

US EPA Method ILM05.2D Using the XSERIES 2 ICP-MS

Key Words

- Environmental Analysis
- CLP ILM05.2
- US EPA
- Productivity Pack

1. Introduction

This Application Note describes the use of the Thermo Scientific XSERIES 2 ICP-MS for CLP method ILM05.2D 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.

Contract Laboratory Program

The US EPA Contract Laboratory Program (CLP) is a national network of EPA personnel, commercial laboratories, and support contractors. The CLP supports the EPA's Superfund program, created under the 1980 Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA), and currently under the 1986 Superfund Amendments and Reauthorization Act

(SARA). The CLP's primary service is the provision of analytical data of known and documented quality, through its routine analytical services (RAS), to its customers. Currently, the CLP offers three RAS services: multi-media, multi concentration organic analytical services; multi-media, multi-concentration inorganic analytical services; and low concentration organic analytical services. All analytical services are performed by EPA-approved contract laboratories that must meet stringent requirements and standards in order to be a part of the CLP. Each sample processed by the CLP is properly documented to ensure timely and accurate analysis for all requested parameters. This process creates sample data that can be used in potential enforcement actions.

CLP data is used for a variety of purposes such as defining the nature and extent of contamination at Superfund sites, determining appropriate cleanup actions, determining emergency response and remedial actions, and enforcement/litigation activities. Furthermore, the data may be used in all stages of hazardous waste site investigations including site inspections, Hazardous Ranking System (HRS) scoring, remedial investigation/feasibility studies, and remedial design.

The CLP analytical contractors come from the nationwide community of chemical analytical laboratories. In order to become a CLP laboratory, a lab must first be awarded a contract. Fixed price contracts are awarded through the Government's bid process after bidders pass performance tests. Bidders must successfully analyze Performance Evaluation (PE) samples and pass a pre-award laboratory audit. Awards are then made to the lowest bidders. In addition, laboratories must meet stringent requirements and standards for equipment, personnel, laboratory practices, and analytical and Quality Control (QC) operations. EPA and CLP support contractors also continue to monitor CLP laboratory performance after contracts are awarded.

Each CLP laboratory plays an important role and is responsible for:

- Logging and maintaining all CLP samples received at their facilities;
- Documenting all processes and procedures associated with CLP samples;
- Analyzing samples and compiling data according to CLP requirements; and
- Submitting data deliverables in the specified time-frame.

All data deliverables are reviewed to ensure that the laboratories are meeting the administrative and technical requirements of their contracts.

The inorganic analysis undertaken by CLP laboratories is described in the document ILM05.2 - *US EPA Contract Laboratory Program Statement of Work for Inorganic Analysis, Multi-Media, Multi-Concentration*. Exhibit D, Part B describes the use of ICP-MS instrumentation for determining a variety of metallic elements.

Method ILM05.2 D¹

This method provides guidelines on general laboratory practices such as sample preparation, instrument setup, calibration of analytes, and interference correction equations. It also provides specific rules on various analytical practices that must be followed, including elements covered, required isotopes, quality control practices and instrument validation. Since EPA 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 aim of the protocol is to ensure a consistently high quality of analytical data by enforcing compliance with a variety of stringent instrument and analytical performance checks outlined in Tables 1 and 2.

¹ ILM05.2 can be downloaded from the EPA CLP website: <http://www.epa.gov/superfund/programs/clp/ilm5.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 <0.75amu at 5 % 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 5 measurements
-	Calibration	calibrates the instrument response for measurement	daily or when required	-
MDL	Method detection limit	assesses the detection limit of the method according to 40CFR136	annually or after major instrument maintenance or hardware replacement	50 % of Contract Required Quantitation Limit (CRQL)
LDR	Linear Dynamic Range	assesses the linear range of the instrument using 3 standards or more	quarterly or after major instrument maintenance or hardware replacement	high standard <±10 % of the expected value extrapolated from the low standards

