Simple, Reliable Analysis of High Matrix Samples According to US EPA Method 6020A using the Agilent 7700x ICP-MS

Combining the advantages of helium mode and aerosol dilution for superior performance

Application Note

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Abstract

The Agilent 7700x ICP-MS combines the simplicity of a single collision cell mode (helium mode) for polyatomic interference removal with the superior matrix tolerance of its unique High Matrix Introduction (HMI) system. Third generation Octopole Reaction System (ORS^3) cell technology provides higher sensitivity and more effective interference removal than ever before in complex, high matrix samples, eliminating the need for reactive cell gases in routine analysis. Helium mode on the ORS^3 is so effective that interference correction equations can also be eliminated. These two factors redefine ease of use in ICP-MS, removing two of the most common causes of errors in multi-element analysis of complex samples. A challenging 15-hour sequence of high matrix soils, waters, seawaters and sediments was analyzed according to US Environmental Protection Agency (EPA) Method 6020A. The Agilent 7700x ICP-MS delivered excellent recovery of certified values for six standard reference materials, with no quality control failures throughout the entire sequence.

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Introduction

US EPA Method 6020A (Rev 4, February 07) is applicable to the determination of sub-µg/L concentrations of a large number of elements in water samples and in waste extracts or digests. The EPA has carried out multi-laboratory studies to validate Method 6020A for 23 elements in aqueous and solid wastes (Table 1).

*Table 1. Elements Currently Validated by EPA for Method 6020A. *Chemical Abstract Services Registry Number*

Element	CASRN*
Aluminum (Al)	7429-90-5
Antimony (Sb)	7440-36-0
Arsenic (As)	7440-38-2
Barium (Ba)	7440-39-3
Beryllium (Be)	7440-41-7
Cadmium (Cd)	7440-43-9
Calcium (Ca)	7440-70-2
Chromium (Cr)	7440-47-3
Cobalt (Co)	7440-48-4
Copper (Cu)	7440-50-8
Iron (Fe)	7439-89-6
Lead (Pb)	7439-92-1
Magnesium (Mg)	7439-95-4
Manganese (Mn)	7439-96-5
Mercury (Hg)	7439-97-6
Nickel (Ni)	7440-02-0
Potassium (K)	7440-09-7
Selenium (Se)	7782-49-2
Silver (Ag)	7440-22-4
Sodium (Na)	7440-23-5
Thallium (Tl)	7440-28-0
Vanadium (V)	7440-62-2
Zinc (Zn)	7440-66-6

However, the method can be used for the analysis of any element(s) for which the performance can be shown to meet the project data quality objectives. Unlike Method 200.8 for drinking water compliance, Method 6020A does not place any restrictions on the use of advancements in ICP-MS technology such as collision/reaction cells (CRCs) for the removal of polyatomic interferences. As a result, Method 6020A permits the use of helium (He) mode on the Agilent 7700x ICP-MS to provide simple, efficient removal of all polyatomic interferences, even in complex and unknown sample types.

This is especially important for Method 6020A, due to the wide variety of sample types and concentrations for which the method is applicable. Table 2 illustrates the challenges presented by the range of samples typically analyzed using Method 6020A. Nearly every element from scandium through selenium is subject to multiple polyatomic interferences in common environmental matrices. No reactive cell gas can simultaneously remove all these interferences, but He mode is universal. It uses the size difference between polyatomic and monatomic ions to remove all polyatomic interferences, eliminating the need for unreliable interference correction equations.

Table 2. Polyatomic Interferences on Elements Between Mass 40 and 80 Resulting from a Common Mixed Matrix Containing Na, Ca, C, S, P, Cl in Nitric Acid

