The Impact of ILM05.3 on ICP-MS
TRENDS AND OPPORTUNITIES

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ENVIRONMENTAL
Analysis

The United States Environmental Protection Agency (US EPA) was formed in 1970 in order to cope with increasing public demand to improve environmental quality. Among its many activities is the monitoring of contaminated or potentially contaminated sites within the 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). In order to do this, the EPA's Office of Superfund Remediation and Technology Innovation (OSRTI) use contract laboratories within their Contract Laboratory Program (CLP) to provide analytical services by following statements of work (SOWs) that include comprehensive, prescriptive analytical methodologies. In 2001 the inorganic SOW, ILM05.2, was released. This gave full methodological details on the analysis of various parameters including metallic analytes, cyanide and mercury using techniques such as atomic absorption spectrophotometry (AAS), inductively coupled plasma atomic emission spectrometry (ICP-AES) and inductively coupled plasma mass spectrometry (ICP-MS) (see Box 1). In February of this year, this SOW was superseded by ILM05.3. This article describes the update as it affects ICP-MS and shows how current ICP-MS instrumentation can be used to comply with this latest US EPA methodology. This methodology is also important to non-CLP labs that want to offer a CLP-like service to their customers.

Summary of ILM05.3

ILM05.3 is the inorganic SOW used to define the analytical procedure for metallic contaminants in waters found at potentially hazardous contaminated or suspected contaminated sites. Samples supplied are digested and analyzed for 16 analytes on the ICP-MS target analyte list (TAL): antimony, arsenic, barium, beryllium, cadmium, chromium, cobalt, copper, lead, manganese, nickel, selenium, silver, thallium, vanadium and zinc. The previous SOW, ILM05.2, also included aluminum. In ILM05.3, aluminum was removed from the TAL and is now determined by ICP-AES instead.

The method is quality control (QC) intensive, requiring the user to establish the linear dynamic range (LDR) and method detection limit (MDL) prior to reporting results. Within each analytical run, data quality has to be checked rigorously according to the following procedure. A "Tune" sample is analyzed to demonstrate the sensitivity and stability, and verify the mass calibration of the instrument. Initially, a calibration verification sample (ICV) and a blank sample (ICB) are analyzed to confirm the validity of the calibration. In order to independently check the prepared calibration concentrations, the ICV is prepared from an alternative source of starting materials. A standard (CRI), prepared at the contract required quantitation limit (CRQL), is also analyzed. This is followed by a pair of solutions (ICSA and ICSAB) containing a variety of potentially interfering elements: one to check freedom from interference at blank levels and the second to check accuracy by calculating the recovery of target analytes added to the first solution. Next, a continuing calibration verification sample (CCV) and blank (CCB) are analyzed to re-check accuracy. The CCV and CCB pair are analyzed once every ten subsequent samples to confirm continuing accuracy and the CRI standard is analyzed once every 20 samples to confirm accuracy at the CRQL level. Sample-based quality checks are also performed. These consist of the analysis of a laboratory control sample (LCS) (a known sample that has been taken through the same sample preparation procedure as the unknown samples), the duplicate analysis of an unknown sample (to check repeatability), a spike recovery of target analytes to the unknown sample (to check for accuracy), and a serial dilution of an unknown sample (to check for matrix effects).

SUMMARY OF CHANGES

General Changes

Some new contract required quantitation limits (CRQLs) have been implemented, and the current CRQL list is shown in Table 1. This has a knock-on effect on some of the QC checks that are based on the CRQL values, e.g. the CRI, ICSA and blank checks (ICB, CCB, etc).

The criteria for dilution of samples that produce results above the calibration or LDR has been changed to state that the diluted concentration must be within the upper 75% of the calibrated or linear range. This is to ensure the quality of data from the dilution is not reduced by the effect of over-dilution.

