

Maximizing Productivity in High Matrix Samples using the Agilent 7700x ICP-MS with ISIS Discrete Sampling

EPA 6020A Compliant Analysis in Less Than 2 Minutes per Sample

Application Note

Environmental

Authors

Steve Wilbur
Agilent Technologies, Inc.
3380 146th Place SE, Suite 300
Bellevue Washington, 98007
USA

Craig Jones
Agilent Technologies, Inc.
5301 Stevens Creek Blvd
Santa Clara, CA 95051
USA

Abstract

Discrete sampling, also known as flow injection, has been shown to significantly reduce run-to-run time in ICP-MS analysis. By fully integrating discrete sampling into the Agilent 7700x (and 7500cx) hardware and software using ISIS-DS, difficult, high matrix analyses can be performed in a fraction of the time typically required, with no compromise in analytical performance.



Agilent Technologies

Introduction

With the advent of helium (He) mode collision cell ICP-MS and the more recent introduction of the Agilent High Matrix Introduction (HMI) system, robust, accurate analysis of complex, high matrix samples such as soils and sludges has become routine [1]. However, increased competition and financial pressure has led to a greater focus on the productivity of contract environmental laboratories. At the same time, it is essential that data quality and ease-of-use are not compromised. In response to the need for the highest possible productivity, Agilent has reworked the Integrated Sample Introduction System (ISIS), allowing users to perform high speed discrete sampling (ISIS-DS) analysis while maintaining full compliance with US Environmental Protection Agency (EPA) requirements for data acquisition.

By combining the unique benefits of a collision cell that operates effectively with an inert cell gas (helium), the HMI and discrete sampling, a rare synergy has been achieved. This has resulted in a much faster system with improved ease-of-use and superior matrix tolerance. This work demonstrates the benefits of combining helium collision mode, aerosol dilution using HMI, and discrete sampling to achieve the best possible productivity and data quality.

Experimental

Instrumentation

An Agilent 7700x ICP-MS fitted with standard nickel cones, and glass concentric nebulizer was used. All 7700x instruments are equipped with the HMI system that maximizes plasma robustness using a combination of aerosol dilution and automated plasma temperature optimization. The system was also fitted with an optional ISIS Discrete Sampling system (ISIS-DS) to deliver the required productivity gains, and further improve long-term matrix tolerance. This was

achieved by reducing run time and sample exposure as much as possible. Instrument conditions are shown in Table 1.

Details of ISIS-DS operation are covered in Agilent Technologies publication 5990-3678EN [2]. Figure 1 shows the basic operation of the ISIS-DS system. The sample is rapidly drawn into the sample loop using the high speed ISIS pump while blank carrier with online internal standards are constantly pumped to the nebulizer (upper left). Rotation of the 6-port valve then diverts the carrier through the loop pushing the sample ahead of it to the nebulizer. At the same time, the autosampler probe goes to rinse position and begins rinsing before the next sample (upper right).

Accuracy, productivity and long term stability were tested by analyzing a long sequence of samples. These samples consisted of water, soil, and sediment Standard Reference Materials (SRMs), with spiked seawater samples and the Quality Control (QC) samples required by EPA method 6020A to simulate a typical sample load in a contract environmental laboratory (Figure 2). Calibration standards were prepared in a 1% HNO₃ and 0.5% HCl matrix. No matrix matching was required and no recalibrations were performed.

Table 1. Agilent 7700x ICP-MS and ISIS-DS Operating Conditions

Agilent 7700x Parameters

RF power (W)	1550
Carrier gas flow (L/min)	0.5
Dilution gas flow (L/min)	0.5
Extract 1 (V)	0
Cell gas/Flow (mL/min)	He/2.3
Kinetic Energy Discrimination (V)	10.0
Number of elements/Internal Standards	26 analytes, 6 ISTDs
Total acquisition time (3 reps) (seconds)	63

Agilent ISIS-DS Parameters

Loop volume (μL)	600
Uptake time (seconds)	10
Acquisition delay (seconds)	25
Rinse time	Pre-emptive rinse during acquisition

