Application Note: 40619

US EPA SW-846 Method 6020A Using the XSERIES 2 ICP-MS

Key Words

- Environmental Analysis
- SW-846 Method 6020/6020A
- Productivity Pack
- US EPA

1. Introduction

This Application Note describes the use of the Thermo Scientific XSERIES 2 ICP-MS for SW-846 Method 6020A compliant analysis. It gives data showing compliance with each of the requirements and highlights the integrated system tools specifically designed to aid compliance. The data shown was generated using the procedures and solutions supplied in the Thermo Scientific EPA Methods Productivity Pack (Part Number 4600430). See also BR40715, *XSERIES 2 ICP-MS: EPA Methods Productivity Pack*.

2. Background

EPA History

In 1970, the United States government established the Environmental Protection Agency (EPA) in response to growing public demand for cleaner water, air and land. Prior to this, the national government was not structured to deal with pollution that caused harm to human health and degraded the environment. The EPA was tasked with repairing the damage already done and moving towards a cleaner environment. Its mission is to protect human health and to safeguard the natural environment. The Agency consists of 18,000 people in Headquarters, program offices, 10 regional offices and 17 labs across the US. The EPA provides leadership in the nation's environmental science, research, education and assessment efforts and works closely with other federal agencies and local government to develop and enforce regulations under existing environmental law. The Agency is responsible for researching and setting national standards for a variety of environmental programs and delegates the responsibility for issuing permits, and monitoring and enforcing compliance, to local government. Where national standards are not met, the EPA can issue sanctions and take other steps to assist local government in reaching the desired levels of environmental quality. The Agency also works with industries and all levels of government in a wide variety of voluntary pollution prevention programs and energy conservation efforts.

Office of Solid Waste

The EPA's Office of Solid Waste (OSW) regulates all waste under the Resource Conservation and Recovery Act (RCRA). The RCRA's goals are to:

1. Protect the public from the hazards of waste disposal
2. Conserve energy and natural resources by recycling and recovery
3. Reduce or eliminate waste, and
4. Clean up waste, which may have spilled, leaked, or been improperly disposed of.

Hazardous wastes come in many varieties. Chemical, metal, and furniture manufacturing are some examples of processes that create hazardous waste. The RCRA tightly regulates all hazardous waste from production to disposal. The RCRA also controls garbage and industrial waste. Common garbage is municipal waste, which consists mainly of paper, yard trimmings, glass, and other materials. Industrial waste is process waste that comes from a broad range of operations. Some wastes are managed by other federal agencies or state laws. Examples of such wastes are animal waste, radioactive waste, and medical waste.

The EPA publication SW-846, entitled *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods*, is the OSW's official compendium of analytical and sampling methods that have been evaluated and approved for use for analysis relating to the RCRA regulations. SW-846 functions primarily as a guidance document setting forth acceptable, although not required, methods for the regulated and regulatory communities to use in responding to RCRA-related sampling and analysis requirements. SW-846 is a multi-volume document that changes over time as new information and data are developed. It was first issued by the EPA in 1980 and is currently in its fourth edition. Advances in analytical instrumentation and techniques are continually reviewed by the OSW and incorporated into periodic updates to SW-846 to support changes in the regulatory program and to improve method performance and cost effectiveness. To date, the EPA has finalized Updates I, II, IIA, IIB, III and IIIA of the SW-846 manual, and the updated and fully integrated manual contains approximately 3500 pages. The Methods Team of OSW has also made Draft Updates IVA and IVB available for public use.

The SW-846 volume 6020 describes the use of ICP-MS instrumentation for determining a variety of metallic elements in aqueous and solid media. In draft edition IVA, the method was replaced with 6020A.

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Methods 6020 and 6020A[1]

Both methods provide guidelines on general laboratory practices such as sample preparation, instrument setup, calibration of analytes, and interference correction equations. They also provide specific rules on various analytical practices that must be followed, including elements covered, required isotopes, quality control practices and instrument validation. Since both methods are well established and readily available in the public domain they have become widely adopted as templates for methodologies used by a host of laboratories undertaking environmental analysis world-wide. The requirements of these two important methods are broadly similar with the aim of the protocol being to ensure a consistently high quality of analytical data by enforcing compliance with a variety of stringent instrument and analytical performance checks, as outlined in Tables 1 and 2. Method 6020A extends the protocol scope to include mercury (after fixing all analytical solutions with 2 mg/L gold) and contains an alteration on interference checking in that the concentration of interferent species is increased in the interference check solutions.

[1]Note that Method 6020A, along with all Draft Update IVA SW-846 methods, may be downloaded from the EPA OSW website: http://www.epa.gov/SW-846/up4a.htm#6_series. Update III methods, including 6020, may be downloaded from the following webpage: http://www.epa.gov/epaoswer/hazwaste/test/6_series.htm.