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 each calibration	90-110 %
ICB	Initial Calibration Blank	initial check of read-back at blank level	After each calibration	<CRQL
CRI	Contract Required Quantitation Limit Check	checks accuracy at the required limit of quantitation	After each calibration and every 20 samples	70-130 % 50-150% for Co, Mn, Zn
ICSA	Interference Check Solution A	checks for freedom from interference	After each calibration	±3CRQL or ±20 % of the true value (whichever is the greater)
ICSAB	Interference Check Solution AB	checks that analytes are accurately measured in an interference-producing matrix	After each calibration	80-120 %
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	<CRQL
MXS	Matrix Spike	checks the recovery of a pre-preparation (digestion) spike on an unknown sample	1 per batch of samples	75-125 %
PDS	Post Digestion Spike	checks the recovery of analytes spiked into an unknown sample after preparation (digestion)	1 per batch of samples	75-125 %
DUP	Duplicate	checks the reproducibility of results by analyzing an unknown sample in duplicate	1 per batch of samples	±20 % Relative Percentage Difference (RPD)
SER	Serial Dilution	checks for matrix effects by assessing the variation of results for an unknown sample before & after dilution	1 per batch of samples	±10 % of the original undiluted result after dilution correction
LCS	Laboratory Control Sample	checks the accuracy of the entire analytical process	1 per batch of samples	80-120 %

Table 2 - Summary of Quality Control Requirements

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 minutes 45 seconds

Table 3 - XSERIES 2 Parameters

3.2 Calibration Solutions

High purity reagents were used throughout. Ultra pure water of resistivity >18MΩ 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, Ti, Pb
Low Concentration Elements - Standard 2	500 µg/L Be, Al, V, Cr, Mn, Co, Ni, Cu, Zn, As, Se, Ag, Cd, Sb, Ba, Ti, 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 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 0.75 amu. However, these settings may be adjusted within 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.

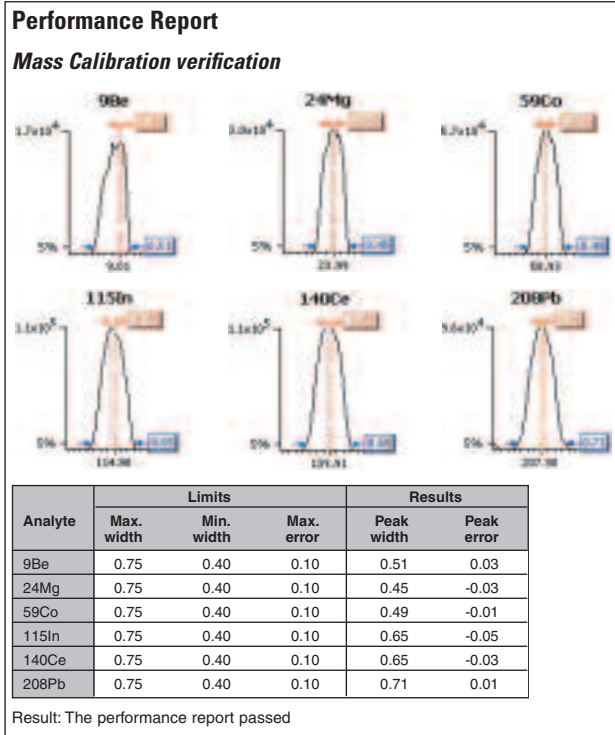


Figure 1 - Performance Report Results for Mass Calibration and Resolution Checks

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	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

3.4 Method Development

Prior to running real samples, ILM05.2 D requires that several checks are performed. This section outlines the method requirements and details proof work to validate the instrument.

Interference Study

Appropriate interference correction 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 an a standard 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
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	= 108M - 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)

Method ILM05.2D requires that the LDR of the instrument is assessed for each analyte by determining the signal responses from a minimum of three different concentration standards, one of which is close to the upper limit of the linear range. The linear calibration range used for the analysis of samples is determined from the resulting data. The upper LDR limit is defined as the point at which the observed signal is no more than 10 % below the level extrapolated from lower standards. Determined sample analyte concentrations that are

greater than 90 % of the determined upper LDR limit must be diluted and re-analyzed. The LDRs must be verified whenever changes in instrument hardware operating conditions indicate they should be re-determined, or verified quarterly.

The LDR for the 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 shows that the XSERIES 2 was linear up to at least the highest standards measured.