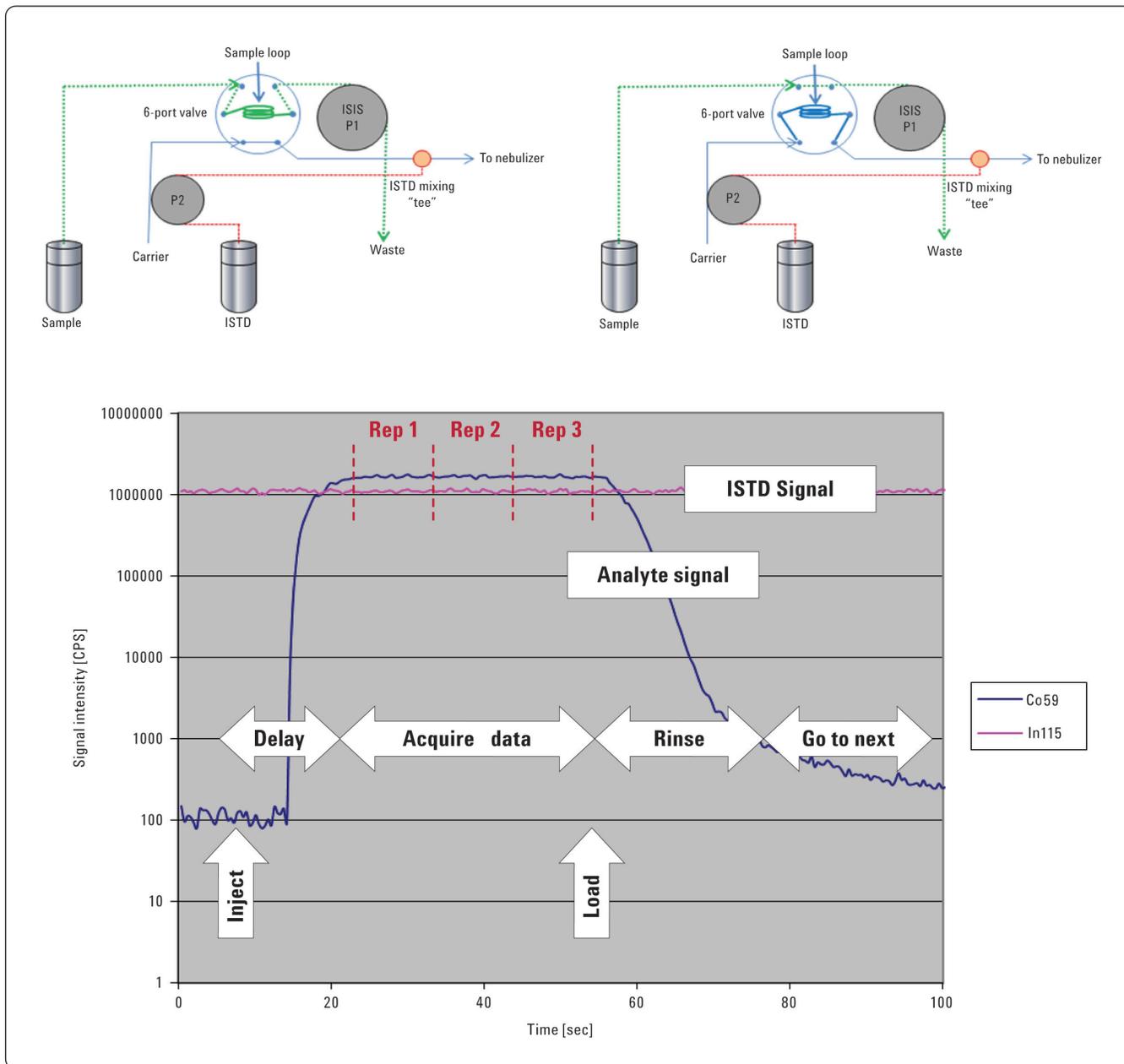


Figure 1. Overview of ISIS-DS operation. Valve in load position (upper left) and inject position (upper right). Actual analyte and internal standard signals during ISIS operation are shown in lower plot with annotation.