Sample Preparation

Various changes have been made in the preparation methodology for samples. ILM05.3 allows the use of polymeric beakers and watchglasses for digestion procedures, which are often desirable for ICP-MS to minimize contamination. Fluoropolymers, in particular, are a desirable choice of material for use in the preparation of samples for ICP-MS analyses, as they reduce the likelihood of contamination due to their hydrophobic surface properties. The previous SOW specified a need for ultra purity acids for the preparation of sample and standard solutions. ILM05.3 removes this requirement as the cost of ultra purity grade reagents can be prohibitively expensive for routine analytical work. Furthermore, super purity grades are normally sufficient for analytical work at the 1 part per billion (ppb) concentration level. ILM05.2 had a sample preparation option allowing "direct analysis", whereby the sample was only acidified and filtered/centrifuged prior to analysis (preparation code NP1). ILM05.3 removes this option and adds a further preparation option (HW3), that essentially consists of heating (93-95⁰C, covered) 100 mL of sample with 1 mL of nitric acid and 1 mL of hydrochloric acid, until the volume is reduced by half. The solution is then refluxed for a further 30 minutes, then cooled, filtered and made to a final volume of 100 mL.

QC

The instructions for running the "Tune" sample have been re-written to clarify the procedure: the sample must be run five times, which can be defined as either five replicate integrations, or as five individual, consecutive analyses. In both cases, the relative standard deviation (RSD) of the analyses must be <5%. Within the "Tune" analysis, ILM05.2 specified a resolution check, whereby the peak width at 5% peak height had to be <0.75 amu. This requirement has been changed to allow the resolution to be checked in line with the instrument manufacturers' recommendations. This amendment was made as some instruments struggled to comply with the old peak width specification.

The sequence of analysis of QCs has been clarified to indicate the proper running order, which was difficult to interpret in ILM05.2. The correct sequence is: Tune, Calibration Blank, Calibration Standard(s), ICV, ICB, CRI, ICSA, ICSAB, CCV, CCB, 10 samples, CCV, CCB, 7 samples, CRI, CCV, CCB, 10 samples, etc.

The reporting requirements for ICS solutions have changed to exclude the reporting of interferent species – these must be analyzed, but not reported.

Internal Standards

The minimum number of internal standards to be used has been increased from three to five, spanning the mass-range of interest. The instructions have also been clarified to state that internal standards should not be run in the "Tune" sample and that the internal standard species used must be consistent throughout the run.

Clarification is also given as to the action to be taken when the internal standard recoveries are outside the allowed range for serial dilution samples (since the normal action is to perform a dilution) and the requirement to re-analyze the blank, when internal standard recoveries are outside specification is removed. This is to facilitate automated analytical runs.

EXAMPLE OF COMPLIANCE WITH ILM05.3

An X Series ICP-MS (Thermo Electron Corp., Winsford, UK) was used to compare the performance of a commercial instrument with the requirements of ILM05.3.

Meeting the CRQL Requirements

The ILM05.3 document specifies that method detection limits (MDLs) must be less than half the CRQL (see Table 1). MDLs must be determined in accordance with the instructions given in 40 CFR, Part 136, Appendix B. Data for MDL calculation must contain all the calculations, e.g. interference correction equations as these can have a substantial influence on the MDL. Table 1 lists MDL values obtained in the HW3 matrix of 2% nitric acid, 1% hydrochloric acid and shows that the requirement of 50% of the CRQL is easily obtained.

MDLs (3 batches of 7 full analyses)

Element	Units	2% HNO3, 1% HCl	CRQL
9Be	μg/L	0.03	1
51V	μg/L	0.3	1
52Cr	μg/L	0.3	2
55Mn	μg/L	0.03	1
59Co	μg/L	0.004	1
60Ni	μg/L	0.03	1
65Cu	μg/L	0.03	2
66Zn	μg/L	0.05	2
75As	μg/L	0.1	1
78Se	μg/L	1	5
82Se	μg/L	0.3	5
107Ag	μg/L	0.2	1
111Cd	μg/L	0.05	1
114Cd	μg/L	0.005	1
121Sb	μg/L	0.03	2
137Ba	μg/L	0.02	10
205Tl	μg/L	0.003	1
208Pb	μg/L	0.005	1

Table 1 – MDLs in 2% HNO3, 1% HCl (HW3 preparation)