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

Table 6 - Linear Ranges

Method Detection Limit (MDL)

The ILM05.2D document specifies that MDLs must be determined annually for each instrument and must be less than half of the contract required quantitation limit (CRQL) specified (see Table 7). An MDL study must also be performed after major instrument maintenance, or changes in instrumentation or instrumental conditions. MDLs must be determined in accordance with the instructions given in 40 CFR, Part 136, Appendix B. This specifies that the instrument hardware and method must be set up as intended for sample analysis. The instrument detection limit (IDL) is then estimated as 3 times the standard deviation of a multiple replicate blank analysis, in concentration units. A reagent blank is then prepared with a spike at 2-5 times the estimated IDL. Seven repeat measurements of the fortified blank sample per dataset are required over three non-consecutive days. The standard deviation (SD) is determined for each of the sets and the mean SD is multiplied by 3.14 (for 7 replicate measurements) to arrive at the MDL. The data for MDL calculation must have all the required calculations included, e.g. interference correction equations as these can have a substantial influence on the MDL. Table 7 lists MDL values obtained. The instruments these data were obtained on were 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.

MDLS (3 BATCHES OF 7 FULL ANALYSES)

ELEMENT	UNITS	1 % HNO3	2 % HCl	CRQL
9Be	µg/L	0.02	0.03	1
23Na	mg/L	0.002	0.01	5
25Mg	mg/L	0.0001	0.0008	5
27Al	µg/L	0.1	0.7	30
39K	mg/L	0.005	0.04	5
44Ca	mg/L	0.004	0.02	5
51V	µg/L	0.03	1	1
52Cr	µg/L	0.04	0.3	2
55Mn	µg/L	0.009	0.05	0.5
56Fe	mg/L	0.002	0.003	0.1
59Co	µg/L	0.004	0.005	0.5
60Ni	µg/L	0.03	0.05	1
65Cu	µg/L	0.02	0.03	2
66Zn	µg/L	0.04	0.1	1
75As	µg/L	0.09	0.7	1
77Se	µg/L	0.2	5	5
78Se	µg/L	0.7	3	5
82Se	µg/L	0.3	0.4	5
107Ag	µg/L	0.2	2	1
111Cd	µg/L	0.05	0.3	1
114Cd	µg/L	0.004	0.005	1
121Sb	µg/L	0.004	0.07	2
137Ba	µg/L	0.02	0.02	10
205Tl	µg/L	0.003	0.006	1
208Pb	µg/L	0.003	0.01	1

Table 7 - MDLs in 1 % HNO₃ and 2 % HCl and CRQLs

3.5 Performance Evaluation

The performance of an XSERIES 2 was evaluated by running the quality control system required for ILM05.2D. Data were acquired over three non-consecutive days, at the same time as acquiring the MDL data. Samples representing a variety of matrices were analysed. Each sample was subjected to the QC requirements of ILM05.2D, 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	Calibration
LoCal1	Fully Quant Standard	
LoCal2	Fully Quant Standard	
HiCal1	Fully Quant Standard	
HiCal2	Fully Quant Standard	
ICV/ICB	QC Sample	Calibration accuracy check with 2nd source standard
ISCA ILM05.2	QC Sample	Blank check in the presence of interferences
ISCAB ILM05.2	QC Sample	Recovery check in the presence of interferences
CCV/CCB	QC Sample	Calibration accuracy/drift check

SAMPLE NAME	SAMPLE TYPE	PURPOSE
CRI	QC Sample	Accuracy check at the CRQL level
LCS	QC Sample	Accuracy check with NIST 1640 River Water
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/CCB	QC Sample	Calibration accuracy/drift check

*Spiked with analytes to the levels dictated in ILM05.2D

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 method suggests that this should be set at a concentration close to the mid-point of the calibration but not equal to any of the calibration standard concentrations. 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 method suggests that this should be set at a concentration close to the mid-point of the calibration but not equal to any of the calibration standard concentrations or the ICV concentration. 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 the CCV measurements from 99 determinations over 3 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/L	304	300	101
56Fe	mg/L	62	60	103
59Co	µg/L	299	300	100
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

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: 100 mg/L Al, Ca, Fe, Mg, Na, P, S, K, 200 mg/L carbon, 1000 mg/L chloride, and 2 mg/L Mo, Ti. ICSAB additionally contains the following analytes at 20 µg/L: As, Cd, Cr, Co, Cu, Mn, Ni, Ag, and Zn. The method requires that the target analyte results for ICSA are within 3CRQL, whilst the analytes in ICSAB must be within 20 % of the known value. Table 11 gives the results for the ICS solutions, measured 30 times over three non-consecutive days.