CHECK CODE	CHECK NAME	PURPOSE	FREQUENCY	LIMITS
-	Mass Calibration/ resolution setting	ensures the correct mass is measured at its maximum and that peaks are properly resolved	prior to each analytical run (daily)	masses measured must not deviate by more than 0.1 amu from their nominal position and peak width must be <0.9amu at 10 % peak height
-	Stability and precision	ensures the instrument is properly optimised and thermally stable	prior to each analytical run (daily)	<5 % RSD on at least 4 measurements
-	Calibration	calibrates the instrument response for measurement	daily or when required	-
IDL	Instrument detection limit	estimates the detection limit of the instrument from 7 analyses of a blank over 3 non-consecutive days	every 3 months or after major instrument maintenance or hardware replacement	-

Table 1 - Summary of Instrument Calibration and Check Requirements

QC CODE	QC NAME	PURPOSE	FREQUENCY	LIMITS
ICV	Initial Calibration Verification	checks the calibration against a second calibration source	After initial calibration	90-110 %
ICB	Initial Calibration Blank	initial check of read-back at blank level	After initial calibration	<3* IDL
ICSA	Interference Check Solution A	checks for freedom from interference	After initial calibration	No specific requirements
ICSAB	Interference Check Solution AB	checks that analytes are accurately measured in an interference-producing matrix	After initial calibration	No specific requirements

Table 2 - Summary of Quality Control Requirements

QC CODE	QC NAME	PURPOSE	FREQUENCY	LIMITS
CCV	Continuing Calibration Verification	a continuing periodic check on accuracy and drift	After each calibration and every 10 samples	90-110 %
CCB	Continuing Calibration Blank	a continuing periodic check on the read-back at blank levels	After each calibration and every 10 samples	<3* IDL
PDS	Post Digestion Spike	checks the recovery of analytes spiked into an unknown sample after preparation (digestion)	1 per 20 samples per matrix	75-125 %
DUP	Duplicate	checks the reproducibility of results by analysing an unknown sample in duplicate	1 per 20 samples per matrix	±20% RPD
SER	Serial Dilution	checks for matrix effects by assessing the variation of results for an unknown sample before & after dilution	1 per 20 samples per matrix	±10 % of the original undiluted result after dilution correction
LCS	Laboratory Control Sample	checks the accuracy of the entire analytical process	Every 20 samples	80-120 %

Table 2 - Summary of Quality Control Requirements (continued)

3. Experimental

3.1 Equipment

An XSERIES 2 ICP-MS (Thermo Fisher Scientific, Bremen, Germany) was setup in the standard configuration, using an ASX-510 autosampler (Cetac, Omaha, Nebraska, USA). Internal standard was added on-line, using a Y-piece (On-line Internal Standard Addition Kit P/N 4600431). The instrument was optimized using the autotune function when required. The instrument parameters are given in Table 3.

PARAMETER	VALUE
RF Power (W)	1400
Cool Gas Flow (L/min)	13
Auxiliary Gas Flow (L/min)	0.8
Nebuliser Gas Flow (L/min)	0.85-0.90
Sample Uptake Rate (mL/min)	0.4 approx.
Sample Introduction System	Concentric nebulizer with low-volume impact bead spraychamber (not cooled) and one-piece torch (1.5mm ID injector)
Cones	Nickel, Xi Design
Detector	Simultaneous pulse/analogue
Uptake Time	25 seconds at 50 rpm
Stabilization Delay	10 seconds at 17 rpm
Wash Time	40 seconds at 50 rpm
Survey Runs	1 - scanning
Main Runs	3 - peak jumping
-Number of Points per Peak	1
-Dwell Time / Point	5 - 50 ms
-Number of Sweeps / Replicate	25
Internal Standardization Technique	Interpolation, using ^{6}Li, ^{45}Sc, ^{115}In, ^{159}Tb
Total Time per Sample	2:45 minutes

Table 3 - XSERIES 2 Parameters

3.2 Calibration Solutions

High purity reagents were used throughout. Ultra pure water of resistivity >18 M cm (Milli-Q) was used, along with super purity grade nitric and hydrochloric acids (Romil, Cambridge, UK). All analytical solutions were prepared from ICP-MS grade stock standards from the EPA Productivity Pack solutions (Thermo Scientific P/N 4600430) and reference samples (NIST, Gaithersburg, MD, USA) were analysed along with known and unknown samples courtesy of the Environment Agency, UK. Table 4 gives the calibration concentrations.

STANDARD	CONCENTRATION
Low Concentration Elements - Standard 1	250 µg/L Be, Al, V, Cr, Mn, Co, Ni, Cu, Zn, As, Se, Ag, Cd, Sb, Ba, Tl, Pb
Low Concentration Elements - Standard 2	500 µg/L Be, Al, V, Cr, Mn, Co, Ni, Cu, Zn, As, Se, Ag, Cd, Sb, Ba, Tl, Pb
High Concentration Elements - Standard 1	50 mg/L Na, Mg, K, Ca, Fe
High Concentration Elements - Standard 2	100 mg/L Na, Mg, K, Ca, Fe

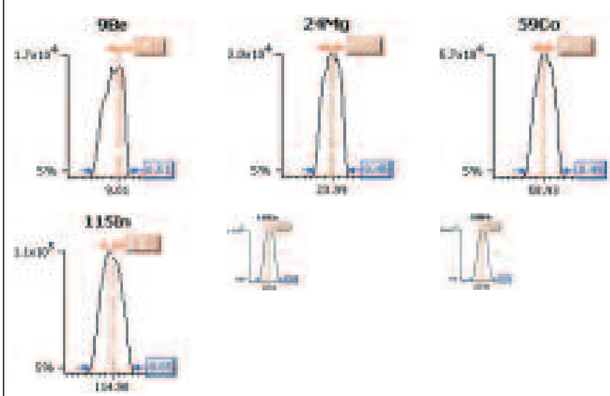
Table 4 - Calibration Standards - Concentrations

3.3 Instrument Checks

To ensure that the mass-calibration, resolution and stability requirements are met, the XSERIES 2 has critical hardware and PlasmaLab software features built-in. The hardware has two variable resolution modes allowing high and standard resolution settings to be defined. Standard resolution is typically set to give peaks of approximately 0.75 amu width at 5 % peak height, whilst high resolution is typically set to give around 0.4 amu. Normally the excellent abundance sensitivity specification of the XSERIES 2 quadrupole will allow low concentration analytes to be measured next to very large interferences at peak width settings of 0.75amu. However, these settings may be adjusted within the software to ensure no peak-tailing from high concentration species affects measurement of adjacent-mass low concentration analytes. PlasmaLab allows the instrument to be mass-calibrated whenever required. The mass calibration, the peak widths, and the precision over five measurements may be checked using a *Performance Report*. The *Performance Report* is a user definable test that may be run as part of an analytical method or separately as a setup function. Figures 1 and 2 show data from a Performance Report in the format in which it is generated.

