

Introduction

US EPA Method 6020A (Rev 4, February 07) is applicable to the determination of sub- $\mu\text{g/L}$ 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).

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

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.

⁴⁵ Sc	¹³ C ¹⁶ O ₂ , ¹² C ¹⁶ O ₂ H, 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, 1

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

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 (ORS³) 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.

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.

$$I = \frac{I_i}{I_j} \cdot \left(\frac{r_i}{r_j} \right) \cdot U = \frac{I_i}{I_j} \cdot \left(\frac{r_i}{r_j} \right)$$

Parameter	Value	Value
	No gas mode	He mode

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.

$$I = \frac{ii}{l} (\%) \quad I = \frac{li}{i} (\%)$$

* $r = \frac{li}{i}$

Mean n=5

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].

	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

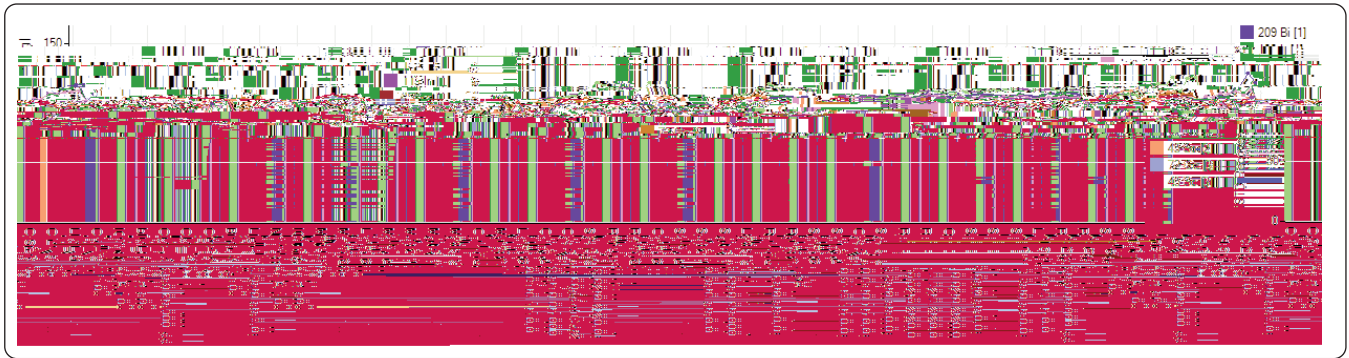
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$$\frac{C_{spike}}{C_{matrix}} = \frac{I_{spike}}{I_{matrix}} \cdot \frac{1}{k}$$

$$\frac{C_{spike}}{C_{matrix}} = \frac{I_{spike}}{I_{matrix}} \cdot \frac{1}{\frac{I_{matrix}}{C_{matrix}}}$$

$$C_{matrix} = \frac{I_{matrix}}{k}$$

	Matrix Spike			Matrix Spike Duplicate			RPD
	Mean	%RSD	%Recovery	Mean	%RSD	%Recovery	
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



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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