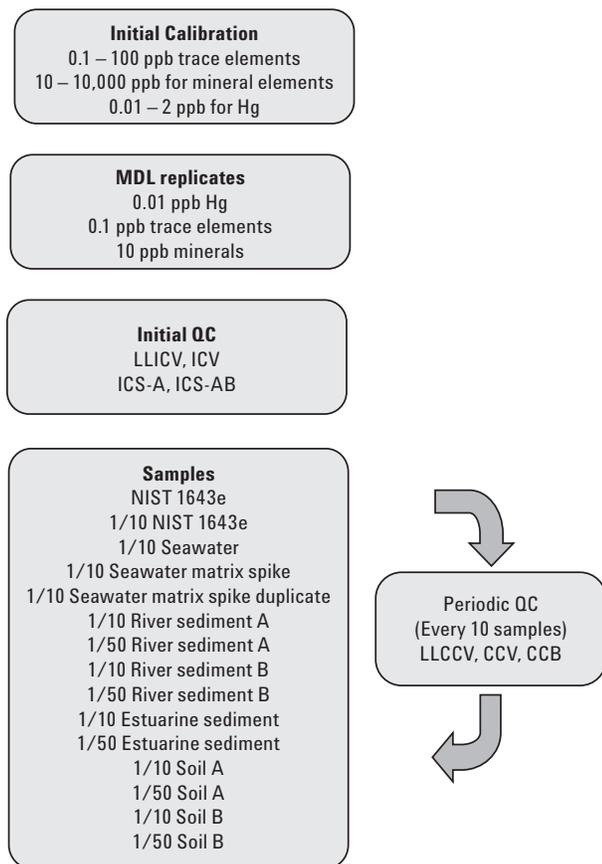


Figure 2. Sequence of samples analyzed in a single eight-hour sequence. Sample Block was repeated continuously with automatic insertion of Periodic QC Block after every 10 sample runs. Number of analyses in eight hours totaled 275.

Table 2. 3 sigma Method Detection Limits (n=7) Calculated From Replicates of the Low Calibration Standard

Isotope/ Element	Integration Time (s)	3 sigma MDL (ppb)	Isotope/ Element	Integration Time (s)	3 sigma MDL (ppb)
9 Be	1.0	0.040	66 Zn	0.3	0.058
23 Na	0.1	19.228	75 As	1.0	0.040
24 Mg	0.1	1.622	78 Se	1.5	0.386
27 Al	0.1	1.674	95 Mo	0.3	0.062
39 K	0.1	9.245	107 Ag	0.3	0.040
44 Ca	0.1	7.784	111 Cd	0.3	0.033
51 V	0.3	0.037	121 Sb	0.3	0.051
52 Cr	0.3	0.034	137 Ba	0.3	0.048
55 Mn	0.3	0.033	201 Hg	1.5	0.006
56 Fe	0.3	3.082	205 Tl	0.1	0.033
59 Co	0.3	0.021	208 Pb	0.1	0.024
60 Ni	0.3	0.018	232 Th	0.1	0.018
63 Cu	0.3	0.028	238 U	0.1	0.011

Results

In a contract environmental laboratory, a successful analytical run is measured by:

- Accuracy (is the answer correct?)
- Precision (how reproducible is the result?)
- Regulatory compliance (will it hold up to legal scrutiny?)
- Expense (how much did it cost to obtain?)

Note that absolute instrument sensitivity is not essential for successful routine analysis. As long as the sensitivity meets the accuracy requirement and project needs, it can be compromised in order to achieve the four more important criteria. To that end, all analytes were analyzed using a single He cell mode. Simply by eliminating the no gas mode, which would have improved the sensitivity for low mass, non-interfered elements, the throughput was increased by ~ 30%. In all, 275 analyses were performed in 8 hours, 8 minutes with a run-to-run time of 1.99 minutes per sample.

Method Detection Limits

Three sigma Method Detection Limits (MDLs) were calculated from seven replicates of the low standard (trace elements: 0.1 ppb, mineral elements: 10 ppb, Hg: 0.01 ppb) (Table 2). All elements were acquired in He mode and integration times were kept as short as possible in order to minimize the total acquisition time. These are not “best possible” detection limits but are more than sufficient for the method requirements.

Lower detection limits would require significantly more effort in reducing blank contamination with a commensurate increase in the cost of analysis.

Meeting EPA QA/QC Requirements

EPA method 6020A is a performance-based method. Consequently, unlike method 200.8 for drinking water analysis, the EPA has not restricted the use of collision/reaction cell (CRC) technology for method 6020 applications.

The most recent version of EPA 6020A (Feb 2007) has added the requirement for a Low Level Initial Calibration Verification (LLICV) check at approximately the method reporting limit. The recommended control limits are $\pm 30\%$ of the actual value. The results for the LLICV are shown in Table 3. These results confirm sub ppb reporting limits for all trace elements and reporting limits in the 10–50 ppb range for the mineral elements. Reducing laboratory contamination for the mineral elements would allow lower reporting limits if required.

