Ultra High Throughput Analysis of Mineral Digests Using a Novel, Multi-Loop Sample Introduction System with ICP-MS (PC 094)

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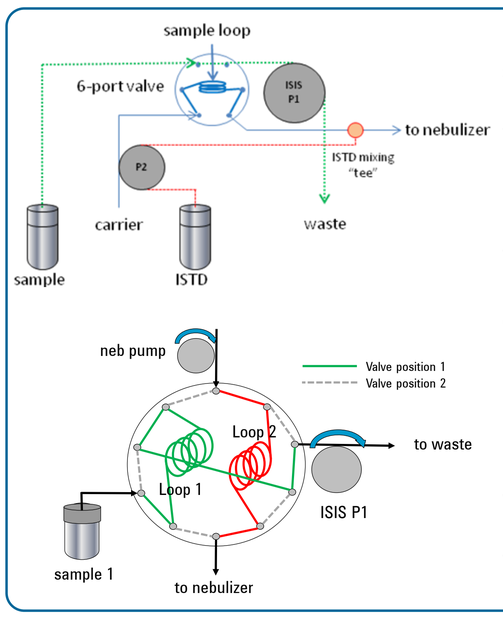
Ultra High Throughput ICP-MS *the next frontier*

In a typical ICP-MS sample analysis, total analysis time per sample is the sum of several serial steps including autosampler movement, sample uptake and stabilization, data acquisition, sample rinseout and data analysis. For many applications including those in the geological environmental and clinical industries, the actual data acquisition is a small fraction of the total analysis time, often as short as 15 seconds or even less for a multi-element scan. In recent years, much work has been done to improve the throughput of ICP-MS for these applications, by eliminating or minimizing some of these pre and post measurement steps mainly through the use of discrete sampling. However typical discrete sampling using a 6 port valve and single, low volume sample loop cannot completely eliminate non-acquisition overhead. By designing a discrete sampling system with multiple sample loops, it is possible in some cases to virtually eliminate wasted time between analyses by overlapping the entire sample handling overhead with the simultaneous measurement of the previous sample. A sequence analysis therefore consists of back to back data acquisition of subsequent samples with almost no non-measurement overhead.

Analytical System Configuration



Conventional discrete sampling configuration (upper left) still suffers from time required to load and rinse the loop and then transport the sample from the loop to the nebulizer.

2-loop, 10 port valve configuration (lower left) eliminates most non-acquisition overhead by performing most tasks associated with sample handling during the analysis of the previous sample.

Conventional (non DS) sample uptake and analysis

Uptake	Stabilization	Acquisition	Rinseout	Autosampler Overhead

5-6 minutes or more (~2.5 ml sample to nebulizer)

Typical discrete sampling analysis (single loop)

Uptake	Stabilization	Acquisition	Rinseout	Autosampler Overhead

< 2 mins (~0.2 ml sample to neb)

Ultra high throughput discrete sampling analysis (2 loops)

Sample 2 handling	<< 1 min	Acquisition 1	Acquisition 2	<< 1 min	Sample 3 handling...

Figure 1 Comparison of conventional and discrete sampling configurations

Method Development and Validation

Since no commercial 10 port valve, 2 sample loop system is available for the Agilent 7000 Series ICP-MS, a prototype system was built using a standard Valco Cheminert 10 port valve and a Gilson peristaltic pump. Control software was written using Microsoft® Visual Basic which communicated with the Cetac ASX 520 autosampler, the 10 port valve and the Agilent 7700x ICP-MS via a CK1104 - 4-Port USB Relay Controller with 6-Channel Analog/Digital I/O Interface (canakit.com). The prototype device and VB user interface are pictured in figure 2.