Tune Sample

The criteria for the Tune sample are easily fulfilled, and some instruments include software specifically designed to cope with the requirements of performing and reporting this check. Figure 1 and tables 2-4 show compliant results for a Tune sample, including the peak resolution check as specified in ILM05.2. Data were collected using an automated, custom defined performance check sequence within the instrument software.
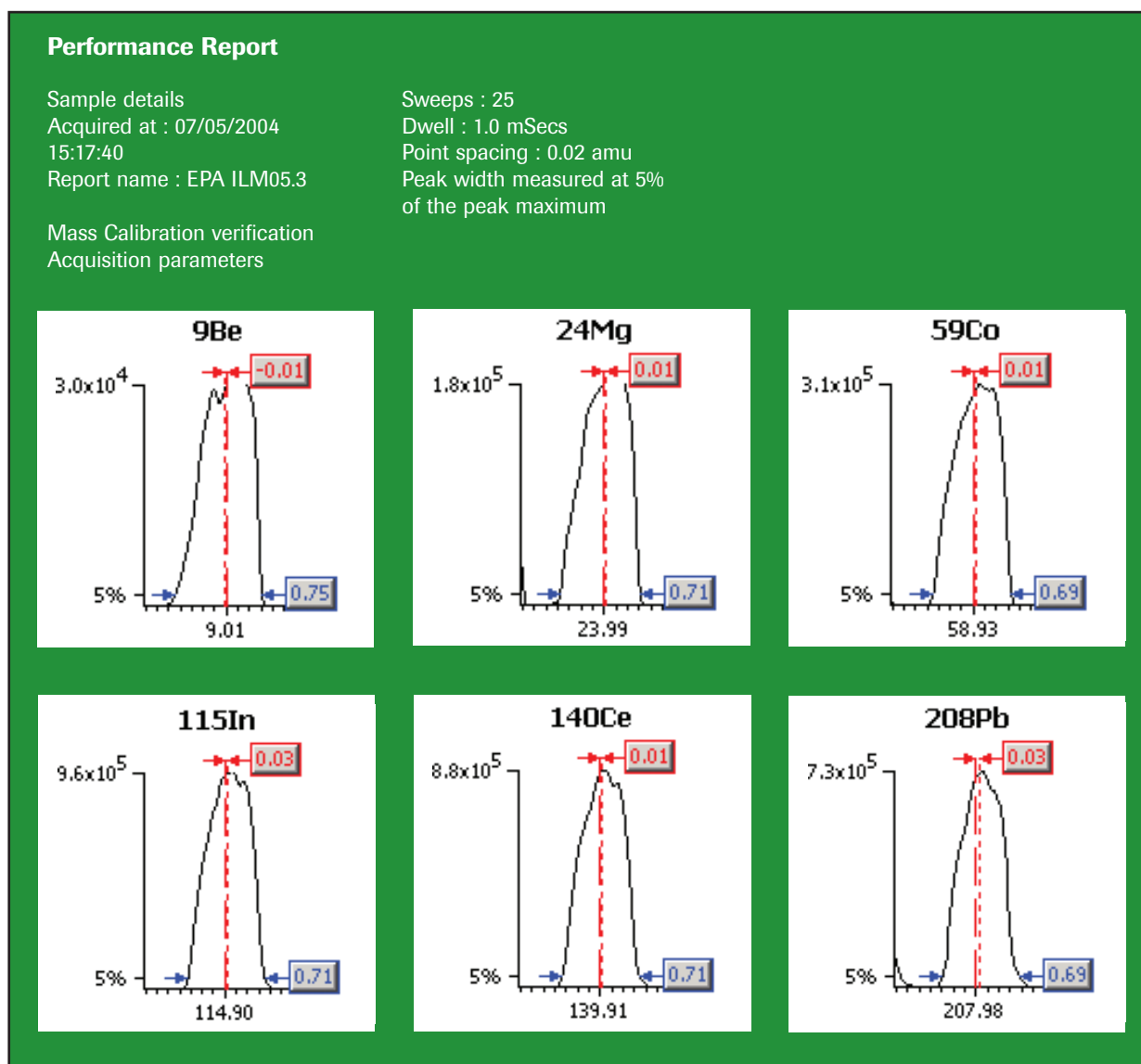
Figure 1 – Performance Report Results for Mass Calibration and Resolution Checks

