table 2).

A two gram sample of each CRM was digested in 20 mL of 75% aquaregia with gentle boiling for 60 minutes in PFA digestion bottles using a hot plate.

After cooling, the samples were transferred to 50 mL polypropylene autosampler tubes and brought to 50 g total weight and allowed to settle overnight.

The clear supernatant was analyzed directly without filtration. Each sample was prepared in 4 replicates.

Table 2. Six geological reference materials were used. 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.

CRM	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
MRGeoO8	Mid-Range Multi-Element CRM

Two preparation blanks were prepared for each batch. Butanol (1%) was added via the online internal standard solution, 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, [6]Li, may be present in mineral samples.

Results and Discussion

Table 3 includes several 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. 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 which would normally require mathematical correction to control polyatomic interferences (Ti, V, Cr, Ni, Cu, As and Se). Figures 1 and 2 show example calibration curves for a range of analytes. Figure 3 also demonstrates the efficiency of He mode at removing polyatomic interferences by comparing calibrations for several interfered elements in both no-gas and He mode.
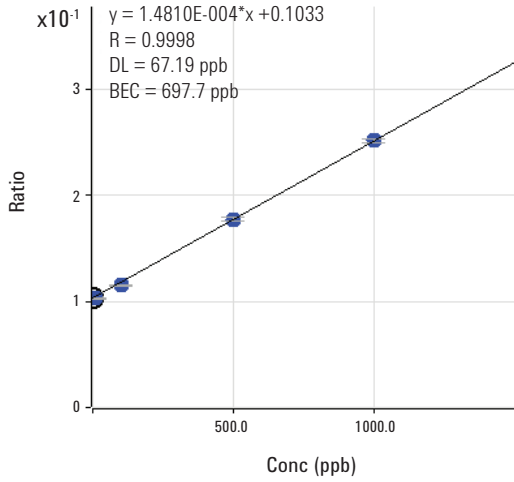
Internal standard recoveries
Three internal standard elements were chosen to match the analyte mass as closely as possible from among elements that are not commonly present in acid digests of geological samples. They were ^{13}C, [103]Rh and [193]Ir as indicated in Table 3.

Internal standard recoveries relative to the initial calibration blank for the entire 9 hour sequence of rock digests are shown in Figure 3.
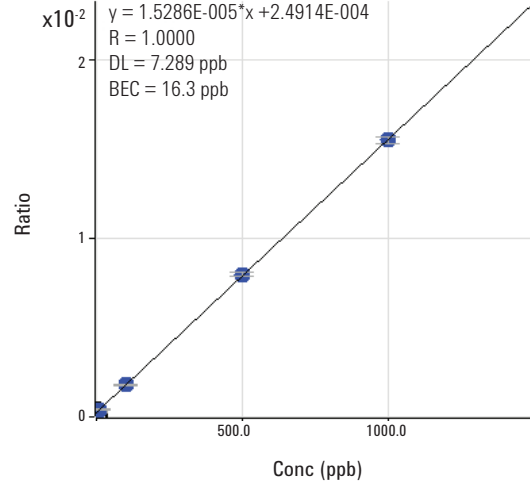
Table 3. Analyte elements and isotopes, internal standards, cell mode, calibration linearity and method detection limits. "On instrument" detection limits are in the solutions as measured, "in sample" detection limits are corrected for initial sample weight and final volume and reflect the actual concentration in the undigested rock samples.