Isotope/ Element	Common Polyatomic Interferences in Mixed Matrix Samples
^{45}Sc	$^{13}C^{16}O_2$, $^{12}C^{16}O_2H$, ^{44}CaH, $^{32}S^{12}CH$, $^{32}S^{13}C$, $^{33}S^{12}C$
^{47}Ti	$^{31}P^{16}O$, ^{46}CaH, $^{35}Cl^{12}C$, $^{32}S^{14}NH$, $^{33}S^{14}N$
^{49}Ti	$^{31}P^{18}O$, ^{48}CaH, $^{35}Cl^{14}N$, $^{37}Cl^{12}C$, $^{32}S^{16}OH$, $^{33}S^{16}O$
^{50}Ti	$^{34}S^{16}O$, $^{32}S^{18}O$, $^{35}Cl^{14}NH$, $^{37}Cl^{12}CH$
^{51}V	$^{35}Cl^{16}O$, $^{37}Cl^{14}N$, $^{34}S^{16}OH$
^{52}Cr	$^{36}Ar^{16}O$, $^{40}Ar^{12}C$, $^{35}Cl^{16}OH$, $^{37}Cl^{14}NH$, $^{34}S^{18}O$
^{53}Cr	$^{36}Ar^{16}OH$, $^{40}Ar^{13}C$, $^{37}Cl^{16}O$, $^{35}Cl^{18}O$, $^{40}Ar^{12}CH$
^{54}Fe	$^{40}Ar^{14}N$, $^{40}Ca^{14}N$, $^{23}Na^{31}P$
^{55}Mn	$^{37}Cl^{18}O$, $^{23}Na^{32}S$, $^{23}Na^{31}PH$
^{56}Fe	$^{40}Ar^{16}O$, $^{40}Ca^{16}O$
^{57}Fe	$^{40}Ar^{16}OH$, $^{40}Ca^{16}OH$
^{58}Ni	$^{40}Ar^{18}O$, $^{40}Ca^{18}O$, $^{23}Na^{35}Cl$
^{59}Co	$^{40}Ar^{18}OH$, $^{43}Ca^{16}O$, $^{23}Na^{35}ClH$
^{60}Ni	$^{44}Ca^{16}O$, $^{23}Na^{37}Cl$
^{61}Ni	$^{44}Ca^{16}OH$, $^{38}Ar^{23}Na$, $^{23}Na^{37}ClH$
^{63}Cu	$^{40}Ar^{23}Na$, $^{12}C^{16}O^{35}Cl$, $^{12}C^{14}N^{37}Cl$, $^{31}P^{32}S$, $^{31}P^{16}O_2$
^{64}Zn	$^{32}S^{16}O_2$, $^{32}S_2$, $^{36}Ar^{12}C^{16}O$, $^{38}Ar^{12}C^{14}N$, $^{48}Ca^{16}O$
^{65}Cu	$^{32}S^{16}O_2H$, $^{32}S_2H$, $^{14}N^{16}O^{35}Cl$, $^{48}Ca^{16}OH$
^{66}Zn	$^{34}S^{16}O_2$, $^{32}S^{34}S$, $^{33}S_2$, $^{48}Ca^{18}O$
^{67}Zn	$^{32}S^{34}SH$, $^{33}S_2H$, $^{48}Ca^{18}OH$, $^{14}N^{16}O^{37}Cl$, $^{16}O_2{}^{35}Cl$
^{68}Zn	$^{32}S^{18}O_2$, $^{34}S_2$
^{69}Ga	$^{32}S^{18}O_2H$, $^{34}S_2H$, $^{16}O_2{}^{37}Cl$
^{70}Zn	$^{34}S^{18}O_2$, $^{35}Cl_2$
^{71}Ga	$^{34}S^{18}O_2H$, $^{35}Cl_2H$, $^{40}Ar^{31}P$
^{72}Ge	$^{40}Ar^{32}S$, $^{35}Cl^{37}Cl$, $^{40}Ar^{16}O_2$
^{73}Ge	$^{40}Ar^{32}SH$, $^{40}Ar^{33}S$, $^{35}Cl^{37}ClH$, $^{40}Ar^{16}O_2H$
^{74}Ge	$^{40}Ar^{34}S$, $^{37}Cl_2$
^{75}As	$^{40}Ar^{34}SH$, $^{40}Ar^{35}Cl$, $^{40}Ca^{35}Cl$, $^{37}Cl_2H$
^{77}Se	$^{40}Ar^{37}Cl$, $^{40}Ca^{37}Cl$
^{78}Se	$^{40}Ar^{38}Ar$
^{80}Se	$^{40}Ar_2$, $^{40}Ca_2$, $^{40}Ar^{40}Ca$, $^{32}S_2{}^{16}O$, $^{32}S^{16}O_3$

Additionally, samples analyzed by Method 6020A can range from very low to very high Total Dissolved Solids (TDS) and a single sequence may cover the entire TDS range. The ICP-MS method must therefore accommodate both the wide range of unknown matrix interferences and the wide range of analyte concentrations; and for the method to be simple and routine, this must all be achieved without any prior knowledge about the samples. The Agilent 7700x ICP-MS achieves this through the use of advanced, third generation helium collision technology (ORS^3) coupled with a unique High Matrix Introduction (HMI) system that is fitted as standard.