ANALYTE UNITS	ICSA				ICSAB		
	MEAN (N=30)	3CRQL	KNOWN	% REC	MEAN (N=30)	KNOWN	% REC
6Li %	76				75		
9Be µg/L	0.088	3.0					
23Na mg/L	101		100	101	103	100	103
25Mg mg/L	101		100	101	103	100	103
27Al µg/L	99752		100000	100	101148	100000	101
39K mg/L	102		100	102	104	100	104
44Ca mg/L	104		100	104	105	100	105
45Sc %	76				76		
51V µg/L	2.0	3.0			21.4	20	107
52Cr µg/L	0.99	6.0			20.2	20	101
55Mn µg/L	2.6	1.5			21.7	20	108

Table 11 - ICS Solution Results

ANALYTE UNITS	ICSA			ICSAB		
	MEAN (N=30)	3CRQL	KNOWN % REC	MEAN (N=30)	KNOWN	% REC
56Fe mg/L	104		104	104	100	104
59Co µg/L	0.63	1.5		19.2	20	96
60Ni µg/L	0.05	3.0		17.7	20	88
65Cu µg/L	1.4	6.0		18.3	20	91
66Zn µg/L	11	3.0		26.7	20	133
75As µg/L	0.20	3.0		18.1	20	90
77Se µg/L	3.0	15.0		19.6	20	98
78Se µg/L	5.7	15.0		22.6	20	113
82Se µg/L	0.038	15.0		16.4	20	82
107Ag µg/L	2.1	3.0		9.77	20	49
111Cd µg/L	0.43	3.0		18.2	20	91
114Cd µg/L	1.2	3.0		18.6	20	93
115In %	78			79		
121Sb µg/L	1.3	6.0		1.26		
137Ba µg/L	1.3	30.0		1.37		
159Tb %	86			86		
205Tl µg/L	0.059	3.0		0.0585		
208Pb µg/L	1.7	3.0		1.73		

Table 11 - ICS Solution Results (continued)

The results given in Table 11 show that accurate results are consistently achieved for the high concentration elements such as Na, Ca, Mg, K, Fe at the 100 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 interferences do not contribute dramatically to the analyte signals at the blank level, with the majority of the results far less than the requirement of 3*CRQL. 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. 77 Se in the presence of chloride (ArCl interference). Two exceptions to the generally excellent ICSA results are Zn and Mn which are slightly above the requirement due to the presence of contamination. This was confirmed by analyzing an alternative source of single element Fe, Mg, Ca and K, finding results much less than the CRQL in each case. The results of ICSAB show that accurate data may be achieved at the 20 µg/L level in the presence of interferences, with the exception of Zn and Ag. The Zn result is high due to the presence of the 11 µg/L of contamination found in the ICSA solution, while Ag is low due to the precipitation of AgCl as the solution contains 1000 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 less than 25 % signal loss.

4.5 CRQL Check (CRI)

This solution is a standard prepared at the CRQL level. This is analysed to check the accuracy of the method at low concentration. The method requires that the results are within the range 70-130 % for all analytes, except Co, Mn and Zn, which must be within the range 50-150 %.

Table 12 gives the results for the CRI.