Performance Report

Mass Calibration verification



Analyte	Limits			Results	
	Max. width	Min. width	Max. error	Peak width	Peak error
9Be	0.75	0.40	0.10	0.51	0.03
24Mg	0.75	0.40	0.10	0.45	-0.03
59Co	0.75	0.40	0.10	0.49	-0.01
115In	0.75	0.40	0.10	0.65	-0.05
140Ce	0.75	0.40	0.10	0.65	-0.03
208Pb	0.75	0.40	0.10	0.71	0.01

Figure 1 - Performance Report Results for Mass Calibration and Resolution Checks

Sample details

Acquired at : 12/12/2002 14:08:12
Report name : EPA ILM05.2 / 6020A 2.1 [12/12/2002 13:56:01]

Sensitivity and stability results
Acquisition parameters

Sweeps : 180

run	time	5Bkg	9Be	24Mg	59Co	115In	140Ce	156Ce o	208Pb	220Bkg
Dwell (mSecs)		100.0	10.0	10.0	10.0	10.0	10.0	30.0	10.0	100.0
Limits	% RSD	-	2.0 %	2.0 %	2.0 %	2.0 %	2.0 %	-	2.0 %	-
	Countrate	<2	>5000	>5000	>10000	>50000	>10000	-	>25000	<2
1	14:08:24	0.000	16797	33832	61243	112879	116767	1962	100691	0.222
2	14:09:23	0.000	16640	33338	61235	113079	116573	1935	100713	0.111
3	14:10:23	0.000	16894	33514	61133	113174	117136	1964	100805	0.444
4	14:11:23	0.167	17027	33294	61436	112328	117146	1948	100657	0.000
5	14:12:23	0.056	16536	33001	61020	112235	116563	1998	100517	0.056
x		0.044	16779	33396	61214	112739	116837	1961	100677	0.167
SD		0.07	195	305	153	432	289	23	104	0.18
% RSD		162.980	1.168	0.916	0.252	0.383	0.248	1.209	0.104	105.409

Ratio results

RUN	TIME	156Ce O/140Ce
	Ratio limits	< 0.0200
1	14:08:24	0.017
2	14:09:23	0.017
3	14:10:23	0.017
4	14:11:23	0.017
5	14:12:23	0.017
x		0.0168
SD		0.00
% RSD		1.2931

Result : The performance report passed.

Figure 2 - Performance Report Results for Sensitivity and Stability Checks

3.4 Method Development

Prior to running real samples, 6020A requires that several checks are performed. This section outlines the method requirements and details proof work to validate the instrument.

Interference Study

Appropriate interference corrections must be implemented and although the EPA methods suggest many theoretical correction equations including factors, they recommend that the actual factors used should be empirically determined for each individual instrument.

An interference correction strategy was formulated and assessed on a standard XSERIES 2 instrument by running high purity single element calibrations reflecting likely environmental sample matrix components. Potential interferents studied include Ca, Na, Fe, Al, Mg, Ti, Mo, P, K, S, C, and Cl. Interferences were observed by inspecting the countrates for analyte species as a function of increasing concentration of the interferent species. Appropriate ratios were used to calculate correction factors where necessary. Table 5 gives the interference correction equations used during the XSERIES 2 analytical performance assessment. Note that these correction factors were derived during several days of tests on two different instruments. The same set of factors were used for all subsequent analysis on two instruments after the evaluation, showing that the interference corrections are extremely stable and accurate from day to day, even with different instruments.

PARAMETER	VALUE
Analyte	Correction Equation
51V	= 51M - 3.0460 * 53Cl O
53Cl O	= 53M - 0.1140 * 52Cr
52Cr	= 52M - 0.0050 * 13C
56Fe	= 56M - 0.1500 * 43Ca
60Ni	= 60M - 0.0020 * 43Ca
75As	= 75M - 2.9000 * 77ArCl
77ArCl	= 77M - 0.8000 * 82Se
82Se	= 82M - 1.0010 * 83Kr
108MoO	= 1805M - 0.7120 * 106Cd
111Cd	= 111M - 0.9820 * 108MoO
114Cd	= 114M - 0.0270 * 118Sn
115In	= 115M - 0.0140 * 118Sn
123Sb	= 123M - 0.1240 * 125Te
208Pb	= 208M + 1.0000 * 206Pb + 1.0000 * 207Pb

Table 5 - Interference Correction Equations

Linear Dynamic Range (LDR)

The LDR for the XSERIES 2 instrument was assessed in the analytical configuration used for analysis by measuring standards of increasing decades of concentration, from 1 µg/L - 10 mg/L (50 µg/L - 500 mg/L for Na, Mg, K, Ca, Fe). Table 6 gives the linear range found for the XSERIES 2.