Experimental

A sequence of samples representing the types of matrices typically encountered by a contract environmental laboratory was analyzed according to Method 6020A requirements. The sequence consisted of a range of water (NIST, Gaithersburg MD, USA), soil, and sediment standard reference materials (High-Purity Standards, Charleston SC, USA), analyzed at both 1/10 and 1/50 dilutions, as well as synthetic seawater (SPEX Certiprep, Metuchen NJ, USA) and spiked seawater, (Figure 1). Additionally a set of low-level standards was analyzed to calculate the method detection limits (MDL). In total, 156 samples, standards and blanks were analyzed over the course of almost 15 hours, after a single initial calibration. Continuing calibration blanks (CCBs) and continuing calibration verification (midpoint) standards (CCVs) were automatically run after every 10 samples. Low level CCVs (LLCCVs) were also analyzed with each CCV block, as required by this most recent update to Method 6020A.

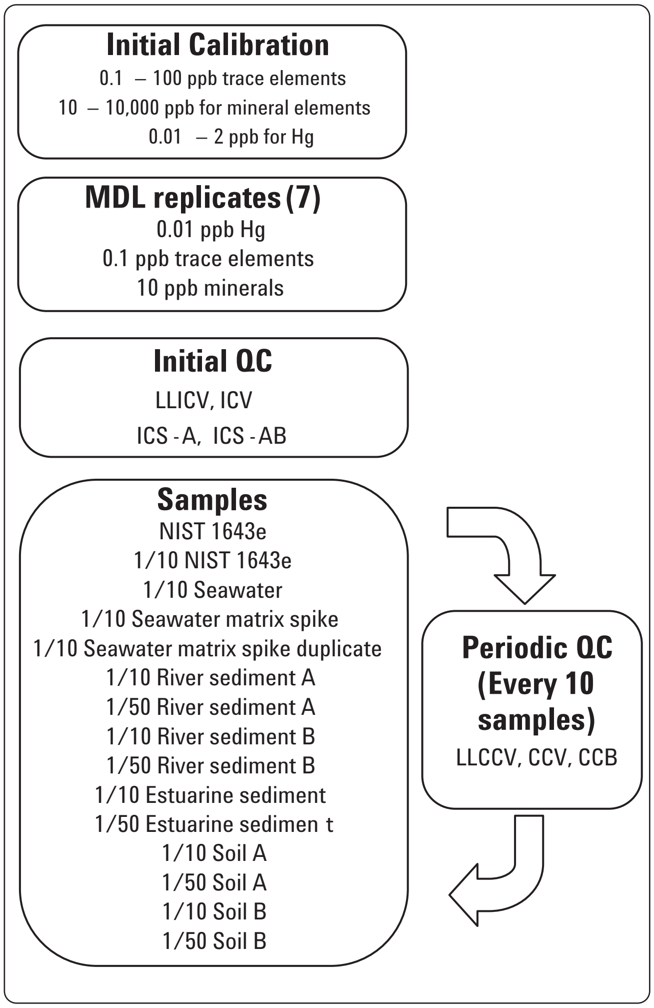

Figure 1. Sequence simulating a typical environmental analysis of a complex mixture of samples, analyzed according to the requirements of EPA Method 6020A.

Instrument Acquisition Parameters

The Agilent 7700x ICP-MS was operated in standard robust plasma conditions (less than 1% CeO/Ce) using the integrated HMI system to effectively eliminate matrix suppression and maintain long term stability in high matrix samples (Table 3). All analytes were acquired using He mode with the exception of the low and high mass elements that do not suffer from polyatomic interferences in any common matrices; these elements were acquired in no gas mode. Table 4 lists the acquisition mode for each element.

Note that the preferred, most abundant isotope was used for every analyte, and the reliable removal of interferences in He mode means that the same isotopes are used regardless of the sample matrix; furthermore, no interference correction equations were applied for any analyte in any matrix. This provides simplified method setup across a wide range of sample types.

*Table 3. 7700x ICP-MS Operating Conditions Used for Both No Gas Mode and He Mode (*He Flow for Se and V = 12 mL/min)*

Parameter	**Value No gas mode**	**Value He mode**
Forward power (W)	1550	same
Sample depth (mm)	8	same
Nebulizer pump speed (rps)	0.1	same
Carrier gas (L/min)	0.6	same
Dilution gas (L/min)	0.4	same
Dilution mode	On	same
Extract 1 (V)	0	same
Kinetic Energy Discrimination (KED) (V)	3	4
Cell gas flow (mL/min He)	0	4*

Results

Method Detection Limits

Table 4 shows the 3 sigma MDLs (µg/L) determined from seven replicates of a low level multi-element standard (3-5 times the estimated MDL for each analyte) measured immediately after the initial calibration. In nearly all cases, single digit to low double digit ppt MDLs were achieved, significantly below the typical requirements for this analysis. Even the common mineral elements, Na, K and Ca showed single digit ppb MDLs.