ANALYTE	UNITS	MEAN (N=30)	KNOWN	% REC	ALLOWED RANGE
9Be	µg/L	1.03	1	103	70-130
27Al	µg/L	33.3	30	111	70-130
51V	µg/L	1.01	1	101	70-130
52Cr	µg/L	2.01	2	101	70-130
55Mn	µg/L	0.538	0.5	108	50-150
59Co	µg/L	0.533	0.5	107	50-150
60Ni	µg/L	1.04	1	104	70-130
65Cu	µg/L	2.03	2	102	70-130
66Zn	µg/L	1.01	1	101	50-150
75As	µg/L	1.05	1	105	70-130
77Se	µg/L	5.30	5	106	70-130
78Se	µg/L	6.07	5	121	70-130
82Se	µg/L	4.90	5	98	70-130
107Ag	µg/L	1.00	1	100	70-130
111Cd	µg/L	1.03	1	103	70-130
114Cd	µg/L	1.02	1	102	70-130
121Sb	µg/L	1.93	2	97	70-130
137Ba	µg/L	9.81	10	98	70-130
205Tl	µg/L	1.01	1	101	70-130
208Pb	µg/L	1.02	1	102	70-130

Table 12 - CRI Results

The results in Table 12 show that accurate results are consistently achieved at the CRQL level with the measured range being well within the allowable range.

4.6 Sample AQC

The method requires that for each sample delivery group (batch) or each sample matrix, one 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 5*CRQL. The PlasmaLab software is able to automatically disqualify results from having this test applied due to the result being less than 5*CRQL. 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 13-17 give the results and AQC results for a variety of sample types treated in this way. Table 14 gives the results for a sediment reference material digested using aqua regia.

BOREHOLE WATER (N=9)

ANALYTE	UNITS	SAMPLE RESULT	DUP (% RPD)	SER (% RPD)	SPIKE AMOUNT (µg/L)	SPIKE REC %
9Be	µg/L	0.03			50	97
23Na	mg/L	27.8	0.5	3.6		
25Mg	mg/L	27.8	0.1	4.9		
27Al	µg/L	5.28			2000	94
39K	mg/L	3.55	0.4	2.5		
44Ca	mg/L	76.9	0.4	1.0		
51V	µg/L	0.289			500	99
52Cr	µg/L	0.118			200	94
55Mn	µg/L	1.71			500	97
56Fe	mg/L	0.00				
59Co	µg/L	0.24			500	97
60Ni	µg/L	0.11			500	92
65Cu	µg/L	4.05	0.3		250	91
66Zn	µg/L	12.0			500	88
75As	µg/L	6.56	0.9	4.6	40	96
82Se	µg/L	0.54			10	90
107Ag	µg/L	0.65				
111Cd	µg/L	0.036			50	95
114Cd	µg/L	0.038			50	94
121Sb	µg/L	0.263			100	93
137Ba	µg/L	79.6	0.6	4.2	2000	103
205Tl	µg/L	0.025				
208Pb	µg/L	0.432			20	92

Table 13 - Borehole Water Results

Very few analytes in the borehole water were above 5*CRQL and therefore few duplicate or serial dilution tests could be applied. Those that were, 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 levels of chloride.

CLYDE SEDIMENT REFERENCE MATERIAL 2 (N=9)

ANALYTE	UNITS	SAMPLE RESULT	KNOWN mg/kg	%REC	DUP (% RPD)	SER (% RPD)	SPIKE AMOUNT (µg/L)	SPIKE REC %
9Be	mg/kg	1.91			9.4		50	98
23Na	mg/kg	4940	4515	110	1.1	2.9		
25Mg	mg/kg	5300	4667	113	2.3	4.5		
27Al	mg/kg	32150	24975	129	2.3	2.5	2000	125
39K	mg/kg	2020	1982	102	0.7	5.1		
44Ca	mg/kg	3910	3455	113	6.4	6.3		
51V	mg/kg	32.4	30.9	105	1.6	4.0	500	101
52Cr	mg/kg	153	153	100	1.6	5.2	200	99
55Mn	mg/kg	378	364	104	1.9	4.6	500	102
56Fe	mg/kg	24700	23786	104	1.3	4.2		
59Co	mg/kg	10.0	10.5	95	0.5	7.4	500	100
60Ni	mg/kg	27.1	28	97	0.1	7.1	500	97
65Cu	mg/kg	94.5	96	98	1.9	8.0	250	96

Table 14 - Sediment Sample Results

CLYDE SEDIMENT REFERENCE MATERIAL 2 (N=9)