ANALYTE	LINEAR RANGE (mg/L)
Be, Al, V, Cr, Mn, Co, Ni, Cu, Zn, As, Se, Ag, Cd, Sb, Ba, Tl, Pb	10
Na, Mg, K, Ca, Fe	500

Table 6 - Linear Ranges

Instrument Detection Limit (IDL)

The 6020A document specifies that IDLs must be determined every three months for each instrument. There are no specific requirements, but the IDLs form the basis of subsequent QC blank checking

6020A describes a protocol for determining the MDL as follows. The instrument hardware and method must be set up as intended for sample analysis. The instrument detection limit (IDL) is estimated from the mean standard deviation of a multiple replicate blank analysis, in concentration units. Seven repeats are required over three non-consecutive days. The data for IDL calculation must have all the required calculations included, e.g. interference correction equations as these can have a substantial influence on the IDL. Table 7 lists IDL values obtained. The ICP-MS systems these data were obtained from were instruments in regular use in an open laboratory environment. The hardware components were exposed to a wide range of sample types, i.e. the cones, spraychamber and sample introduction system were conditioned with environmental matrices before data collection. These method detection limits represent achievable data using a basic XSERIES 2 instrument in a standard laboratory environment using ultra pure water and super pure acids.

IDLS (3 BATCHES OF 7 FULL ANALYSES)

ELEMENT	UNITS	1% HNO3	2 % HCL
9Be	µg/L	0.006	0.01
23Na	mg/L	0.0006	0.003
25Mg	mg/L	0.00003	0.0003
27Al	µg/L	0.03	0.2
39K	mg/L	0.002	0.01
44Ca	mg/L	0.001	0.006
51V	µg/L	0.01	0.3
52Cr	µg/L	0.01	0.1
55Mn	µg/L	0.003	0.02
56Fe	mg/L	0.0006	0.001
59Co	µg/L	0.001	0.002
60Ni	µg/L	0.01	0.02
65Cu	µg/L	0.006	0.01
66Zn	µg/L	0.01	0.03
75As	µg/L	0.03	0.2
77Se	µg/L	0.06	2
78Se	µg/L	0.2	1
82Se	µg/L	0.1	0.1
107Ag	µg/L	0.06	0.6
111Cd	µg/L	0.02	0.1
114Cd	µg/L	0.001	0.002
121Sb	µg/L	0.001	0.02
137Ba	µg/L	0.006	0.006
205Tl	µg/L	0.001	0.002
208Pb	µg/L	0.001	0.003

Table 7 - IDLs in 1 % HNO3 and 2 % HCl

3.5 Performance Evaluation

The performance of an XSERIES 2 was evaluated by running the quality control system required for 6020A. Data were acquired over three non-consecutive days, at the same time as acquiring the IDL data. Samples representing a variety of matrices, including tap water, river water, industrial effluent, digestates of soil, sediment and biota (liver tissue), were analysed. Each sample was subjected to the QC requirements of 6020A, i.e. analysed in duplicate, after serial dilution and after spike addition.

The sample list was as follows:

SAMPLE NAME	SAMPLE TYPE	PURPOSE
Instrument Cal and cross-cal	Instrument Setup	Mass calibration, detector voltage set-up
Tune	Instrument Setup	Performance report and Autotune if required
Blank	Blank	
LoCal1	Fully Quant Standard	
LoCal2	Fully Quant Standard	Calibration
HiCal1	Fully Quant Standard	
HiCal2	Fully Quant Standard	
ICV	QC Sample	Calibration accuracy check with 2nd source standard
ICB	QC Sample	Initial blank check
CCV	QC Sample	Calibration accuracy/drift check
CCB	QC Sample	Blank check
LCS	QC Sample	Accuracy check with NIST 1640 River Water
ISCA 6020A	QC Sample	Blank check in the presence of interferences
ICSAB 6020A	QC Sample	Recovery check in the presence of interferences
CCV	QC Sample	Calibration accuracy/drift check
CCB	QC Sample	Blank check
Sample 1	Unknown	Unknown sample 1
Sample 1 DUP	QC Sample	Unknown sample 1 repeated
Sample 1 SER	QC Sample	Unknown sample 1 diluted 1+4 with 1 % nitric acid
Sample 1 SPK	QC Sample	Unknown sample 1 spiked
Sample 2	Unknown	Unknown sample 2
TO		
Sample n	Unknown	Unknown sample n
CCV	QC Sample	Calibration accuracy/drift check
CCB	QC Sample	Blank check

4. Results and Discussion

4.1 Initial Calibration Verification (ICV)

The ICV sample is a solution prepared from an alternative source of starting materials to those of the calibration. Its purpose is to check the accuracy immediately after calibration. The ICV was set at 40 % of the top standard in this case. The measured concentrations must be within 10 % of the known values. Table 8 gives the results of ICV measurements from 36 determinations over three non-consecutive days.

ANALYTE	UNITS	MEAN (N=36)	KNOWN	% REC
9Be	µg/L	191	200	96
23Na	mg/L	40	40	100
25Mg	mg/L	40	40	101
27Al	µg/L	198	200	99
39K	mg/L	40	40	100
44Ca	mg/L	40	40	100
51V	µg/L	201	200	101
52Cr	µg/L	198	200	99
55Mn	µg/L	196	200	98
56Fe	mg/L	40	40	101
59Co	µg/L	196	200	98
60Ni	µg/L	191	200	95
65Cu	µg/L	187	200	94
66Zn	µg/L	186	200	93
75As	µg/L	205	200	102
77Se	µg/L	956	1000	96
78Se	µg/L	957	1000	96
82Se	µg/L	959	1000	96
107Ag	µg/L	183	200	91
111Cd	µg/L	192	200	96
114Cd	µg/L	190	200	95
121Sb	µg/L	191	200	96
137Ba	µg/L	201	200	100
205Tl	µg/L	195	200	98
208Pb	µg/L	190	200	95

Table 8 - ICV Results

The results in Table 8 show that the calibration was consistent with the second source stock used for the ICV. The results (91-102 %) are within the required limits of 90-110 %. The result for Ag is slightly low at 91 %, although there are well known stability problems with this element due to precipitation as AgCl in the presence of chloride.