Analyte element	Isotope	Internal Standard	Cell mode	Correlation coefficient (r)	MDL (µg/L) on instrument	MDL (µg/kg) in sample
Li	7	^{13}C	No gas	1.0000	0.2	5
Be	9	^{13}C	No gas	1.0000	0.2	5
B	11	^{13}C	No gas	1.0000	0.7	20
Ca	44	^{103}Rh	He	1.0000	40	1000
Sc	45	^{103}Rh	No gas	0.9999	0.3	7
Ti	47	^{103}Rh	He	0.9999	8	200
V	51	^{103}Rh	He	0.9999	0.5	13
Cr	52	^{103}Rh	He	1.0000	0.3	7
Mn	55	^{103}Rh	No gas	1.0000	0.1	3
Fe	56	^{103}Rh	He	1.0000	1	30
Co	59	^{103}Rh	No gas	1.0000	0.05	1.3
Ni	60	^{103}Rh	He	1.0000	0.4	10
Cu	63	^{103}Rh	He	1.0000	0.1	3
Zn	66	^{103}Rh	No gas	1.0000	0.4	10
Ga	71	^{103}Rh	No gas	1.0000	0.2	5
Ge	74	^{103}Rh	No gas	1.0000	0.2	5
As	75	^{103}Rh	He	1.0000	0.2	5
Se	78	^{103}Rh	He	1.0000	0.5	13
Rb	85	^{103}Rh	No gas	1.0000	0.04	1
Sr	88	^{103}Rh	No gas	1.0000	0.03	0.7
Y	89	^{103}Rh	No gas	1.0000	0.02	0.5
Zr	90	^{103}Rh	No gas	1.0000	0.08	1
Nb	93	^{103}Rh	No gas	1.0000	0.03	0.7
Mo	95	^{103}Rh	No gas	1.0000	0.2	5
Ag	109	^{103}Rh	No gas	1.0000	0.02	0.5
Cd	111	^{103}Rh	No gas	1.0000	0.04	1
In	115	^{103}Rh	No gas	1.0000	0.01	0.3
Sn	118	^{103}Rh	No gas	1.0000	0.06	1.5
Sb	121	^{103}Rh	No gas	1.0000	0.1	3
Te	125	^{103}Rh	No gas	1.0000	0.03	0.7
Cs	133	^{103}Rh	No gas	1.0000	0.03	0.7
Ba	138	^{103}Rh	No gas	1.0000	0.07	2
La	139	^{103}Rh	No gas	1.0000	0.02	0.5
Ce	140	^{103}Rh	No gas	1.0000	0.03	0.7
Hf	178	^{193}Ir	No gas	1.0000	0.04	1
Ta	181	^{193}Ir	No gas	1.0000	0.02	0.5
W	182	^{193}Ir	No gas	1.0000	0.05	1.3
Re	187	^{193}Ir	No gas	1.0000	0.003	0.7
Au	197	^{193}Ir	No gas	1.0000	0.02	0.5
Hg	201	^{193}Ir	No gas	0.9999	0.02	0.5
Tl	203	^{193}Ir	No gas	1.0000	0.07	2
Pb	208	^{193}Ir	No gas	1.0000	0.08	2
Bi	209	^{193}Ir	No gas	1.0000	0.02	0.5
Th	232	^{193}Ir	No gas	1.0000	0.02	0.5
U	238	^{193}Ir	No gas	1.0000	0.02	0.5

47 Ti [No gas] ISTD:103 Rh [No gas]

$x10^{-1}$ | y = 1.4810E-004*x +0.1033
R = 0.9998
DL = 67.19 ppb
BEC = 697.7 ppb

Ratio

Conc (ppb)

47 Ti [He] ISTD:103 Rh [He]

$x10^{-2}$ | y = 1.5286E-005*x +2.4914E-004
R = 1.0000
DL = 7.289 ppb
BEC = 16.3 ppb

Ratio

Conc (ppb)

51 V [No gas] ISTD:103 Rh [No gas]

$x10^{-1}$ | y = 0.0022*x +0.3294
R = 0.9993
DL = 38.02 ppb
BEC = 178 ppb

Ratio

Conc (ppb)

51 V [He] ISTD:103 Rh [He]

$x10^{-2}$ | y = 5.5098E-004*x +0.0021
R = 1.0000
DL = 0.5337 ppb
BEC = 3.807 ppb

Ratio

Conc (ppb)

52 Cr [No gas] ISTD:103 Rh [No gas]

y = 0.0023*x +1.2047
R = 0.9899
DL = 32.74 ppb
BEC = 514.3 ppb

Ratio

Conc (ppb)

52 Cr [He] ISTD:103 Rh [He]

$x10^{-1}$ | y = 7.4947E-004*x +0.0022
R = 1.0000
DL = 0.6439 ppb
BEC = 2.986 ppb