Table 4. 3-Sigma Method Detection Limits in µg/L (ppb) Calculated from Seven Replicate Analyses of a Low Standard at the Beginning of the Sequence

Mass	Element	Mode	MDL (µg/L)
9	Be	no gas	0.019
23	Na	He	2.134
24	Mg	He	0.582
27	Al	He	0.214
39	K	He	1.873
44	Ca	He	3.171
51	V	He	0.007
52	Cr	He	0.012
55	Mn	He	0.012
56	Fe	He	0.157
59	Co	He	0.004
60	Ni	He	0.011
63	Cu	He	0.012
66	Zn	He	0.028
75	As	He	0.013
78	Se	He	0.034
95	Mo	no gas	0.016
107	Ag	no gas	0.007
111	Cd	no gas	0.009
121	Sb	no gas	0.008
137	Ba	no gas	0.015
201	Hg	no gas	0.005
205	Tl	no gas	0.005
208	Pb	no gas	0.005
232	Th	no gas	0.009
238	U	no gas	0.004

Low Level Performance Verification – LLCCV

A new requirement for Method 6020A (Feb 2007) is the analysis of a low level continuing calibration verification (LLCCV) sample in order to verify that the system continues to accurately measure samples at the reporting limit over the course of the entire sample sequence. The recommended recovery limits are ±30% of the actual value. A LLCCV sample was included in the periodic QC block along with the CCV and CCB standards. The LLCCV concentration was 0.5 ppb for most elements, 50 ppb for the mineral elements (Na, K, Ca, Mg and Fe) and 0.05 ppb for Hg. The LLCCV was analyzed five times over the 15-hour sequence. RSDs for the five replicates were mostly <3% and recoveries were easily within the ±30% limits (mostly within ±10%) for all elements (except Hg, due to low level contamination) (Table 5). This demonstrates the superior sensitivity and accuracy of the Agilent 7700x ICP-MS, and its exceptional long-term stability.

Dynamic Range

In order to provide the simplest, most accurate analysis, the instrument must possess a dynamic range sufficient to analyze typical samples without excessive dilution or over-range results. Table 4 establishes the lower end of the dynamic range as single digit ppt for nearly all elements under typical environmental laboratory conditions, validated by the LLCCV recoveries shown in Table 5.

*Table 5. Precision (%RSD) and Accuracy (% Recovery) of Replicate Low Level CCV (LLCCV) Analyses Over the Duration of the 15 hour Sequence. *Some Contamination was Evident in the Hg LLCCV, Expected Value = 50 ppt*

	Mean n=5 (µg/L)	%RSD	Recovery (%)
Be	0.492	4.1	98.4
Na	43.146	11.0	86.3
Mg	48.160	0.9	96.3
Al	0.416	17.6	83.2
K	48.106	6.7	96.2
Ca	39.387	9.3	78.8
V	0.489	0.9	97.9
Cr	0.504	1.7	100.8
Mn	0.485	1.5	97.1
Fe	49.210	1.4	98.4
Co	0.489	2.0	97.8
Ni	0.509	3.0	101.9
Cu	0.508	2.3	101.6
Zn	0.433	4.1	86.7
As	0.498	1.1	99.7
Se	0.482	5.3	96.4
Mo	0.470	2.4	94.0
Ag	0.471	2.2	94.2
Cd	0.489	0.9	97.8
Sb	0.479	1.2	95.8
Ba	0.492	4.9	98.4
Hg	0.068	10.4	135.7*
Tl	0.461	1.5	92.1
Pb	0.480	1.3	96.0
Th	0.461	1.6	92.3
U	0.461	1.6	92.1

The upper limit is established either by the highest calibration concentration (100 ppb for trace elements and 10 ppm for minerals), or by linear range standards. In this work, any of the certified reference materials (CRMs) can be used as a linear range standard. The certified concentrations for the six CRMs are listed in Table 6. The highest concentration for each element is shown in the "Maximum" column. For those samples that were diluted 1/10, the on-instrument concentration is shown in the final column. Documented dynamic range under the simple conditions used in this work ranged from 2 ppt to more than 120 ppm, while other work has shown upper range in excess of 1000 ppm for some elements [1].

Accuracy and Precision

Recovery of Certified Values

In all, six CRMs were analyzed repeatedly over the course of the 15-hour sequence (Table 6). These included NIST 1643e (water), and High-Purity Standards CRM-ES (estuarine sediment), CRM-RS-A, CRM-RS-B (river sediments), CRM-Soil-A and CRM-Soil-B (soils). All CRMs were analyzed without further preparation, either undiluted (NIST 1643e), diluted ten times in 1% HNO_3/0.5% HCl (NIST 1643e, and all High Purity Standards CRMs), or diluted 50x (all High Purity Standards CRMs). The results are shown in Table 7.