4.2 Continuing Calibration Verification (CCV)

The CCV sample is designed to continuously check accuracy by periodic analyses interspersed between analyses of unknowns. The CCV was set at 60 % of the top standard in this case. Again, the measured concentrations must be within 10 % of the known values. Table 9 gives the results of CCV measurements from 99 determinations over three non-consecutive days.

ANALYTE	UNITS	MEAN (N=99)	KNOWN	%REC
9Be	µg/L	284	300	95
23Na	mg/L	61	60	102
25Mg	mg/L	61	60	102
27Al	µg/L	310	300	103
39K	mg/L	62	60	103
44Ca	mg/L	62	60	103
51V	µg/L	304	300	101
52Cr	µg/L	299	300	100
55Mn	µg/	304	300	101
56Fe	mg/L	62	60	103
59Co	µg/L	299	300	100

Table 9 - CCV Results.

ANALYTE	UNITS	MEAN (N=99)	KNOWN	% REC
60Ni	µg/L	289	300	96
65Cu	µg/L	284	300	95
66Zn	µg/L	280	300	93
75As	µg/L	295	300	98
77Se	µg/L	282	300	94
78Se	µg/L	284	300	95
82Se	µg/L	282	300	94
107Ag	µg/L	289	300	96
111Cd	µg/L	287	300	96
114Cd	µg/L	285	300	95
121Sb	µg/L	293	300	98
137Ba	µg/L	304	300	101
205Tl	µg/L	297	300	99
208Pb	µg/L	293	300	98

Table 9 - CCV Results (continued)

The results given in Table 9 show that the instrument consistently gives accurate results, even after running the ICS solutions and real samples. The determined range (93-103 %) is well within the required range of 90-110 %.

4.3 Laboratory Control Sample (LCS)

In this case the River Water reference material, NIST 1640, was analyzed as a LCS. The results from 36 determinations over 3 non-consecutive days are summarized in Table 10. These must lie within 10 % of the known value.

ANALYTE	UNITS	MEAN (N=36)	REF VALUE	% REC
9Be	µg/L	36.58	34.94	105
23Na	mg/L	30.39	29.35	104
25Mg	mg/L	6.14	5.819	106
27Al	µg/L	52.23	52	100
39K	mg/L	0.98	0.994	99
44Ca	mg/L	7.15	7.045	101
51V	µg/L	12.86	12.99	99
52Cr	µg/L	37.73	38.6	98
55Mn	µg/L	122.5	121.5	101
59Co	µg/L	20.79	20.28	102
60Ni	µg/L	27.66	27.4	101
65Cu	µg/L	85.28	85.2	100
66Zn	µg/L	53.19	53.2	100
75As	µg/L	27.34	26.67	103
82Se	µg/L	22.82	21.96	104
111Cd	µg/L	23.26	22.79	102
114Cd	µg/L	22.93	22.79	101
121Sb	µg/L	13.42	13.79	97
137Ba	µg/L	149.9	148	101
208Pb	µg/L	27.06	27.89	97

Table 10 - LCS Results

The results given in Table 10 show that the instrument consistently produces accurate data for real environmental samples, such as the NIST River Water reference material, 1640. All measured values (97-106 %) are well within the allowable range of 90-110 %.

4.4 Interference Check Solutions (ICSA & ICSAB)

Solution ICSA is analysed to check the effect of interference on the results at blank levels, whilst ICSAB checks the recovery of analytes in the presence of interference. Both solutions contain the following interferent species: 2000 mg/L chloride, 300 mg/L Ca, 250 mg/L Na, Fe, 200 mg/L carbon, 100 mg/L Al, Mg, P, S, K, and 2 mg/L Mo, Ti. ICSAB additionally contains the following analytes: 50 µg/L Ag, 100 µg/L As, Cd, Se, Zn, 200µg/L Co, Cr, Cu, Mn, Ni, V. There are no specific requirements for the results of the interference checks. Table 11 gives the results for the ICS solutions.

		ICSA			ICSAB		
ANALYTE	UNITS	MEAN (N=30)	KNOWN	%REC	MEAN (N=30)	KNOWN	% REC
6Li	%	*71.74*			*70.94*		
9Be	µg/L	0.12			0.091		
23Na	mg/L	240	250	96	242	250	97
25Mg	mg/L	102	100	102	103	100	103
27Al	µg/L	100115	100000	100	100819	100000	101
39K	mg/L	104	100	104	105	100	105
44Ca	mg/L	318	300	106	323	300	108
45Sc	%	*70.87*			*70.71*		
51V	µg/L	2.0			205	200	103
52Cr	µg/L	0.90			199	200	99
55Mn	µg/L	2.9			199	200	99
56Fe	mg/L	253	250	101	255	250	102
59Co	µg/L	0.73			191	200	96
60Ni	µg/L	-1.14			175	200	88
65Cu	µg/L	1.9			169	200	84
66Zn	µg/L	13			89	100	89
75As	µg/L	0.49			91	100	91
77Se	µg/L	4.7			85	100	85
78Se	µg/L	4.6			86	100	86
82Se	µg/L	-0.30			80	100	80
107Ag	µg/L	1.9			32	50	64
111Cd	µg/L	0.33			87	100	87
114Cd	µg/L	1.14			87	100	87
115In	%	*74.00*			*73.71*		
121Sb	µg/L	0.66			0.58		
137Ba	µg/L	2.6			2.4		
159Tb	%	*77.80*			*78.51*		
205Tl	µg/L	0.033			0.025		
208Pb	µg/L	1.9			1.9		