Ratio

Conc (ppb)
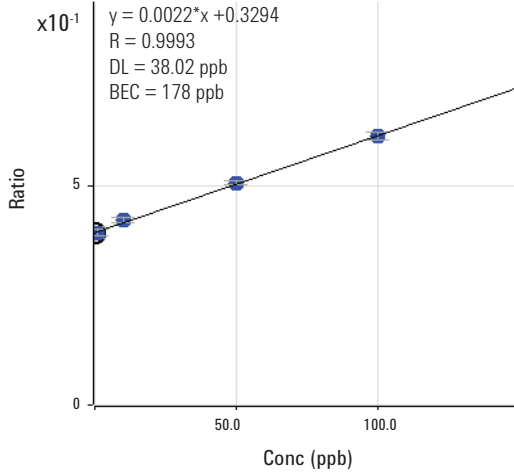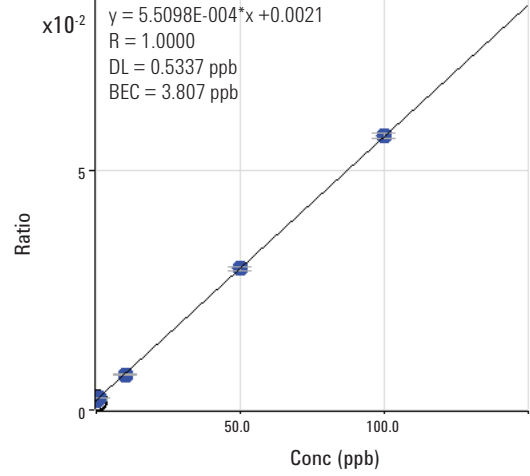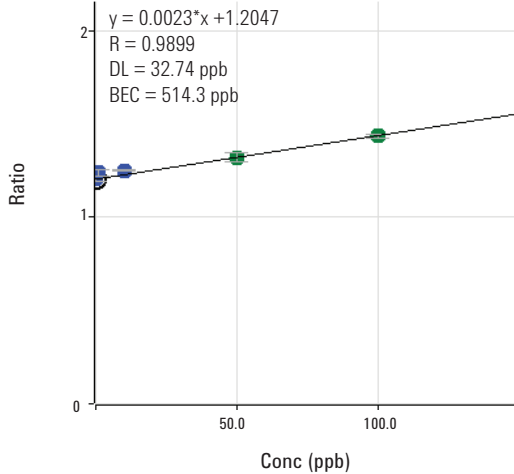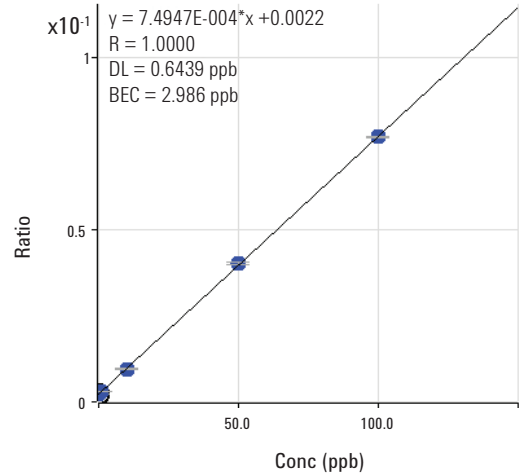
Figure 1. Comparative calibration curves for Ti, V and Cr in no-gas mode (left) and He mode (right). The effectiveness of helium mode at