Table 6. Composition of Six Certified Reference Materials Analyzed (µg/L in Original Aqueous Solutions as Provided). The Last Two Columns Show the Highest Concentration by Element Across the Six CRMs to Illustrate the Dynamic Range Encountered in this Sequence.

	NIST 1643e (µg/L)	CRM-ES (µg/L)	CRM-RS-A (µg/L)	CRM-RS-B (µg/L)	CRM-Soil-A (µg/L)	CRM-Soil-B (µg/L)	Maximum (µg/L)	Diluted 1/10 (µg/L)
Be	13.98	20	0	0	0	0	20	2
Na	20740	200000	0	50000	70000	100000	200000	20000
Mg	8037	100000	70000	120000	70000	80000	120000	12000
Al	141.8	700000	250000	600000	500000	700000	700000	70000
K	2034	150000	150000	200000	200000	210000	210000	21000
Ca	32300	80000	300000	300000	350000	125000	350000	35000
V	37.86	1000	250	1000	100	800	1000	100
Cr	20.4	800	300000	15000	0	400	300000	30000
Mn	38.97	4000	8000	6000	100	100000	100000	10000
Fe	98.1	350000	1200000	400000	200000	350000	1200000	120000
Co	27.06	100	100	150	0	100	150	15
Ni	62.41	300	500	500	300	200	500	50
Cu	22.76	200	1000	1000	300	3000	3000	300
Zn	78.5	1500	15000	5000	1000	70000	70000	7000
As	60.45	100	600	200	200	6000	6000	600
Se	11.97	50	20	10	10	0	50	5
Mo	121.4	0	0	0	0	0	121.4	12.14
Ag	1.062	0	0	0	0	0	1.062	0.1062
Cd	6.568	0	100	30	0	200	200	20
Sb	58.3	0	500	40	30	400	500	50
Ba	544.2	0	500	4000	5000	7000	7000	700
Tl	7.445	0	10	10	0	0	10	1
Pb	19.63	300	7000	2000	400	60000	60000	6000
Th	0	100	20	100	100	100	100	10
U	0	0	10	30	10	250	250	25

Table 7 Recovery of Certified Values for 6 Certified Reference Materials. Note Excellent Agreement Between Both 10x Diluted and 50x Diluted Samples Indicating Excellent Sensitivity, Matrix Tolerance, Precision and Linear Range.

	NIST 1643e	NIST 1643e (10×)	Estuarine Sediment (10×)	Estuarine Sediment (50×)	River Sediment "A" (10×)	River Sediment "A" (50×)	River Sediment "B" (10×)	River Sediment "B" (50×)	Soil "A" (10×)	Soil "A" (50×)	Soil "B" (10×)	Soil "B" (50×)
9 Be	107.6%	106.6%	95.8%	102.1%								
23 Na	94.9%	92.9%	96.7%	96.8%			102.8%	117.1%	95.0%	97.8%	91.9%	93.4%
24 Mg	101.5%	91.7%	101.0%	101.9%	97.8%	94.8%	102.2%	104.9%	99.5%	93.2%	96.4%	90.6%
27 Al	103.9%	105.9%	99.6%	100.9%	100.8%	99.1%	101.8%	104.1%	98.0%	100.1%	96.1%	97.8%
39 K	99.7%	88.5%	100.5%	99.5%	99.3%	103.9%	102.8%	104.0%	97.8%	98.7%	95.5%	95.6%
44 Ca	101.9%	100.1%	97.3%	99.4%	100.1%	101.7%	97.7%	99.7%	97.2%	100.0%	96.7%	99.0%
51 V	102.3%	100.0%	97.8%	97.2%	99.8%	102.0%	97.3%	98.2%	99.3%	99.3%	96.8%	96.5%
52 Cr	103.5%	102.1%	96.5%	97.5%	102.7%	106.1%	101.8%	104.8%			94.3%	96.1%
55 Mn	101.4%	98.5%	104.2%	95.8%	105.9%	100.1%	104.5%	97.7%	99.1%	100.9%	98.5%	99.6%
56 Fe	104.0%	108.8%	99.2%	100.8%	101.1%	104.4%	98.8%	101.5%	97.8%	99.9%	96.1%	97.8%
59 Co	99.0%	96.7%	99.4%	100.9%	112.4%	116.9%	98.1%	101.4%			99.4%	101.3%
60 Ni	101.8%	100.7%	96.8%	100.0%	101.2%	105.7%	96.0%	100.3%	96.0%	99.4%	96.8%	100.4%
63 Cu	100.5%	98.8%	94.8%	98.6%	98.1%	102.5%	94.6%	99.1%	94.6%	98.0%	100.4%	97.1%
66 Zn	98.7%	101.8%	94.5%	99.2%	105.1%	102.5%	94.4%	100.1%	96.2%	100.5%	100.0%	106.2%
75 As	101.0%	102.1%	99.9%	101.8%	101.7%	105.6%	100.0%	102.1%	100.2%	102.2%	99.3%	100.7%
78 Se	94.9%	101.0%	99.2%	101.4%			93.6%	95.0%	93.8%	94.3%		
95 Mo	107.3%	96.5%										
107 Ag	93.1%	91.3%										
111 Cd	99.2%	100.9%			99.6%	101.3%	97.8%	100.3%			96.8%	98.4%
121 Sb	102.2%	99.7%			100.6%	100.5%	100.0%	99.2%	101.2%	99.5%	101.8%	101.5%
137 Ba	107.9%	99.8%			100.0%	101.2%	107.9%	101.4%	107.1%	99.9%	105.5%	98.0%
205 Tl	95.5%	94.1%			88.0%	95.7%	84.0%	95.1%				
208 Pb	101.3%	104.6%	94.2%	98.6%	107.4%	110.6%	104.3%	101.6%	102.1%	99.8%	104.8%	108.8%
232 Th			94.6%	97.8%	98.4%	98.9%	93.9%	94.8%	96.5%	97.9%	97.3%	98.8%
238 U					97.1%	98.1%	91.3%	93.6%	94.1%	96.6%	107.7%	97.4%