In addition to calculating and verifying MDLs and reporting limits, method 6020A requires that internal standard (ISTD) recoveries for all samples exceed 70% of the ISTD response in the calibration blank. Continuing Calibration Verification (CCV) samples at the midpoint concentration of the calibration must be analyzed after every 10 real samples and must recover within $\pm 10\%$ of the true value. If either of these criteria is not met, the affected samples must be re-analyzed, either after dilution, in the case of ISTD failure, or after recalibration, in the case of CCV failure. CCV recoveries for all 19 CCV replicates run over the course of the sequence are shown in Figure 3. Only sodium exceeded the +10% limit towards the end of the sequence, as a result of gradual cross contamination from repeated seawater analysis. Internal standard recoveries are shown in Figure 4. The flat slope of

the ISTD curve indicates that there was no loss in sensitivity due to matrix accumulation on the interface or lenses for the entire sequence. In addition, there were no internal standard failures in any sample, which demonstrates the exceptional matrix tolerance delivered by the 7700x ICP-MS system with HMI.

Table 3. Low Level Initial Calibration Verification (LLICV) Concentrations and Recoveries. The EPA Limit for LLICV Recoveries is ± 30 Percent of Actual

Element	[LLICV] (ppb)	Recovery (%)
9 Be	0.10	96
23 Na	50.00	89
24 Mg	10.00	97
39 K	50.00	103
44 Ca	50.00	93
51 V	0.10	101
52 Cr	0.10	101
55 Mn	0.20	102
56 Fe	0.20	92
59 Co	0.20	101
60 Ni	0.20	97
63 Cu	0.20	100
66 Zn	0.50	102
75 As	0.10	97
78 Se	0.50	121
107 Ag	0.10	96
121 Sb	0.10	81
201 Hg	0.10	92
208 Pb	0.20	103
232 Th	0.50	103
238 U	0.02	104

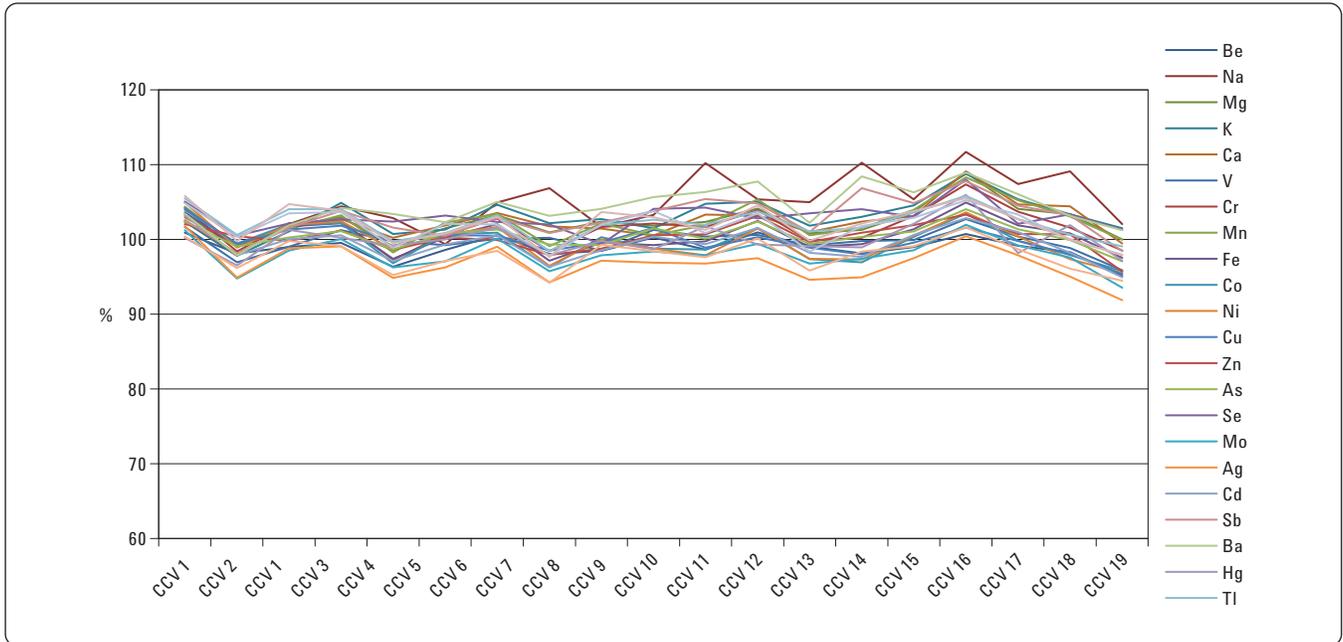


Figure 3. Continuing calibration verification (CCV) recoveries over the course of the sequence. Only Na exceeded the $\pm 10\%$ limit. No recalibrations were performed.