removing common polyatomic interferences from P, Cl and C is evident in the significantly lower BECs and DLs on the right.
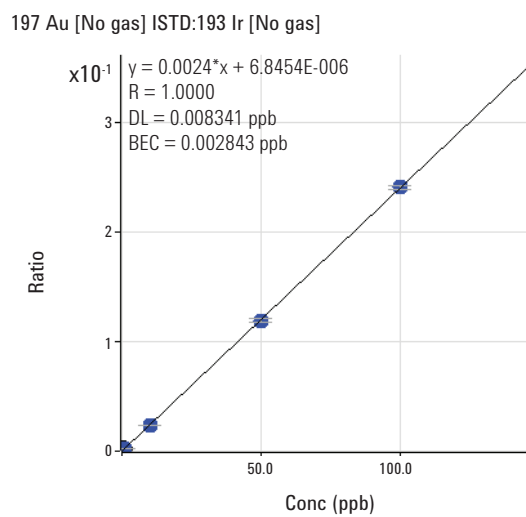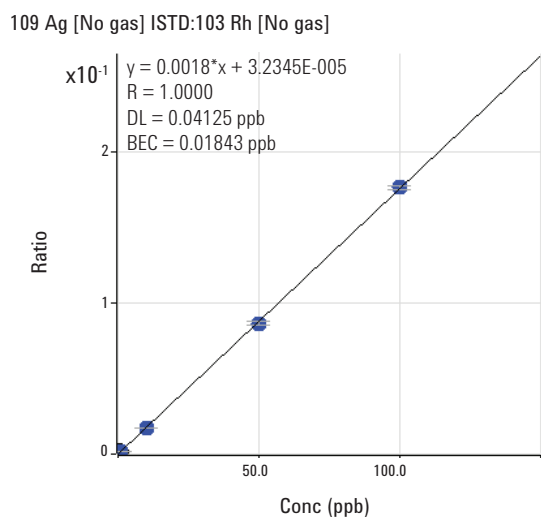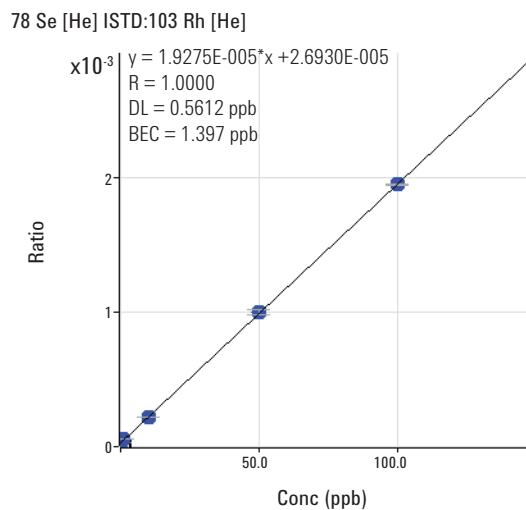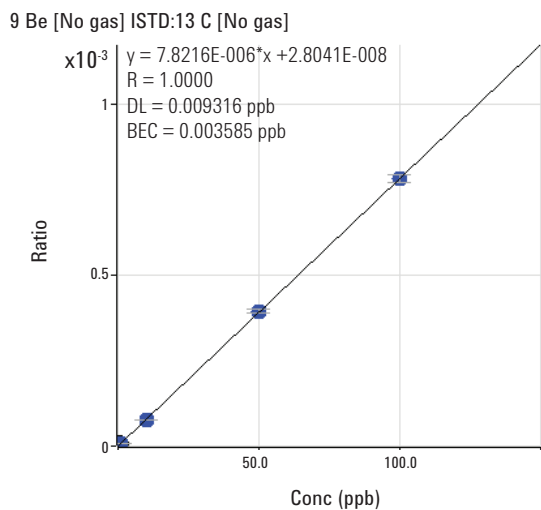
9 Be [No gas] ISTD:13 C [No gas]