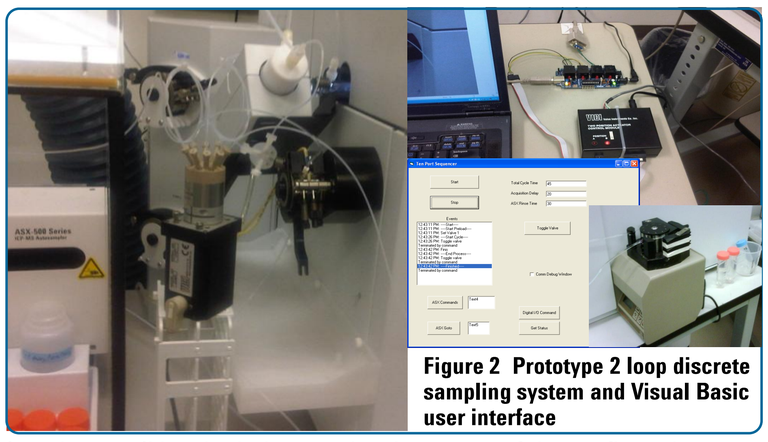


Figure 2 Prototype 2 loop discrete sampling system and Visual Basic user interface

In order to validate both the speed and accuracy of the configuration, a sequence of digested mineral samples was analyzed along with typical quality control samples and calibration checks (Figure 3).

5 point calibration
0 – 50 ppb for trace elements
0 – 20 ppm for mineral elements (Na, Mg, Al, P, K, Ca and Fe)

Memory Check Block (2 successive calibration blanks)

Initial QC Block (NIST 1643, 50 ppb CCV, 2 CCB blanks, digestion blank)

Sample Block (digested rock samples in duplicate and digestion blank)

Periodic QC Block (CCV, CCB, digestion blank)

Figure 3 Analytical validation sequence

In total, 58 isotopes were acquired resulting in a total integration time of 23.4 seconds per sample. A single point per peak was acquired and all elements were measured in helium collision mode to eliminate the potential of matrix based polyatomic interferences. Representative calibration curves are displayed in figure 4 below.

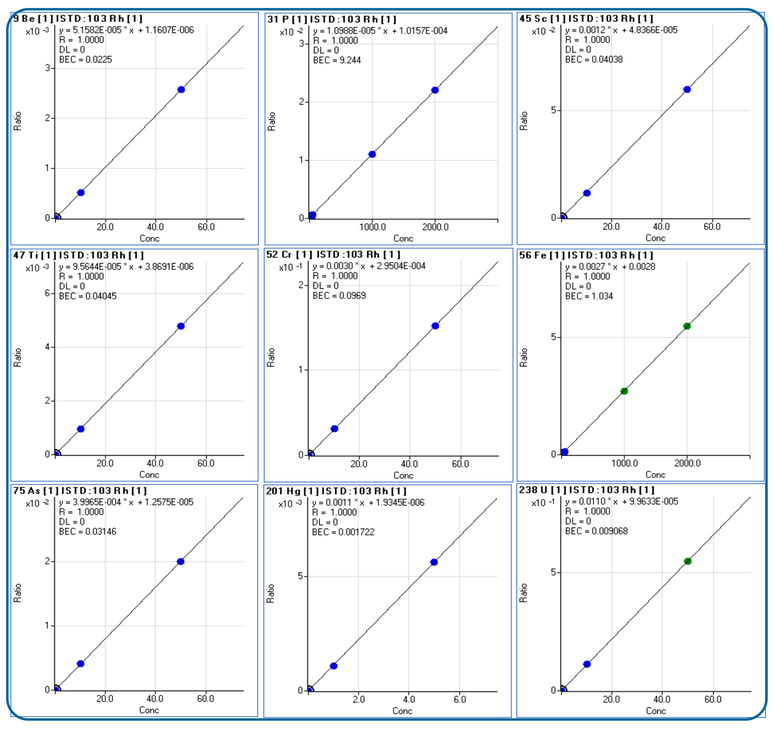


Figure 4 Representative calibration curves for elements ranging from Be to Pb – All elements' calibration data below