☐ no certified value

Matrix Spike (MS) and Matrix Spike Duplicates (MSD) in 1/10 Seawaters

Seawater is a challenging matrix for several reasons. Neat seawater contains approximately 3% total dissolved solids, mainly NaCl, which can accumulate on the nebulizer tip, torch injector, and interface cones, causing signal instability and gradual loss of sensitivity. Additionally, Na is an easily ionized element (first ionization potential (IP) = 5.14 eV) that can significantly reduce the response of higher IP elements such as Zn, As, Se, Cd and Hg in non-robust plasmas. Synthetic seawater (3% high purity NaCl) was diluted 1/10 and spiked in duplicate (MS and MSD) with the calibration standard mix at 10 ppb (1 ppm for mineral elements). Each MS and MSD was measured four times over the course of the sequence. The mean results of the four measurements are presented in Table 8. Most recoveries were well within ±10%, and %RSDs over the 15-hour sequence were typically a few percent. In all cases, the RPD values were within the EPA limit of ±20%.

Table 8. 1/10 Seawater Matrix Spike (MS) and Matrix Spike Duplicate (MSD) Results for 10 ppb Spike (1 ppm Ca, Fe) Showing Mean Value of Replicate Measurements (n=4), %RSD and % Recovery of Both MS and MSD Samples. RPD = Relative Percent Difference Between the Mean MS and Mean MSD values.

	Matrix Spike			**Matrix Spike Duplicate**			
	Mean	**%RSD**	**%Recovery**	**Mean**	**%RSD**	**%Recovery**	**RPD**
9 Be	10.513	4.0	105.1	10.572	4.4	105.7	-0.6
24 Mg	928.493	5.4	92.8	921.914	5.4	92.2	0.7
44 Ca	892.134	5.8	89.2	905.386	10.0	90.5	-1.5
51 V	10.246	3.8	102.5	8.848	1.7	88.5	13.6
52 Cr	9.82	6.6	98.2	8.71	1.8	87.1	11.3
55 Mn	9.557	4.9	95.6	9.433	1.9	94.3	1.3
56 Fe	886.110	2.0	88.6	905.780	1.8	90.6	-2.2
59 Co	9.205	3.0	92.1	9.098	2.8	91.0	1.2
60 Ni	9.144	3.1	91.4	9.216	3.6	92.2	-0.8
63 Cu	8.895	4.6	89.0	8.835	4.3	88.3	0.7
66 Zn	9.470	5.1	94.7	8.833	5.0	88.3	6.7
75 As	10.220	1.1	102.2	8.099	0.4	81.0	20.8
78 Se	9.241	6.4	92.4	8.799	2.5	88.0	4.8
95 Mo	9.859	2.6	98.6	8.349	1.5	83.5	15.3
107 Ag	8.826	1.2	88.3	8.774	0.8	87.7	0.6
111 Cd	9.268	1.0	92.7	9.146	2.7	91.5	1.3
121 Sb	9.741	2.5	97.4	9.687	3.1	96.9	0.6
137 Ba	9.990	1.8	99.9	9.998	0.7	100.0	-0.1
205 Tl	8.708	5.4	87.1	8.707	6.0	87.1	0.0
208 Pb	8.879	7.3	88.8	8.698	6.8	87.0	2.0
232 Th	9.397	6.6	94.0	9.316	7.6	93.2	0.9
238 U	9.447	7.6	94.5	9.229	8.2	92.3	2.3

Precision and Long Term Stability

Long term precision was measured by calculating percent relative standard deviation (%RSD) for all replicates of the repeated samples over the course of the 15-hour sequence. The CCV and NIST 1643e were analyzed most frequently (n=8 and n=6 respectively). %RSD values in the range of a few percent indicate excellent precision over a long sequence, without the need for recalibration (Table 9).