Table 11 - ICS Solution Results

The results given in Table 11 show that accurate results are consistently achieved for the high concentration elements such as Mg, Al, K at the 100 mg/L level, Ca at the 300 mg/L, and Fe and Na at the 250 mg/L level. Accurate data were even achieved for Al at 100 mg/L after calibration for this analyte to only 0.5 mg/L. This demonstrates the excellent linear range of the instrument. The results of ICSA show that the presence of interferences do not contribute dramatically to the analyte signals at the blank level, with the majority of results in the single figure µg/L range or lower. This indicates that, where used, the interference correction equations work well, e.g. the case of As in the presence of chloride (ArCl interference) or Ni in the presence of Ca (CaO interference). Furthermore, where not used, the interference contributions are still extremely low due to the characteristics of the Xi interface, e.g. 77Se in the presence of chloride (ArCl interference). Two exceptions to the generally excellent ICSA results are Zn and Mn, which are slightly high due to the presence of contamination. The Mn contamination was confirmed by acquiring a mass spectrum in standard resolution mode for an independently prepared 250 mg/L Fe solution and a 50 ng/L Mn standard (Figure 4). This shows that even in the presence of 250 mg/L Fe, the mass 56 signal for Fe does not contribute to the Mn signal at mass 55.

The results of ICSAB show that accurate data may be achieved at the µg/L level in the presence of interferences, with the exception of Ag. The low Ag value is due to the precipitation of AgCl as the solution contains 2000 mg/L of chloride. The internal standard percentages show that the presence of high matrix levels do not produce excessive signal suppression, with the worst case being Li with approximately 30 % signal loss.

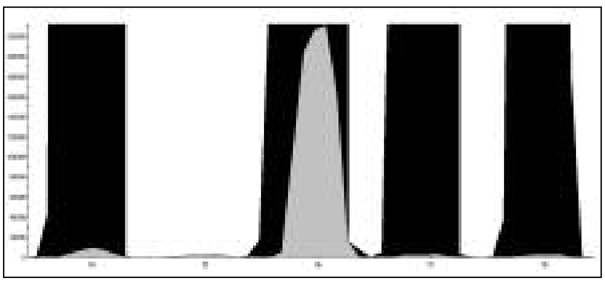


Figure 4 - Spectrum for 250 mg/L Fe (black) and 500 ng/L Mn (grey)

4.5 Sample AQC

The method requires that once every 20 samples per matrix, a sample must be analyzed in duplicate (DUP), after a 1+4 serial dilution (SER) and after the addition of a post digestion spike (PDS). The Relative Percentage Difference (RPD) is calculated for each duplicate and serial dilution (relative to the original sample) - see Equation 1. This test is not applied if either of the results is less than 50*IDL. The PlasmaLab software is able to automatically disqualify results from having this test applied due to the result being less than 50*IDL. Similarly, a spike recovery test will not be applied if the sample result is greater than a user definable percentage of the spiked concentration.

Equation 1 - Calculation of % RPD for Duplicates

$$\% \; RPD = 100 * (i - d) / \{(i + d) / 2\}$$

where i is the initial sample result, and d is the duplicate result

Equation 2 - Calculation of % RPD for Serial Dilutions

$$\% \; RPD = 100 * (i - s) / i$$

where i is the initial sample result, and s is the dilution corrected serial dilution result

Equation 3 - Calculation of % Spike Recovery

$$\% \; REC = 100 * (a - i) / k$$

where i is the initial, unspiked sample result, a is the sample result after spike addition, and k is the known spike concentration

The method requires that the RPD values are less than 20 %, while the spike recoveries are within 25 % of the known addition value. Tables 12-16 give the results and AQC results for a variety of sample types treated in this way. Tables 14 gives the results for multiple analyses of a sediment reference material digested using an aqua regia digestion.

			TAP WATER (N=9)			
ANALYTE	UNITS	SAMPLE RESULT	DUP (% RPD)	SER (% RPD)	SPIKE AMOUNT (µg/L)	SPIKE REC %
9Be	µg/L	0.02			50	118
23Na	mg/L	10.9	0.55	0.64		
25Mg	mg/L	3.86	0.83	0.31		
27Al	µg/L	11.9			2000	89
39K	mg/L	1.63	1.3	2		
44Ca	mg/L	31.9	0.5	4.9		
51V	µg/L	0.278			500	100
52Cr	µg/L	0.147			200	98
55Mn	µg/L	1.92			500	99
56Fe	mg/L	0.05				
59Co	µg/L	0.11			500	99
60Ni	µg/L	2.30			500	98
65Cu	µg/L	199	0.57	0.37	250	98
66Zn	µg/L	189	0.78	3.4	500	97
75As	µg/L	4.82			40	100
82Se	µg/L	0.53			10	93
107Ag	µg/L	0.415				
111Cd	µg/L	0.067			50	98
114Cd	µg/L	0.097			50	97
121Sb	µg/L	0.122			100	93
137Ba	µg/L	89.4			2000	105
205Tl	µg/L	0.005				
208Pb	µg/L	9.82			20	94

Table 12 - Tap Water Results

Very few analytes in the tap water were above 50*IDL and therefore few duplicate or serial dilution tests could be applied. Those that are, show relative percentage differences (RPDs) that were well within the allowable limit of 20 %. The spike recoveries in this matrix are well within the allowable range of 75-125 %. Silver was not tested on these spiked samples due to the presence of high chloride.