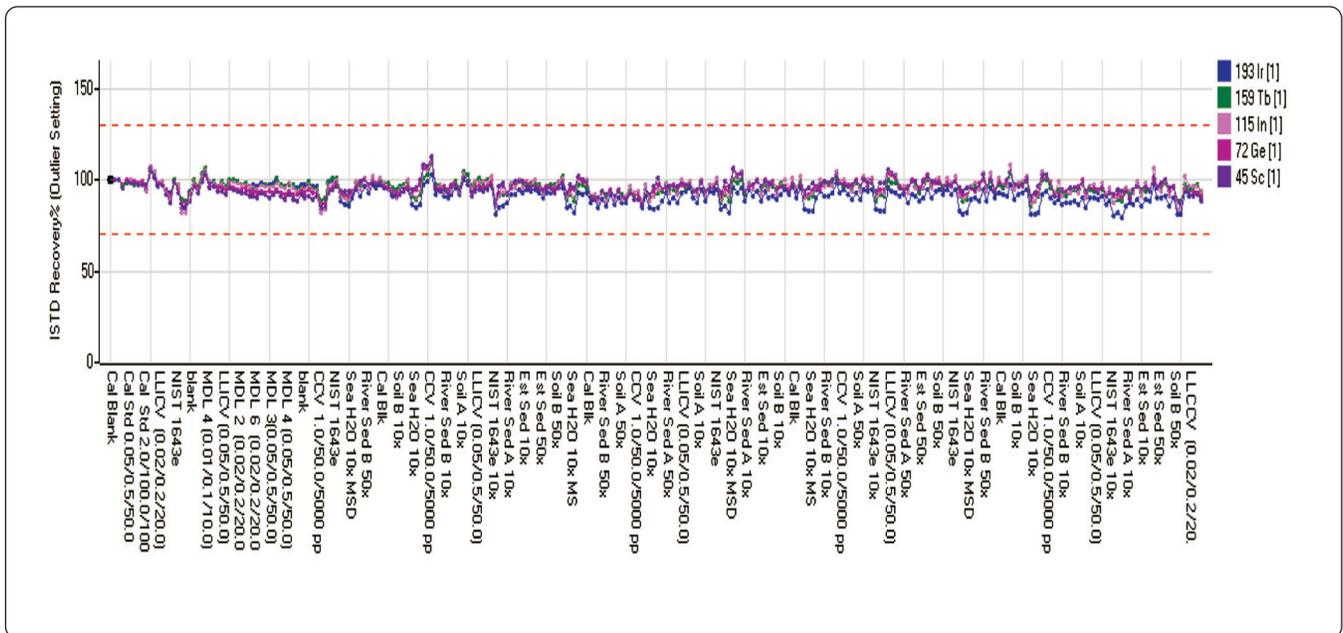


Figure 4. Internal standard recoveries normalized to the calibration blank for all samples. Due to limited space, not all sample names are shown. No internal standard failures occurred.

Seawater Matrix Spike and Matrix Spike Duplicates

Synthetic 1/10 seawater (0.3% high purity NaCl, SPEX Certiprep) was analyzed periodically along with seawater Matrix Spike (MS) and Matrix Spike Duplicates (MSD) spiked at 1 ppb for trace elements and 100 ppb for mineral elements (Mg, K, Ca and Fe). The number of repeats of each of these sample types was 10, interspersed with the other samples throughout the sequence. No matrix matching of the calibration standards and blanks to the 10% seawater samples was required, as HMI effectively eliminates matrix suppression by ensuring very high temperature plasma conditions (around 0.2% CeO/Ce ratio). Results are shown in Table 4.