Element	Mass	R	BEC	Units	Element	Mass	R	BEC	Units
Li	7	1.0000	0.0537	ppb	Cd	111	0.9999	0.0129	ppb
Be	9	1.0000	0.0225	ppb	Sn	118	1.0000	0.1606	ppb
Na	23	1.0000	26.8943	ppb	Sb	121	0.9999	0.0252	ppb
Mg	24	1.0000	2.8398	ppb	Te	125	1.0000	0.0157	ppb
Al	27	1.0000	2.7277	ppb	Cs	133	1.0000	0.0080	ppb
P	31	1.0000	9.2435	ppb	Ba	137	1.0000	0.0390	ppb
K	39	1.0000	61.3057	ppb	La	139	1.0000	0.0082	ppb
Ca	44	0.9997	29.5115	ppb	Ce	140	1.0000	0.0071	ppb
Sc	45	1.0000	0.0404	ppb	Pr	141	1.0000	0.0100	ppb
Ti	47	1.0000	0.0405	ppb	Nd	146	1.0000	0.0133	ppb
V	51	1.0000	0.0769	ppb	Sm	147	1.0000	0.0098	ppb
Cr	52	1.0000	0.0969	ppb	Eu	153	1.0000	0.0076	ppb
Mn	55	1.0000	0.0814	ppb	Gd	157	1.0000	0.0051	ppb
Fe	56	1.0000	1.0343	ppb	Dy	163	1.0000	0.0093	ppb
Co	59	1.0000	0.0127	ppb	Ho	165	1.0000	0.0081	ppb
Ni	60	1.0000	0.1787	ppb	Er	166	1.0000	0.0098	ppb
Cu	63	1.0000	0.1745	ppb	Tm	169	1.0000	0.0081	ppb
Zn	66	1.0000	0.4694	ppb	Yb	172	1.0000	0.0055	ppb
Ga	71	1.0000	0.0177	ppb	Hf	178	1.0000	0.0111	ppb
Ge	72	1.0000	0.0496	ppb	Ta	181	1.0000	0.0093	ppb
As	75	1.0000	0.0315	ppb	W	182	1.0000	0.0133	ppb
Se	78	1.0000	0.1769	ppb	Hg	201	1.0000	0.0017	ppb
Rb	85	0.9999	0.0104	ppb	Pb	206	1.0000	0.0327	ppb
Sr	88	1.0000	0.0305	ppb	Pb	207	1.0000	0.0280	ppb
Y	89	1.0000	0.0049	ppb	Pb	208	1.0000	0.0284	ppb
Zr	90	1.0000	0.0408	ppb	Bi	209	1.0000	0.0491	ppb
Nb	93	1.0000	0.0095	ppb	Th	232	1.0000	0.0249	ppb
Mo	95	1.0000	0.0186	ppb	U	238	1.0000	0.0091	ppb
Ag	107	1.0000	0.0094	ppb	Rh	103	ISTD	N/A	N/A

Table 1 Calibration Linearity as R, and Background Equivalent Concentration for All 58 analyte elements

Analytical Performance

Sample Analysis Time The actual sample to sample time for this method as tested was 50 seconds per sample.
Long Term Stability Long term stability as measured by internal standard recoveries (Figure 5) was excellent, displaying no measurable drift.

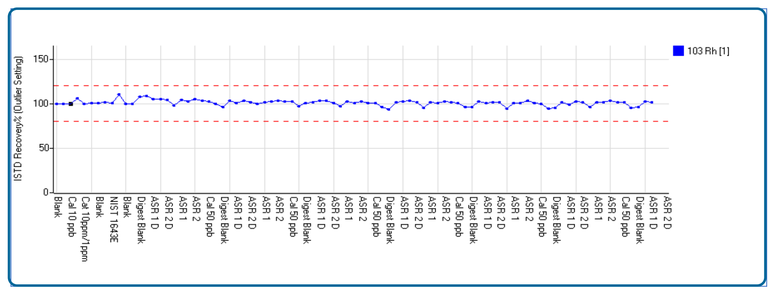


Figure 5 Internal standard recoveries for entire 89 sample sequence

In addition, **CCV checks** over the course of the sequence showed excellent recovery and precision. Figure 6 shows a plot of the measured values for all trace elements (50 ppb except for Hg at 5 ppb). CCV precision (n=7) for all measured trace elements was typically less than 2% RSD over the entire sequence.