Analyte	Limits		Results		
	Max. width	Min. width	Max. error	Peak width	Peak error
9Be	0.75	0.45	0.10	0.75	-0.01
24Mg	0.75	0.45	0.10	0.71	0.01
59Co	0.75	0.45	0.10	0.69	0.01
115In	0.75	0.45	0.10	0.71	0.03
140Ce	0.75	0.45	0.10	0.71	0.01
208Pb	0.75	0.45	0.10	0.69	0.03

Table 2 - Performance Report Results for Mass Calibration and Resolution Checks

Run	Time	5Bkg	9Be	24Mg	59Co	115In	140Ce	156Ce O	208Pb	220Bkg
Limits	%RSD	-	5%	5%	5%	5%	5%	-	5%	-
1	15:17:57	0.167	30443.110	187543.07	306965.94	944942.47	856281.53	13447.160	704913.53	0.000
2	15:18:59	0.056	30316.020	187197.16	306783.84	949769.27	859914.99	13587.183	710217.92	0.333
3	15:20:00	0.000	30322.709	186631.25	303948.73	942207.60	851879.25	13430.469	703479.71	0.056
4	15:21:02	0.000	30382.909	186515.58	304192.81	939275.05	846896.63	13167.307	698503.19	0.167
5	15:22:03	0.056	30288.707	185262.57	303288.90	931283.94	844829.73	13106.107	691993.63	0.000
x		0.056	30350.691	186629.93	305036.04	941495.67	851960.43	13347.645	701821.59	0.111
s		0.07	62.06	871.54	1712.10	6892.94	6293.70	203.10	6899.43	0.14
%RSD		122.474	0.204	0.467	0.561	0.732	0.739	1.522	0.983	127.475

Table 3 - Sensitivity and Stability Results

Ratio results

Run	Time	156CeO/140Ce
	-	
1	15:17:57	0.016
2	15:18:59	0.016
3	15:20:00	0.016
4	15:21:02	0.016
5	15:22:03	0.016
x		0.0157
s		0.00
%RSD		0.8250

Table 4 – Oxide Results

QC Samples

The ICV and CCV samples must measure within 10% of the known value. The measured concentrations in Table 4 are shown to be well within these specifications. The CRI solution is a check of accuracy at the contract required quantitation limit (CRQL) value. The measured values must recover the known value to within the allowed range given in Table 5. Again, these specifications are easily met, with all measured values actually within 10% of the CRQL value.

Interference Checks

The ICSA solution must measure less than three times the CRQL value for each target analyte, whilst the measured values for the ICSAB solution must be within 20% of the known value. Table 6 shows that the measured values are well within the allowed ranges and therefore the analysis is sufficiently free of interferences.

Analyte	Units	ICV Results			CRI Results				CCV Results		
		Mean (n=36)	Known	%Rec	Mean (n=30)	Known	%Rec	Allowed Range %	Mean (n=99)	Known	%Rec
9Be	µg/L	191	200	96	1.03	1	103	70-130	284	300	95
51V	µg/L	201	200	101	1.01	1	101	70-130	304	300	101
52Cr	µg/L	198	200	99	2.01	2	101	70-130	299	300	100
55Mn	µg/L	196	200	98	1.06	1	106	50-150	304	300	101
59Co	µg/L	196	200	98	1.04	1	104	50-150	299	300	100
60Ni	µg/L	191	200	95	1.04	1	104	70-130	289	300	96
65Cu	µg/L	187	200	94	2.03	2	102	70-130	284	300	95
66Zn	µg/L	186	200	93	2.02	2	101	50-150	280	300	93
75As	µg/L	205	200	102	1.05	1	105	70-130	295	300	98
78Se	µg/L	957	1000	96	5.44	5	109	70-130	284	300	95
82Se	µg/L	959	1000	96	4.9	5	98	70-130	282	300	94
107Ag	µg/L	183	200	91	1	1	100	70-130	289	300	96
111Cd	µg/L	192	200	96	1.03	1	103	70-130	287	300	96
114Cd	µg/L	190	200	95	1.02	1	102	70-130	285	300	95
121Sb	µg/L	191	200	96	1.93	2	97	70-130	293	300	98
137Ba	µg/L	201	200	100	9.81	10	98	70-130	304	300	101
205Tl	µg/L	195	200	98	1.01	1	101	70-130	297	300	99
208Pb	µg/L	190	200	95	1.02	1	102	70-130	293	300	98