x10⁻³

y = 7.8216E-006*x +2.8041E-008
R = 1.0000
DL = 0.009316 ppb
BEC = 0.003585 ppb

Ratio

Conc (ppb)

78 Se [He] ISTD:103 Rh [He]

x10⁻³

y = 1.9275E-005*x +2.6930E-005
R = 1.0000
DL = 0.5612 ppb
BEC = 1.397 ppb

Ratio

Conc (ppb)

109 Ag [No gas] ISTD:103 Rh [No gas]

x10⁻¹

y = 0.0018*x + 3.2345E-005
R = 1.0000
DL = 0.04125 ppb
BEC = 0.01843 ppb

Ratio

Conc (ppb)

197 Au [No gas] ISTD:193 Ir [No gas]

x10⁻¹

y = 0.0024*x + 6.8454E-006
R = 1.0000
DL = 0.008341 ppb
BEC = 0.002843 ppb

Ratio

Conc (ppb)

Figure 2. Calibration curves for representative elements across the mass range

- 13 C (ISTD) [No Gas]
- 103 Rh (ISTD) [No Gas]
- 103 Rh (ISTD) [He]
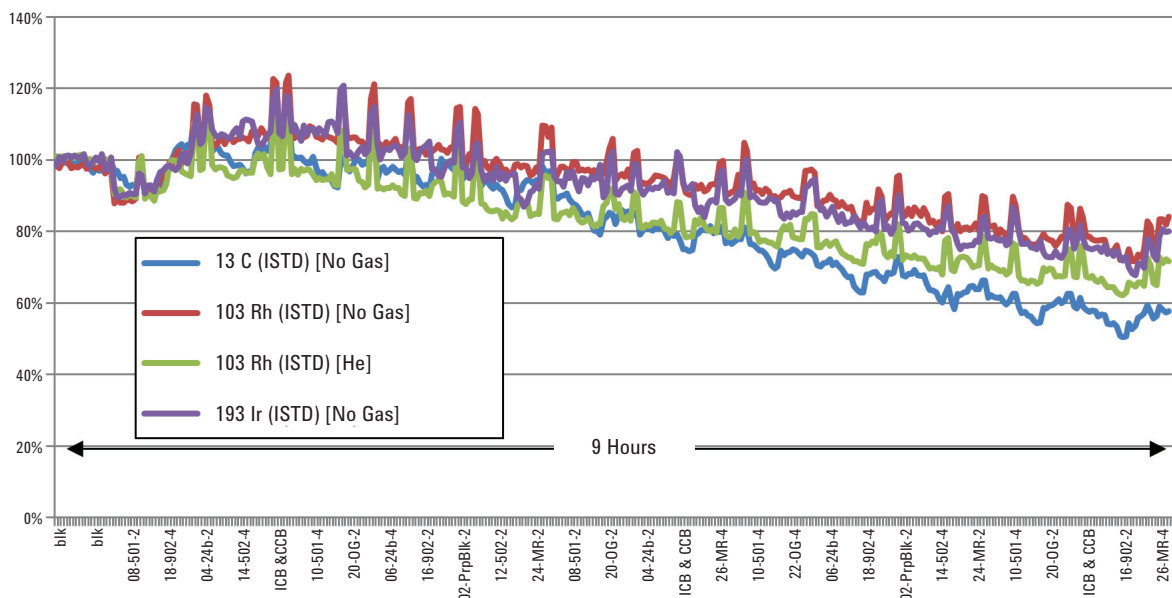- 193 Ir (ISTD) [No Gas]

9 Hours

Figure 3. Internal standard recoveries over a 9 hour sequence of 365 analyses of rock digests

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Internal standard behavior across the mass range was very consistent and downward drift was well within typical specifications used by the industry. Figure 4 shows the skimmer cone after completion of the 9 hour sequence. Very little material has accumulated on the cone surface, and the orifice remains completely unblocked.
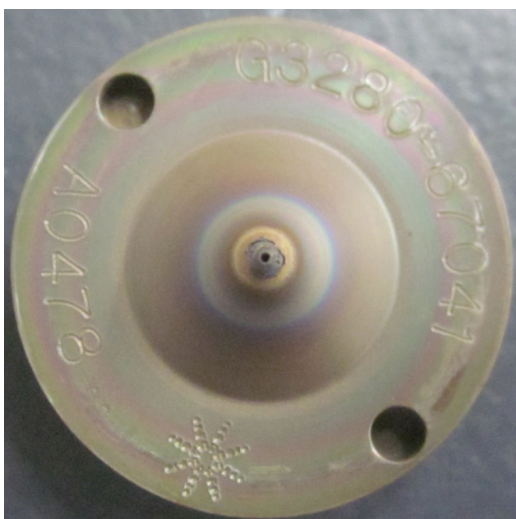
Figure 4. Skimmer cone after 9 hour sequence of minerals digests. Orifice opening is unchanged from original condition.