ANALYTE	UNITS	SAMPLE RESULT	KNOWN mg/kg	%REC	DUP (% RPD)	SER (% RPD)	SPIKE AMOUNT (µg/L)	SPIKE REC %
66Zn	mg/kg	280	290	96	1.3	5.5	500	97
75As	mg/kg	10.5	11.1	94	0.6	0.5	40	97
82Se	mg/kg	0.91					10	100
107Ag	mg/kg	5.14						
111Cd	mg/kg	1.18	1.045	113	1.7	5.9	50	100
114Cd	mg/kg	0.99	1.045	95	0.5	0.2	50	99
121Sb	mg/kg	0.498					100	94
137Ba	mg/kg	261					2000	106
205Tl	mg/kg	0.279						
208Pb	mg/kg	123	123	100	0.9	5.2	20	99

Table 14 - Sediment Sample Results (continued)

Most analytes in the Clyde Sediment Digest 2 were above 5*CRQL 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 levels of chloride from the aqua regia digestion. 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.

WASTE (CONTAMINATED LAND) DIGEST (N=9)

ANALYTE	UNITS	SAMPLE RESULT	DUP (% RPD)	SER (% RPD)	SPIKE AMOUNT (µg/L)	SPIKE REC %
9Be	mg/kg	2.05	2.9	1.8	50	97
23Na	mg/kg	486	0.5			
25Mg	mg/kg	4150	1.2	2.4		
27Al	mg/kg	25483	0.4	2.0	2000	97
39K	mg/kg	3910	0.1	5.8		
44Ca	mg/kg	29000	1.5	3.7		
51V	mg/kg	71.7	1.0	2.2	500	101
52Cr	mg/kg	55.0	0.8	2.3	200	97
55Mn	mg/kg	736	0.9	1.6	500	100
56Fe	mg/kg	50000	1.2	2.4		
59Co	mg/kg	17.3	0.7	2.3	500	100
60Ni	mg/kg	69.0	0.4	4.7	500	95
65Cu	mg/kg	137	1.3	3.1	250	97
66Zn	mg/kg	744	1.4	5.0	500	96
75As	mg/kg	18.3	0.3	1.1	40	97
82Se	mg/kg	0.41			10	97
107Ag	mg/kg	<MDL				
111Cd	mg/kg	10.6	0.3	3.2	50	96
114Cd	mg/kg	10.1	1.4	4.6	50	96
121Sb	mg/kg	3.24	1.9		100	92
137Ba	mg/kg	377	0.0	2.5	2000	106
205Tl	mg/kg	0.202	5.5			
208Pb	mg/kg	478	0.2	2.2	20	95

Table 15 - Waste Digest Results

Most analytes in the Waste Digest were above 5*CRQL 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 levels of chloride from the aqua regia digestion.

SOIL DIGEST (N=9)

ANALYTE	UNITS	SAMPLE RESULT	DUP (% RPD)	SER (% RPD)	SPIKE AMOUNT (µg/L)	SPIKE REC %
9Be	mg/kg	7.05	1.8	5.0	50	97
23Na	mg/kg	1647	0.1	0.6		
25Mg	mg/kg	2830	1.2	2.4		
27Al	mg/kg	12170	0.4	3.0	2000	94
39K	mg/kg	8340	0.4	4.4		
44Ca	mg/kg	205700	0.2	3.1		
51V	mg/kg	39.8	3.8	2.1	500	99
52Cr	mg/kg	81.8	0.8	1.8	200	95
55Mn	mg/kg	418	1.1	2.6	500	97
56Fe	mg/kg	22900	0.7	2.4		
59Co	mg/kg	24.9	2.5	1.5	500	95
60Ni	mg/kg	96.1	0.5	4.1	500	92
65Cu	mg/kg	117	2.7	4.6	250	93
66Zn	mg/kg	1046	0.3	5.5	500	90
75As	mg/kg	31.1	1.2	3.6	40	95
82Se	mg/kg	3.06	5.9		10	96
107Ag	mg/kg	6.95				
111Cd	mg/kg	6.4	0.6	5.6	50	96
114Cd	mg/kg	6.2	3.5	1.8	50	94
121Sb	mg/kg	4.63	0.7	2.2	100	94
137Ba	mg/kg	210	1.9	2.0	2000	107
205Tl	mg/kg	0.808				
208Pb	mg/kg	614	0.6	0.1	20	95

Table 16 - Soil Digest Results

Most analytes in the Soil Digest were above 5*CRQL 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 levels of chloride from the aqua regia digestion.