			EFFLUENT (N=9)			
ANALYTE	UNITS	SAMPLE RESULT	DUP (% RPD)	SER (% RPD)	SPIKE AMOUNT (µg/L)	SPIKE REC %
9Be	µg/L	14.2	5.0	3.9	50	96
23Na	mg/L	23.2	2.2	1.5		
25Mg	mg/L	12.4	0.9	4.9		
27Al	µg/L	440	2.4	1.2	2000	93
39K	mg/L	4.15	1.9	1.9		
44Ca	mg/L	77.1	2.2	0.5		
51V	µg/L	60.7	3.1	3.0	500	96
52Cr	µg/L	32.5	3.4	3.6	200	94
55Mn	µg/L	75.5	4.0	1.7	500	94
56Fe	mg/L	1.81	2.5	5.0		
59Co	µg/L	58.6	2.6	3.3	500	92
60Ni	µg/L	57.7	3.0	4.3	500	91
65Cu	µg/L	82.8	2.8	5.2	250	91
66Zn	µg/L	67.2	4.5	2.8	500	91

Table 13 - Effluent Results

EFFLUENT (N=9)

ANALYTE	UNITS	SAMPLE RESULT	DUP (% RPD)	SER (% RPD)	SPIKE AMOUNT (μg/L)	SPIKE REC %
75As	μg/L	38.6	1.8	1.2	40	93
82Se	μg/L	21.2	1.4	2.3	10	95
107Ag	μg/L	2.72				
111Cd	μg/L	14.6	0.3	3.7	50	93
114Cd	μg/L	14.5	1.9	5.6	50	93
121Sb	μg/L	18.6	2.5	0.3	100	93
137Ba	μg/L	456	1.4	4.7	2000	102
205Tl	μg/L	12.5	1.1	3.9		
208Pb	μg/L	12.3	1.4	4.4	20	96

Table 13 - Effluent Results (continued)

Most analytes in the effluent were above 50*IDL and all show relative percentage differences (RPDs) that are well within the allowable limit of 20 %. The spike recoveries in this matrix are well within the allowable range of 75-125 %. Silver was not tested on these spiked samples due to the presence of high chloride.

CLYDE SEDIMENT REFERENCE MATERIAL 1 (N=9)

ANALYTE	UNITS	SAMPLE RESULT	KNOWN (mg/kg)	%REC	DUP (% RPD)	SER (% RPD)	SPIKE AMOUNT (μg/L)	SPIKE REC %
9Be	mg/kg	1.95			0.4		50	98
23Na	mg/kg	5030	4515	111	1.5	1.7		
25Mg	mg/kg	5480	4667	117	0.5	5.1		
27Al	mg/kg	33575	24975	134	0.3	2.5	2000	121
39K	mg/kg	2070	1982	104	1.0	4.4		
44Ca	mg/kg	4120	3455	119	0.0	9.3		
51V	mg/kg	32.5	30.9	105	0.9	6.9	500	102
52Cr	mg/kg	157	153	102	0.9	4.5	200	100
55Mn	mg/kg	385	364	106	1.6	4.9	500	102
56Fe	mg/kg	25100	23786	106	1.9	5.1		
59Co	mg/kg	10.2	10.5	97	0.2	5.1	500	102
60Ni	mg/kg	27.7	28	99	0.3	6.1	500	98
65Cu	mg/kg	97.0	96	101	0.8	6.9	250	97
66Zn	mg/kg	294	290	101	0.7	6.2	500	98
75As	mg/kg	10.6	11.1	96	2.5	6.6	40	99
82Se	mg/kg	1.27					10	97
107Ag	mg/kg	5.51						
111Cd	mg/kg	1.18	1.045	113	4.6	1.3	50	99
114Cd	mg/kg	1.04	1.045	100	0.9	5.4	50	100
121Sb	mg/kg	0.516					100	95
137Ba	mg/kg	264					2000	107
205Tl	mg/kg	0.255						
208Pb	mg/kg	125	123	101	1.4	1.0	20	100

Table 14 - Sediment Results

Most analytes in the Clyde Sediment Digest were above 50*IDL and all show relative percentage differences (RPDs) that are well within the allowable limit of 20 %. The spike recoveries in this matrix are well within the allowable range of 75-125 %. Silver was not tested on these spiked samples due to the presence of high chloride from the Aqua Regia extraction. The measured values agree extremely well with the reference values, all being within 20 % of the known value, with the exception of Al which is slightly high, possibly due to contamination.

STONY SOIL DIGEST (N=9)

ANALYTE	UNITS	SAMPLE RESULT	DUP (% RPD)	SER (% RPD)	SPIKE AMOUNT (μg/L)	SPIKE REC %
9Be	mg/kg	3.28	9.4	4.6	50	99
23Na	mg/kg	775	0.2	4.5		
25Mg	mg/kg	11060	2.7	5.7		
27Al	mg/kg	25843	0.6	2.7	2000	95
39K	mg/kg	12690	1.0	2.1		
44Ca	mg/kg	32400	0.8	2.7		
51V	mg/kg	476	0.3	2.3	500	98
52Cr	mg/kg	122.0	0.6	2.2	200	96
55Mn	mg/kg	824	0.0	0.6	500	97
56Fe	mg/kg	7300	2.2	1.2		
59Co	mg/kg	3.3	4.1		500	96
60Ni	mg/kg	20.6	0.9	1.7	500	94
65Cu	mg/kg	486	0.4	2.6	250	93
66Zn	mg/kg	16	3.8	1.1	500	94
75As	mg/kg	1.6	4.9		40	96
82Se	mg/kg	9.64			10	99
107Ag	mg/kg	4.27				
111Cd	mg/kg	0.1			50	96
114Cd	mg/kg	0.2			50	95
121Sb	mg/kg	0.83			100	94
137Ba	mg/kg	31			2000	102
205Tl	mg/kg	0.872				
208Pb	mg/kg	26	2.3	2.8	20	94

Table 15 - Soil Digest Results

Most analytes in the Stony Soil were above 50*IDL and all show relative percentage differences (RPDs) that are well within the allowable limit of 20 %. The spike recoveries in this matrix are well within the allowable range of 75-125 %. Silver was not tested on these spiked samples due to the presence of high chloride from the Aqua Regia extraction.