Table 9. Long Term Precision (%RSD) Over the Course of the 15-hour Sequence, for Both the Continuing Calibration Verification (CCV) Standard (Mid-Point of the Calibration Range), and for NIST 1643e Water (Undiluted).

	% Relative Standard Deviation	
Element	**CCV (n=8)**	**NIST 1643e (n=6)**
9 Be	3.7	7.0
23 Na	5.5	5.9
24 Mg	4.1	5.0
27 Al	2.1	4.6
39 K	4.1	9.4
44 Ca	3.5	5.4
51 V	1.3	1.1
52 Cr	4.1	3.9
55 Mn	3.4	4.0
56 Fe	3.3	3.1
59 Co	3.0	2.5
60 Ni	4.0	3.0
63 Cu	4.2	3.1
66 Zn	3.0	2.2
75 As	0.9	0.5
78 Se	0.8	2.0
95 Mo	3.0	2.2
107 Ag	3.2	2.1
111 Cd	1.5	1.3
121 Sb	0.8	3.7
137 Ba	1.9	1.0
205 Tl	3.7	3.6
208 Pb	3.1	4.3
232 Th	4.6	N/A
238 U	5.3	N/A

Calibration accuracy and precision were measured by repeated analysis of the continuing calibration verification (CCV) sample, which is at the midpoint concentration of the calibration curve. Figure 2 shows the percent recoveries for all elements for each of the eight CCV samples. No CCV failed the EPA limit of ± 10% for any analyte. Absolute long term stability (absence of drift) is measured by comparing raw internal standard responses from the beginning of the sequence to the end. Internal standard responses also indicate the degree of suppression from high matrix samples. EPA Method 6020A requires that the internal standard responses be greater than 70% compared to the calibration blank for all samples (lower dashed line – Figure 3). If the internal standard response in any sample falls below 70%, that sample must be diluted and reanalyzed until the internal standards exceed the 70% limit. Figure 3 shows the percent recovery of the raw internal standard responses for the entire 15-hour sequence normalized to the calibration blanks. A single blank recalibration at run # 118 (CCB) compensated for the slight change in internal standard responses due to gradual conditioning of the cones and interface. All samples passed the >70% test, and no samples required additional dilution as a result of an internal standard failure. In addition, the generally flat slope of the internal standard recovery curve shows that there was no gradual loss of sensitivity over time, even when running these high matrix samples.