ROCK DIGEST (N=9)

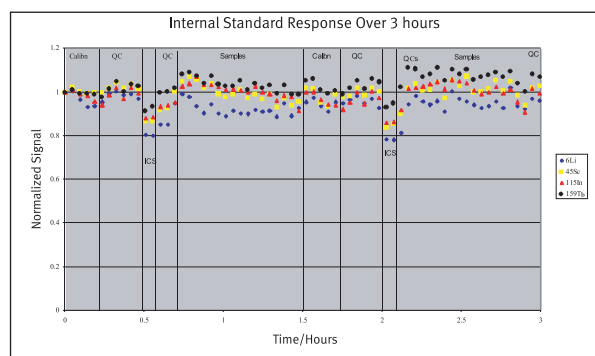
ANALYTE	UNITS	SAMPLE RESULT	DUP (% RPD)	SER (% RPD)	SPIKE AMOUNT (µg/L)	SPIKE REC %
9Be	mg/kg	3.77	3.6	3.7	50	96
23Na	mg/kg	15340	1.9	1.4		
25Mg	mg/kg	76030	0.3	1.0		
27Al	mg/kg	35375	0.2	0.2	2000	80
39K	mg/kg	17050	0.7	1.6		
44Ca	mg/kg	183900	0.8	2.9		
51V	mg/kg	457.0	0.6	0.2	500	98
52Cr	mg/kg	140.0	0.4	0.3	200	94
55Mn	mg/kg	3957	1.2	2.1	500	90
56Fe	mg/kg	71500	1.1	1.0		
59Co	mg/kg	6.1	2.9	2.7	500	95
60Ni	mg/kg	23.8	2.0	2.3	500	92
65Cu	mg/kg	1927	0.9	2.7	250	87
66Zn	mg/kg	21	2.2	0.3	500	90
75As	mg/kg	7.3	0.8	1.7	40	94
82Se	mg/kg	4.31			10	96
107Ag	mg/kg	0.60				
111Cd	mg/kg	<MDL*			50	95
114Cd	mg/kg	0.1			50	93
121Sb	mg/kg	1.83			100	95
137Ba	mg/kg	62	0.9	1.7	2000	106
205Tl	mg/kg	0.312				
208Pb	mg/kg	25	1.6	3.5	20	96

* <MDL = less than method detection limit
Table 17 - Rock Digest Results

Most analytes in the Rock Digest were above 5*CRQL 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 levels of chloride from the aqua regia digestion.

4.7 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 three 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 low suppression of only 10-25 %.



Graph 1 - Internal Standard Response over a 3-Hour Period Running Calibrations, QCs and Samples

5. Conclusions

The XSERIES 2 demonstrates CLP method ILM05.2 D 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 ILM05.2 D compliant analysis as outlined below.

Mass calibration and resolution checking is made simple with the custom Performance Report after peaks are easily set to the required width using the variable resolution function.

The Performance Report also monitors and records the precision over a user definable number of measurements (in this case five), 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 method detection limits (as seen in Table 7), far exceeding the CRQL requirements of ILM05.2 D. It reduces the 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 coupled with the dual mode simultaneous detector, result in unrivalled linear range performance. 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.

The data presented here is a typical for an XSERIES 2 ICP-MS. The data cannot be taken as a guarantee of performance with respect to the detection limits, quality control recoveries or drift characteristics. However, Thermo Fisher Scientific do guarantee that any XSERIES 2 ICP-MS installed to conditions specified in the site planning guide, running solutions prepared from the provided standards within the Thermo Scientific Productivity Pack 4600430 will achieve limit of detection, quality control recoveries and drift criteria that meet or exceed the requirements of ILM05.2D.

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