All elements except silver and thallium met the EPA 75% to 125% recovery for matrix spikes. Ag and Tl showed less than 80 percent recovery due to poor solubility in unacidified seawater, and even in this case, the precision was excellent (6% RSD for Ag and 3% RSD for Tl). Relative Percent Difference (RPD) was calculated between the MS and MSD samples. EPA 6020A requires the RPD to be less than $\pm 20\%$ for analytes whose concentration is greater than 100x the MDL. All elements passed the MS/MSD test. It is also noteworthy that while the 7700x is capable of quickly and accurately measuring trace elements in seawater, it was also able to measure the sodium concentration accurately, under the same analytical conditions and in the same run as all the other mineral and trace elements. The sodium concentration in 1/10 seawater is 1180 ppm. The measured concentration of 1103 ppm represents 93% recovery, even though the highest calibration standard was only 200 ppm.

Table 4. Spike Recoveries and Matrix Spike/Matrix Spike Duplicate Relative Percent Differences for 1/10 Synthetic Seawater Samples

		Matrix spike mean (n=10)	%RSD (n=10)	Mean recovery (%)	RPD MS/MSD (%)
9	Be	0.975	8	97	3.6
23	Na	1102996.6	2	N/A	-2.9
24	Mg	96.1	2	91	-0.7
44	Ca	112.7	8	91	-7.7
51	V	1.007	3	100	-2.1
52	Cr	1.153	8	97	-1.5
55	Mn	1.112	4	111	-7.6
56	Fe	90.2	4	88	-3.1
59	Co	0.984	3	95	-1.2
60	Ni	0.997	3	95	4.3
63	Cu	0.998	4	98	-6.9
66	Zn	1.327	16	114	-1.9
75	As	1.100	7	107	2.0
78	Se	1.555	11	104	0.3
95	Mo	1.018	3	97	3.7
107	Ag	0.642	6	61	-14.1
111	Cd	0.942	4	94	0.1
121	Sb	1.048	4	103	1.6
137	Ba	1.189	13	100	2.9
205	Tl	0.719	3	66	-14.9
208	Pb	1.264	17	108	0.0
232	Th	0.862	2	86	-4.2
238	U	0.891	2	89	-2.3

Recovery of Certified Reference Values

In addition to synthetic seawater spikes, four standard reference samples were analyzed repeatedly. They were NIST 1643e water (NIST, Gaithersburg MD), CRM River Sediment A, CRM Soil A, and CRM Soil B (High Purity Standards – Charleston SC, USA). NIST 1643e was analyzed undiluted, while the other reference materials were analyzed after both

10x and 50x dilutions. Values shown in Table 5 were taken from the 10x dilutions. Each sample was measured multiple times over the sequence and the mean concentration, percent relative standard deviation (% RSD), and mean recovery were calculated for each analyte (Table 5). Not all reference materials are certified for all analytes – blank cells indicate the absence of a certified value.

Table 5. Mean Measured Values, Recoveries, Percent Relative Standard Deviations (%RSDs) for all Certified Elements in the Four Certified Reference Materials Analyzed. Blank Cells Indicate No Certified Value.