### 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 at 10 ppb. Table 4 displays the mean concentration and % relative standard deviation of the 16 replicate CCV measurements for the trace elements. Excellent calibration stability for low mass through high mass elements measured in both no gas and He modes is evident.

Recoveries of CRM analyte elements

As an additional measure on long term quantitative stability, recoveries of CRM analyte elements were monitored over the sequence. Plots of representative elements over the mass range comparing measured value versus certified value for OGGeo08 are shown in Figure 5. Not only are the recoveries very close to certified values documenting excellent accuracy and interference removal, but the precision over the 12 replicate analyses of the sample during the 9 hour sequence is excellent, as shown in Table 5.   Excellent accuracy and precision are evident for elements at concentrations of a few ppb (Te 7.35 ppb), to 100s or 1000s of ppm (Ca, Fe, Ni, Cu, Zn etc.).

Table 4. Continuing Calibration Verification (CCV) recoveries and precision (%RSD, n=16) for trace elements over the 9 hour sequence. Actual concentration is 100 ppb, 10 ppb for Hg.

Analyte	Mean (ppb)	%RSD
7 Li [No Gas]	94.71	4.8%
9 Be [No Gas]	95.23	4.6%
11 B [No Gas]	102.83	4.3%
45 Sc [No Gas]	107.20	3.6%
51 V [He]	115.85	6.7%
52 Cr [He]	116.99	7.1%
55 Mn [No Gas]	124.69	3.8%
59 Co [No Gas]	104.03	7.6%
71 Ga [No Gas]	102.39	1.3%
74 Ge [No Gas]	100.93	1.5%
75 As [He]	113.39	10.1%
78 Se [He]	91.85	6.2%
85 Rb [No Gas]	113.07	3.5%
88 Sr [No Gas]	114.11	3.4%
89 Y [No Gas]	111.51	2.8%
90 Zr [No Gas]	107.03	2.6%
93 Nb [No Gas]	103.25	1.5%
109 Ag [No Gas]	101.76	1.2%
111 Cd [No Gas]	102.78	1.5%
115 In [No Gas]	107.12	1.9%
118 Sn [No Gas]	105.38	2.6%
121 Sb [No Gas]	104.10	2.7%
125 Te [No Gas]	104.16	1.7%
133 Cs [No Gas]	110.63	3.2%
138 Ba [No Gas]	120.07	4.9%
139 La [No Gas]	109.30	2.8%
140 Ce [No Gas]	108.53	2.6%
178 Hf [No Gas]	107.26	1.7%
181 Ta [No Gas]	101.69	1.8%
182 W [No Gas]	105.93	1.5%
187 Re [No Gas]	104.27	1.1%
197 Au [No Gas]	100.64	1.3%
201 Hg [No Gas]	9.74	1.5%
203 Tl [No Gas]	100.14	1.2%
209 Bi [No Gas]	100.28	1.3%
232 Th [No Gas]	99.71	1.9%
238 U [No Gas]	98.59	2.2%
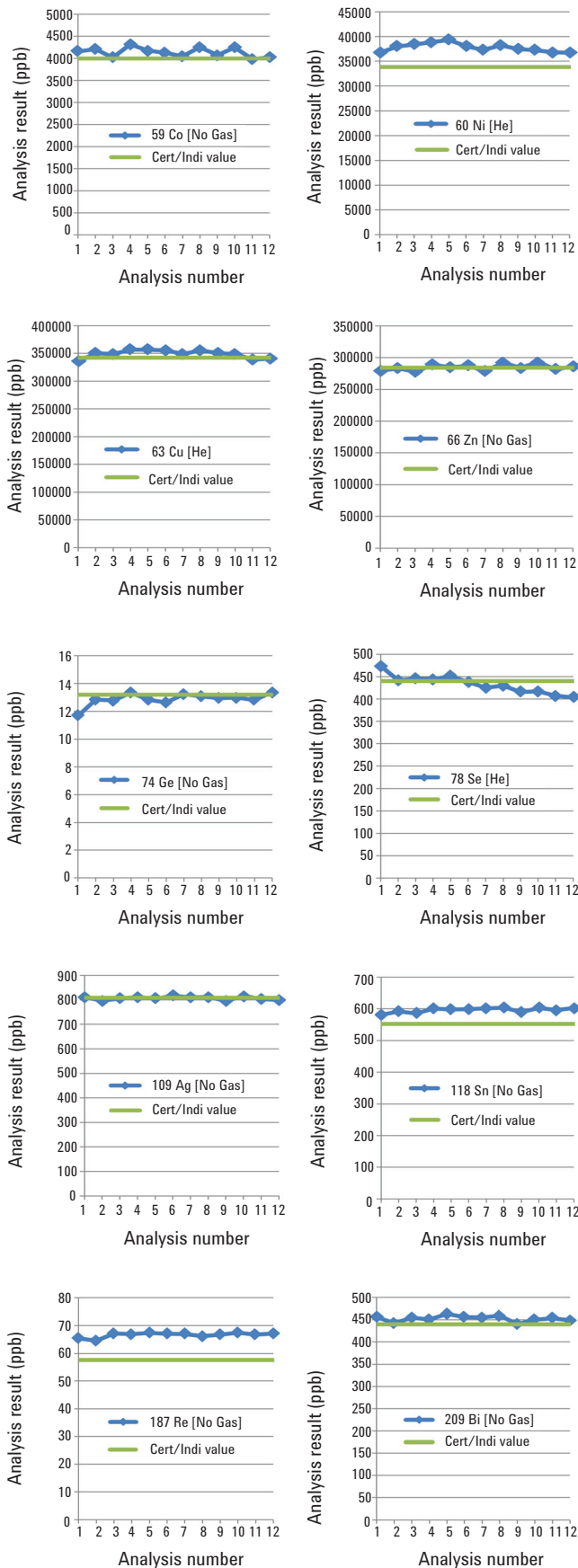
Figure 5. Comparison of measured value versus certified value for Co, Ni, Cu, Zn, Ge, Se, Ag, Sn, Re and Bi in OGGeo08.