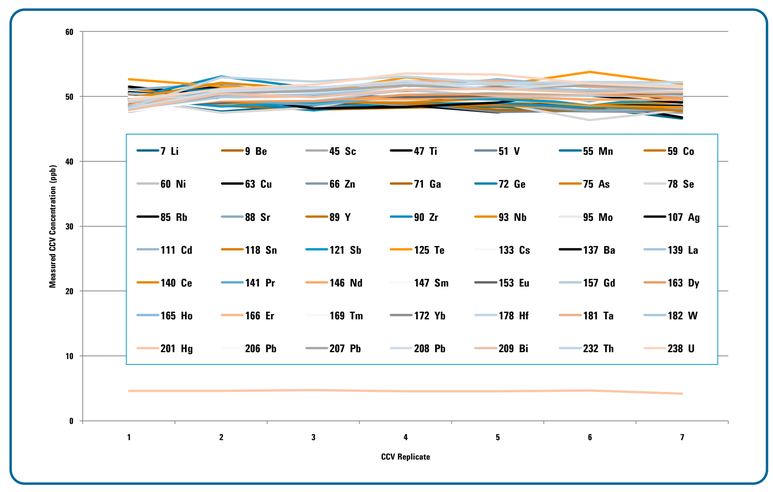


Figure 6 CCV recoveries (n=7) over entire 89 sample sequence. Trace elements = 50 ppb, Hg = 5 ppb (bottom of plot)

Accuracy was initially determined via the measurement of NIST 1643e Standard Reference Water (Table 2).
Washout, which is always a concern for very high throughput methods was evaluated by examining the 2 blanks run immediately after the high calibration standard. In all cases, greater than 3 orders of magnitude washout was achieved in the first blank after a high standard.
Sample precision was determined for each sample through the analysis of duplicates (separate preparations) and replicates (same preparation, but multiple analyses per sample) – Table 2.