Isotope/ Element	NIST 1643e (n=12)			CRM-River Sediment-A (n=11)			CRM-Soil-A (n=11)			CRM-Soil-B (n=9)		
	Mean concentration (ppb)	%RSD	Mean recovery (%)									
9 Be	13.68	2.6	97.8	0.19	58.7		0.14	92.7		0.06	22.8	
23 Na	20421.63	2.9	98.5	61068.28	10.2		74157.80	1.4	105.9	101419.59	2.1	101.4
24 Mg	8028.85	3.0	99.9	73101.89	2.2	104.4	71164.49	1.1	101.7	80629.37	2.2	100.8
27 Al	159.73	7.5	112.6	282728.91	2.1	113.1	531638.05	1.2	106.3	746683.41	2.3	106.7
39 K	2091.16	3.0	102.8	156789.36	2.2	104.5	201262.49	1.3	100.6	212065.38	2.3	101.0
44 Ca	29456.07	2.9	91.2	292739.84	2.0	97.6	327451.76	1.2	93.6	118893.32	1.8	95.1
51 V	38.20	2.2	100.9	254.84	2.3	101.9	100.95	1.8	101.0	796.98	1.9	99.6
52 Cr	20.81	2.6	102.0	320196.72	2.8	106.7	4.44	11.4		396.52	2.0	99.1
55 Mn	40.60	3.8	104.2	9139.62	2.5	114.2	105.51	1.7	105.5	107152.33	2.3	107.2
56 Fe	98.16	5.3	100.1	1228964.31	2.2	102.4	198107.49	1.7	99.1	346586.45	1.7	99.0
59 Co	26.74	2.5	98.8	118.37	3.0	118.4	4.33	3.2		104.02	1.6	104.0
60 Ni	60.90	2.7	97.6	514.45	3.1	102.9	288.51	2.4	96.2	198.52	2.0	99.3
63 Cu	22.25	2.1	97.8	1000.20	2.8	100.0	288.16	2.0	96.1	3164.69	1.5	105.5
66 Zn	77.93	1.7	99.3	16496.33	2.3	110.0	984.66	1.7	98.5	73857.97	1.5	105.5
75 As	60.06	2.1	99.4	617.05	2.0	102.8	202.86	1.5	101.4	6148.47	1.5	102.5
78 Se	12.12	3.5	101.3	28.57	6.4		12.76	11.8		3.66	22.5	
95 Mo	119.30	2.2	98.3	0.81	13.8		0.46	20.1		0.51	16.0	
107 Ag	0.64	13.4	60.0	1.26	29.2		0.43	38.9		0.64	14.5	
111 Cd	6.38	2.8	97.2	102.30	2.4	102.3	0.19	21.7		201.33	1.8	100.7
121 Sb	59.04	2.8	101.3	535.59	1.9	107.1	32.09	2.3	107.0	430.38	2.8	107.6
137 Ba	557.45	3.1	102.4	532.89	1.8	106.6	5192.34	1.4	103.8	8401.48	3.0	120.0
201 Hg	0.38	5.8		0.11	17.7		0.02	68.0		0.02	67.0	
205 Tl	6.53	3.2	87.7	10.23	3.3	102.3	0.18	47.4		0.22	12.7	
208 Pb	19.93	3.5	101.5	7452.60	2.2	106.5	389.62	1.8	97.4	61817.26	2.0	103.0
232 Th	0.01	63.0		18.98	2.2	94.9	92.58	1.5	92.6	91.98	2.1	92.0
238 U	0.01	48.3		9.45	2.5	94.5	9.20	2.6	92.0	258.27	1.8	103.3

Conclusions

This study shows that long sequences of high Total Dissolved Solids (TDS) samples can be analyzed with the highest accuracy, precision, and long term stability possible. This was shown by combining the benefits of He mode for removing polyatomic interferences with the HMI for highly robust plasma conditions, and the ISIS-DS discrete sampling system. The advantages are as follows:

- ISIS-DS eliminates the need for stabilization after high speed uptake via constant flow nebulization reducing the run time by as much as a minute per sample.
- ISIS-DS uncouples uptake and analysis so the system can begin rinsing before the previous analysis is finished, reducing the run time by as much as an additional minute.
- ISIS-DS introduces sample to the mass spectrometer only during actual data acquisition; at all other times, a clean blank solution is being nebulized. This results in a 3-5x reduction in the amount of sample reaching the instrument with a resulting decreased requirement for cleaning and maintenance.
- HMI reduces the total sample load in the aerosol introduced to the plasma by accurately and reproducibly controlling aerosol dilution eliminating costly reruns and reducing system maintenance.
- The high sensitivity and universality of He mode permits all elements to be analyzed in a single cell mode, regardless of the sample matrix composition, thereby reducing total acquisition time.

The net result is simpler operation, higher throughput and improved long term stability over conventional ICP-MS systems.

References

1. Steve Wilbur and Craig Jones, "Simple, Reliable Analysis of High Matrix Samples According to US-EPA Method 6020A using the Agilent 7700x ICP-MS", Agilent Technologies publication 5990-5514EN
2. Steve Wilbur, Takeo Kuwabara and Tetsushi Sakai, "High-Speed Environmental Analysis Using the Agilent 7500cx with Integrated Sample Introduction System – Discrete Sampling (ISIS-DS)," Agilent Technologies publication 5990-3678EN

For More Information

For more information on our products and services, visit our Web site at www.agilent.com/chem/icpms.

www.agilent.com/chem

Agilent shall not be liable for errors contained herein or for incidental or consequential damages in connection with the furnishing, performance, or use of this material.

Information, descriptions, and specifications in this publication are subject to change without notice.

© Agilent Technologies, Inc., 2010
Printed in the USA
March 16, 2010
5990-5437EN



Agilent Technologies