BIOTA DIGEST (N=9)

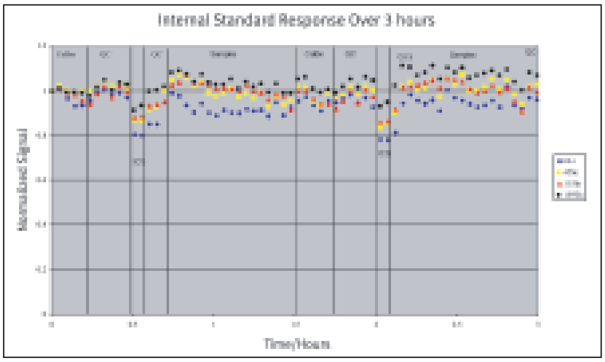
ANALYTE	UNITS	SAMPLE RESULT	DUP (% RPD)	SER (% RPD)	SPIKE AMOUNT (μg/L)	SPIKE REC %
9Be	mg/kg	0.03			50	97
23Na	mg/kg	4700	0.5			
25Mg	mg/kg	510	0.3	4.7		
27Al	mg/kg	22			2000	96
39K	mg/kg	6940	1.2	0.5		
44Ca	mg/kg	400				
51V	mg/kg	1.0			500	96
52Cr	mg/kg	0.7			200	96
55Mn	mg/kg	4			500	97
56Fe	mg/kg	300				
59Co	mg/kg	0.8			500	96
60Ni	mg/kg	1.4			500	95
65Cu	mg/kg	21	1.1	0.6	250	95
66Zn	mg/kg	73	2.1	3.2	500	94
75As	mg/kg	2.3	3.0		40	94
82Se	mg/kg	6.80	5.7		10	97
107Ag	mg/kg	5.54				
111Cd	mg/kg	1.4			50	96
114Cd	mg/kg	1.5	0.2		50	94
121Sb	mg/kg	0.66			100	92
137Ba	mg/kg	5			2000	105
205Tl	mg/kg	0.276				
208Pb	mg/kg	1			20	94

Table 16 - Biota Digest Results

Very few analytes in the Biota digest sample were above 50*IDL and therefore few duplicate or serial dilution tests could be applied. Those that are, show relative percentage differences (RPDs) that are well within the allowable limit of 20 %. The spike recoveries in this matrix are well within the allowable range of 75-125 %. Silver was not tested on these spiked samples due to the presence of high chloride from the Aqua Regia extraction.

4.6 Internal Standard Response and Stability

Graph 1 shows the internal standard responses, (normalized to the initial response for the calibration blank) for a three-hour analytical duration, running real samples. It is seen that the overall drift during the two hour period is negligible and samples rarely produce internal standard responses outside of ±10 % of that of the initial calibration blank. It is also seen that the high matrix ICS solutions produce a fairly modest 10-20 % suppression.



Graph 1 - Internal Standard Response over a 2-Hour Period Running Calibration, QCs and Samples

5. Conclusions

The XSERIES 2 demonstrates SW-846 method 6020A compliant analysis for a wide range of sample types and easily copes with the stringent interference checks and AQC requirements of the method. A combination of specifically designed hardware and software tools enables and simplifies 6020A compliant analysis as outlined below.

Mass calibration and resolution checking is made simple with the custom Performance Report and peaks are easily set to the required width using the variable resolution function. The Performance Report also monitors and records the precision over five measurements, allowing a "Tune" sample to be tagged to each sample run. Any deviations from acceptable performance are clearly flagged in red and the report ends with a simple, unambiguous *Pass* or *Fail* statement.

The unique Xi interface design produces low background equivalent concentrations, resulting in very low instrument detection limits (as seen in Table 7). It reduces the effective contribution of polyatomic species allowing robust, reproducible interference correction (as seen in Table 11), and enhances stability when analyzing solutions containing high levels of matrix components, e.g. Ca, Na, Fe, Mg, K. This is demonstrated by the consistent CCV results (see Table 9) and the stability of the internal standards (see Graph 1). The unique response properties of this interface technology coupled with the dual mode simultaneous detector allow unrivalled linear range. This further improves productivity by reducing the number of dilutions required.

The PlasmaLab software has a built-in QC checking capability that is specifically designed to meet the requirements of EPA methods. Each QC type (ICV, CCV, LCS, etc) is available as a default in the QC set-up page and the user can also define their own QC tests, as required. The results display page visually flags results that are outside the allowed range making validation a simple process. Percentage recoveries can be automatically calculated for any QC sample or spiked sample and percentage differences can be calculated for DUP and SER samples. A variety of user-selectable automated actions can be set-up to ensure fully compliant analysis is achieved during an unattended run.

PlasmaLab enables automated initiation of measurement and completion of washout using the intelligent Monitored Uptake / Washout features. This reduces the amount of non-productive time and maximises useful analytical time. The productivity tools in PlasmaLab in combination with the rapidity of the XSERIES 2 quadrupole and the low-volume sample introduction system result in the fastest analysis with complete compliance. Samples in this study were being processed at a speed of 1 sample every 2 minutes and 45 seconds, or 22 samples per hour. This makes the XSERIES 2 the ultimate ICP-MS for cost-effective elemental analysis.

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