Table 5. Mean concentration determinations and measurement precision (%RSD, n=12) for all certified elements in OGGeo08.

| Element	Mean value (ppb) n=12	%RSD
7 Li	1195.99	3.9%
9 Be	42.77	5.0%
11 B	190.79	4.1%
44 Ca	359661.45	6.3%
45 Sc	345.68	3.3%
47 Ti	150845.34	7.1%
51 V	3815.57	5.3%
52 Cr	3993.09	6.0%
55 Mn	19389.68	2.1%
56 Fe	2367665.55	3.2%
59 Co	4137.04	2.6%
60 Ni	377680.94	2.2%
63 Cu	348886.52	2.0%
66 Zn	284681.31	1.7%
71 Ga	422.64	1.1%
74 Ge	12.88	3.4%
75 As	5280.55	2.8%
78 Se	432.98	4.7%
85 Rb	5702.13	5.5%
88 Sr	4536.99	5.6%
89 Y	895.66	5.4%
90 Zr	1333.75	5.1%
93 Nb	23.79	2.5%
95 Mo	42460.95	3.3%
109 Ag	807.02	0.9%
111 Cd	857.45	0.8%
115 In	64.33	1.4%
118 Sn	596.05	1.2%
121 Sb	561.37	1.8%
125 Te	7.35	2.0%
133 Cs	437.15	5.3%
138 Ba	1024.20	6.2%
139 La	1452.83	6.1%
140 Ce	2991.75	5.3%
178 Hf	46.80	1.9%
197 Au	3.04	2.6%

Optimizing the washout protocol

Washout was also evaluated, because several key analyte elements such as gold are present at very trace levels, and are difficult to rinse out. Several washout schemes were tested to determine the protocol that resulted in the fastest return to baseline concentrations after analysis of a high concentration standard. The optimum protocol used a rinse solution composed of 3% HCl/2% HNO_3 + 20 mM thiourea which was used in the autosampler flow-through rinse port as well as for the discrete sampling carrier solution.