Mass/element [tune mode]	Rock 1 (mean µg/L)	%RSD	Rock 2 (mean µg/L)	%RSD	NIST 1643e	Certified Value	% Recovery
7 Li [1]	7.334	3.3%	5.831	2.7%	17.80	17.4	97.8%
9 Be [1]	0.045	45.0%	0.517	15.1%	13.50	13.980	103.6%
23 Na [1]	104.759	2.9%	50.667	3.2%	20488.29	20740	101.2%
24 Mg [1]	621.477	3.4%	434.419	2.2%	8032.44	8037	100.1%
27 Al [1]	1859.706	2.8%	7874.176	2.9%	144.25	141.8	98.3%
31 P [1]	92.763	5.8%	331.254	2.6%	10.76		
39 K [1]	382.890	2.7%	1836.878	1.6%	2051.28	2034	99.2%
44 Ca [1]	511.542	2.7%	1271.182	2.9%	32719.73	32300	98.7%
45 Sc [1]	0.474	13.6%	1.639	3.4%	0.22		
47 Ti [1]	22.725	3.2%	104.211	1.7%	0.15		
51 V [1]	6.357	1.8%	26.191	1.5%	39.57	37.860	95.7%
52 Cr [1]	1731.171	1.0%	1608.120	1.1%	20.78	20.400	98.2%
55 Mn [1]	183.574	1.3%	198.292	1.2%	40.06	38.970	97.3%
56 Fe [1]	22226.481	1.4%	27752.183	0.9%	97.74	98.100	100.4%
59 Co [1]	4.941	1.4%	5.533	0.9%	26.58	27.060	101.8%
60 Ni [1]	89.272	0.8%	86.159	1.1%	61.78	62.410	101.0%
63 Cu [1]	32.139	1.0%	32.060	0.8%	21.85	22.760	104.2%
66 Zn [1]	3.554	3.6%	5.921	2.9%	79.21	78.500	99.1%
71 Ga [1]	1.888	4.3%	4.987	2.0%	<0.000		
72 Ge [1]	1.150	6.4%	2.176	3.0%	<0.000		
75 As [1]	3.201	2.5%	12.430	2.0%	59.98	60.450	100.8%
78 Se [1]	0.427	26.9%	1.199	19.4%	9.63	11.97	124.3%
85 Rb [1]	1.880	2.0%	3.264	2.0%	15.07	14.140	93.8%
88 Sr [1]	49.414	1.1%	227.678	1.4%	338.84	323.100	95.4%
89 Y [1]	2.844	1.2%	11.186	1.3%	0.00		
90 Zr [1]	17.693	1.8%	126.843	1.2%	0.18		
93 Nb [1]	0.078	21.3%	0.060	6.8%	0.01		
95 Mo [1]	15.847	0.9%	13.911	0.9%	126.45	121.4	96.0%
107 Ag [1]	0.070	18.3%	0.118	6.7%	0.95	1.062	111.5%
111 Cd [1]	0.017	65.0%	0.076	19.8%	6.53	6.568	100.6%
118 Sn [1]	2.249	1.9%	4.001	2.0%	<0.000		
121 Sb [1]	0.262	13.6%	0.227	6.5%	63.72	58.300	91.5%
125 Te [1]	0.036	39.1%	0.037	101.9%	0.85	1.09	128.7%
133 Cs [1]	0.148	3.2%	0.098	6.3%	<0.000		
137 Ba [1]	45.908	0.6%	41.145	0.9%	569.24	544.2	95.6%
139 La [1]	9.395	0.8%	37.026	1.3%	0.00		
140 Ce [1]	20.917	0.8%	79.469	1.0%	0.01		
141 Pr [1]	2.182	1.5%	8.129	1.0%	<0.000		
146 Nd [1]	7.955	1.6%	29.608	1.3%	<0.000		
147 Sm [1]	1.424	2.7%	4.783	1.1%	<0.000		
153 Eu [1]	0.205	10.4%	0.561	2.3%	0.03		
157 Gd [1]	1.180	3.2%	3.846	1.6%	0.00		
163 Dy [1]	0.704	3.0%	2.554	1.9%	<0.000		
165 Ho [1]	0.130	13.5%	0.476	1.6%	<0.000		
166 Er [1]	0.350	3.4%	1.250	1.9%	<0.000		
169 Tm [1]	0.049	36.1%	0.170	2.0%	<0.000		
172 Yb [1]	0.345	7.4%	1.174	1.5%	<0.000		
178 Hf [1]	0.512	5.1%	3.514	1.3%	0.05		
181 Ta [1]	0.028	134.0%	0.001	50.6%	0.00		
182 W [1]	0.703	3.1%	0.265	4.7%	0.40		
201 Hg [1]	0.021	34.3%	0.015	37.1%	0.33		
206 Pb [1]	8.073	1.6%	19.078	1.1%	18.68		
207 Pb [1]	7.378	1.4%	14.388	1.2%	19.77		
208 Pb [1]	7.585	1.3%	19.577	1.1%	19.41	19.630	101.1%
209 Bi [1]	0.056	32.0%	0.340	3.0%	14.12	14.090	99.8%
232 Th [1]	4.360	3.1%	68.590	1.4%	0.45		
238 U [1]	1.499	2.0%	8.264	1.1%	<0.000		

Table 2 Summary QC for Rock Digests 1 and 2 and NIST 1643e Water

Is it Possible to go Even Faster?

Yes, we think so. While the 2 loop method tested successfully reduced or eliminated a lot of the analysis overhead, some significant overhead remained in the tested configuragion.

- **Quadrupole settling time**, which can be significant for large numbers of masses such as this method
- **Autosampler overhead**. The Cetac ASX 520 used for this work was not the high speed version, nor was it optimized for high speed analysis
- **Stabilization time**, which is the time required to achieve a stable, steady state signal after the valve rotates to inject the sample.

All of these overheads are easily reduced or eliminated. We think that by doing so, it will be possible to reduce the total analysis time of this 58 element minerals method to approximately 30 seconds per sample without any degradation of performance.