Table 5: Results Summary for QC Samples ICV, CRI and CCV.
Recoveries for ICV and CCV must be within 90-110% of the known value.

Box 1: ICP-MS Instrumentation

Detection

Filtration

Optimization

Sample introduction

ICP-MS Instrumentation

ICP-MS is a highly sensitive analytical technique that is used to measure elements in the part per trillion to low percent concentration range. The sample (usually a liquid) is sprayed into a high-temperature radio frequency argon plasma which ionises the constituent elements. The ions are sampled into a mass spectrometer (usually a quadrupole) at high vacuum via a pair of cones with small central apertures. Electrostatic lenses focus the ion beam into the mass spectrometer which separates the elements by virtue of mass-to-charge ratio differences. The separated ions are then detected by an electron multiplier which gives a signal that is proportional to the concentration of analyte present in the original sample.

ICP-MS is widely used in chemical analyses relating to environmental quality assessment.

| Analyte | Units | ICSA | | | | ICSAB | | |
		Mean (n=30)	3CRQL	Known	%Rec	Mean (n=30)	Known	%Rec
9Be	µg/L	0.088	3.0			0.101		
23Na	mg/L	101		100	101	103	100	103
25Mg	mg/L	101		100	101	103	100	103
27Al	mg/L	99.7		100	100	101	100	101
39K	mg/L	102		100	102	104	100	104
44Ca	mg/L	104		100	104	105	100	105
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	1.9	3.0			21.7	20	108
56Fe	mg/L	104		100	104	104	100	104
59Co	µg/L	0.63	3.0			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	4.2	6.0			19.9	20	100
75As	µg/L	0.20	3.0			18.1	20	90
78Se	µg/L	3.1	15.0			22.6	20	113
82Se	µg/L	0.038	15.0			16.4	20	82
107Ag	µg/L	2.1	3.0			17.7	20	89
111Cd	µg/L	0.43	3.0			18.2	20	91
114Cd	µg/L	1.2	3.0			18.6	20	93
121Sb	µg/L	1.3	6.0			1.26		
137Ba	µg/L	1.3	30.0			1.37		
205Tl	µg/L	0.059	3.0			0.059		
208Pb	µg/L	1.7	3.0			1.73		

Table 6: ICS Solution Results

Sample QC

At least one unknown sample per sample delivery group (SDG) must be subjected to re-analysis as a duplicate, after serial dilution and after spiking with target analytes for recovery calculation. Spike recoveries must be within 75 – 125%. Table 7 gives an example of the results from these tests with borehole water (a natural water with high calcium content). All the requirements were met.

Conclusion

The US EPA has made some very practical updates to the CLP SOW for ICP-MS in ILM05.3. The X Series ICP-MS has been shown to be suitable for compliance with the requirements of the SOW and has integral software features that facilitate this. Traditionally, performing this complex methodology could be an arduous task. With the X Series ICP-MS from Thermo Electron, conforming with the EPA's stringent requirements it is now hassle-free, thanks to the instrument's user friendliness and easy to use software interface. Moreover this leads to more confidence with better results and efficiencies gained for the modern laboratory.

ILM05.3 may be downloaded free of charge from the following website: http://www.epa.gov/superfund/programs/clp/ilm5.htm.

| Analyte | Units | Borehole Water (n=9) | | | | |
		Sample	DUP (% RPD)	SER (% RPD)	SPIKE AMOUNT (_g/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	mg/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 7: Example Sample QC Results