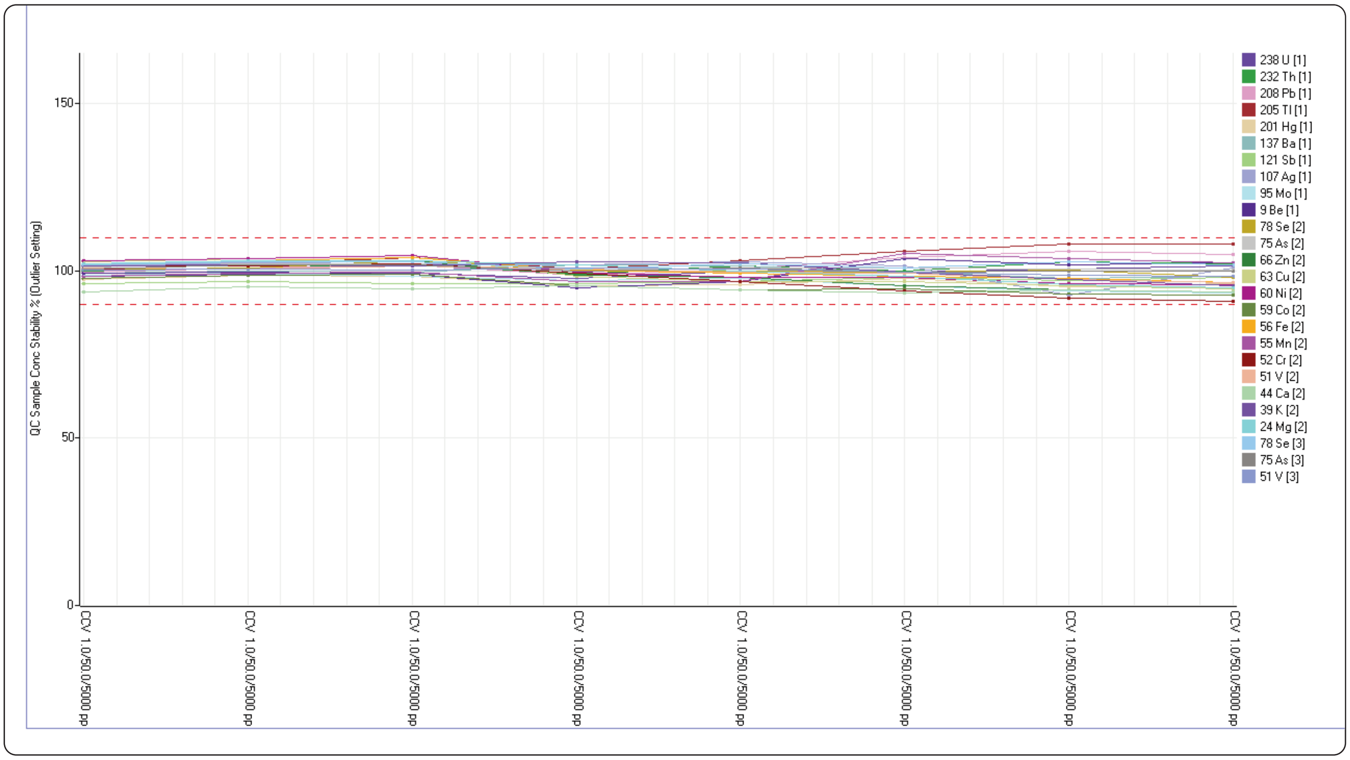

Figure 2. CCV recoveries – all analytes (1 ppb Hg, 50 ppb trace elements, 5 ppm minerals). Control limits at +/- 10% are indicated in by the dashed line.

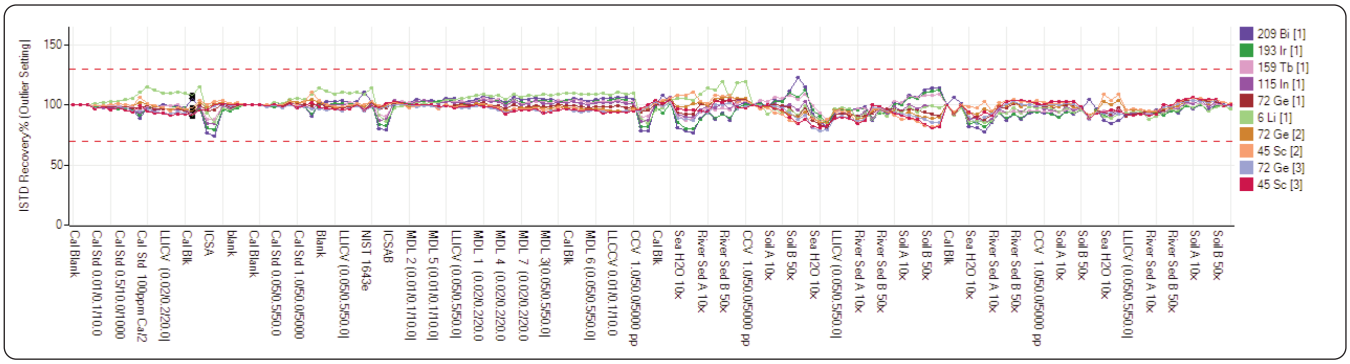

Figure 3. *ISTD stability over 156 runs, 14.8 hours. EPA 6020A lower control limit is 70% (lower dashed line). While there is no upper limit specified in EPA 6020A, 130% is displayed as the upper limit. Due to space limitations, not all sample names are shown.*

Conclusions

EPA Method 6020A is applicable for a wide range of elements in samples ranging from clean waters to highly contaminated soils or sludges. Because of this, contract laboratories running Method 6020A may not have detailed information on the composition and concentration of samples analyzed together in a single sequence. The Agilent 7700x ICP-MS is uniquely qualified to perform this difficult application for a number of reasons. All samples, regardless of composition or concentration can be analyzed using a single cell gas mode (helium mode), and no prior knowledge of the sample is necessary. The built-in High Matrix Introduction system (HMI) allows most samples to be analyzed without the need for further dilution after initial sample preparation. Additionally, the HMI significantly improves plasma robustness, which minimizes internal standard failures and extends the number of samples that can be run between calibrations. All of these benefits translate into simpler, faster, more reliable analysis of complex environmental samples.

Reference

1. Steven Wilbur and Emmett Soffey, "Meeting Worldwide Regulatory Requirements for the Analysis of Trace Metals in Drinking Water Using the Agilent 7500c ICP-MS", Agilent Application Note 5988-8902EN

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