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Carryover %, (blank after high std)/(high std)
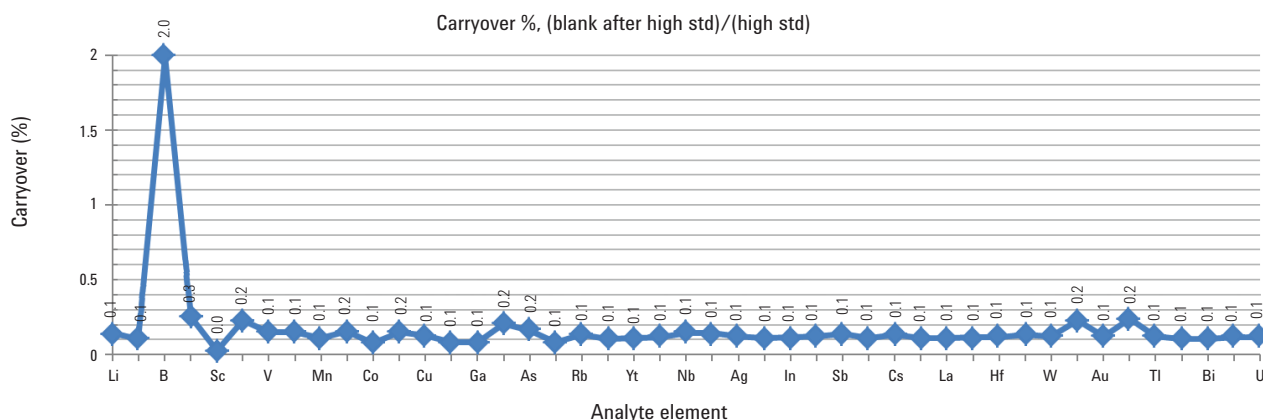
Figure 6. Percent carryover for all analyte elements in the first blank after the high calibration standard.

Figure 6 shows a summary of percent carryover in the first blank after the high calibration standard for all analyte elements. Critical elements Au, Ag, Hg, and Tl washed down to 0.1% or less. Only B demonstrated evidence of significant carryover due to its volatility in acid solutions. However, the level returned to baseline in the subsequent blank. Figure 7 shows a detailed view of Au washout in concentration (ppb) after analysis of a 500 ppb standard.

Gold washout profile after 500 ppb calibration standard
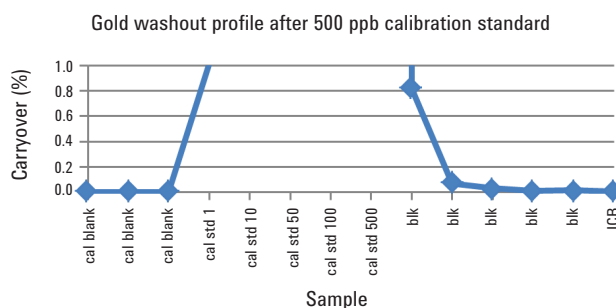
Figure 7. Gold washout profile after analysis of a multi-element standard containing 500 ppb Au.

Conclusions

The Agilent 7700x ICP-MS with ISIS-DS discrete sampling is well suited to high productivity analysis of acid digested geological samples.

- Analysis of 47 elements (3 internal standards and 44 analytes) including several elements normally relegated to ICP-OES due to high concentrations can be achieved in under a minute and a half per sample with excellent stability over more than 9 hours.

- Proprietary HMI system and ISIS discrete sampling provide unsurpassed matrix tolerance and minimum drift for long sequences of high TDS rock digests.

- Helium mode eliminates the need for unreliable mathematical corrections for interfered elements, increasing analytical confidence and lowering detection limits while adding only a small amount of additional measurement time. Additionally the use of He mode can extend the dynamic range for low mass, high concentration elements into the 1000s of ppm range, thereby eliminating the need for ICP-OES determination for these elements.

The analysis is simple and reliable, not requiring complex third party sample introduction systems, or unreliable mathematical interference correction. Detection limits are low ppb in the original ore samples and accuracy as demonstrated by the analysis of a range of mineral certified reference materials is excellent. High concentration elements which are normally relegated to analysis by ICP-OES can be included in the ICP-MS analysis, possibly eliminating the requirement for a separate analysis. As a result, 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.

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