Application Note

Environmental Analysis Using a High Throughput ICP AES

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1 Introduction

Although designed for the United States, the US EPA protocol has been adopted by many countries, especially in Asia, as the basis for their environmental methodology. It is therefore of interest to many countries around the world to understand the changes effecting this protocol.

Recent suggested changes to the US EPA Statement of Work (SOW) ILM04 have produced draft version ILM05, scheduled for release in the near future. The well-established criteria for a compliant analysis under ILM04 will drastically change in ILM05 in the area of detection limits, control limits and in the sample turnaround time. These are briefly described below:

Table 1: Proposed limits for CRQL and MDL in ILM05

Element	CRQL (ppb)	MDL (ppb)	Element	CRQL (ppb)	MDL (ppb)
Al	200	100	Pb	3	1.5
Sb	60	30	Mg	5000	2500
As	10	5	Mn	15	7.5
Ba	200	100	Ni	40	20
Be	5	2.5	K	5000	2500
Cd	5	2.5	Se	5	2.5
Ca	5000	2500	Ag	10	5
Cr	10	5	Na	5000	2500
Co	50	25	Tl	10	5
Cu	25	12.5	V	50	25
Fe	100	50	Zn	20	10

Table 2: Comparison of IDL in ILM04 with MDL in ILM05

Element	IDL-ILM04 (ppb)	MDL-ILM05 (ppb)
Sb	60	30
As	10	5
Be	5	2.5
Cd	5	2.5
Cr	10	5
Pb	3	1.5
Se	5	2.5
Ag	10	5
Tl	10	5

- The Contract Required Quantitation Limits (CRQL) replace the existing Contract Required Detection Limits (CRDL). In addition, the CRQL standard control limits are modified to 70 - 130% of the expected result.

- The Method Detection Limits (MDL) will replace the Instrument Detection Limits (IDL), resulting in a dramatic decrease in detection limits. The MDLs must be less than 50% of the CRQL.

- The time for a sample to be turned around is reduced from 14 - 35 days to 7, 14, or 21 days.

These changes require environmental laboratories to use an ICP AES system that provides not only the detection limits required, but also a fast analysis in order to meet the reduced turnaround time. Many laboratories may consider the purchase of new instrumentation to meet the requirements described above.
The ULTIMA 2 (introduced at the Pittsburgh Conference 2001) and the ULTIMA 2CE provide the environmental laboratory with a choice of ICP AES instrumentation for a fast, fully compliant analysis. No supplemental sample introduction devices, such as an ultrasonic nebulizer or hydride generation system, are required for this compliant analysis. In addition, both spectrometers utilize a radial plasma orientation, which minimizes matrix effects that are typically seen from the variety of environmental samples to be analyzed.

2 Compliant analysis

The ULTIMA 2CE combination ICP is customized for analysis of the elements specified by method 200.7 and the CLP. It adds simultaneous optics to the high performance platform of the ULTIMA 2, to offer an analysis time of less than 4 minutes for the suite of 22 elements.

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The ULTIMA 2 without the simultaneous optical system provides an analysis time of less than 7 minutes, including rinse and flush times.

3 Performance based methods system (PBMS)

Another important feature of ILM05 is the flexibility clause enabling users to request modification to the analytical requirements. Like the Performance Based Methods System (PBMS), this will allow laboratories to justify the use of alternate sample introduction devices and to modify methods to enhance performance. One such device available for the ULTIMA 2 and ULTIMA 2CE is the patented Concomitant Metals Analyzer (CMA) hydride generation system. The CMA provides enhanced sensitivity for the hydride forming elements while also providing the analysis of non-hydride elements without detrimental affects on their limits of detection. All elements can be measured in one analysis run, often without sample pretreatment.

The CMA generates a high efficiency aerosol for the analysis of hydrides that travels with the non-hydride sample aerosol into the plasma.

Detection limits obtained using the ULTIMA 2 and ULTIMA 2CE show an improvement factor of 5 to 20 times. The analyzer is particularly sensitive for Hg with a detection limit of 0.04 ppb.

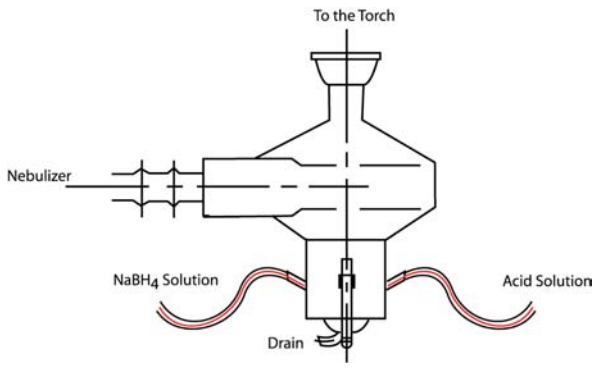

Figure 1: Concomitant Metals Analyser (CMA)

[1] The cycle time is defined using a JY AS421 autosampler and includes both the rinse and flush times
[2] New York Times, November 1, 2001

Table 3: ULTIMA 2 typical detection limits with and without the CMA at 3 sigma in ppb

Element	ULTIMA 2	ULTIMA 2 + CMA
As	1.5	0.2
Be	0.04	0.04
Cd	0.1	0.09
Co	0.2	0.2
Cr	0.2	0.2
Cu	0.2	0.2
Hg	1.5	0.04
Li	0.5	0.7
Mo	0.2	0.2
Mn	0.05	0.05
Ni	0.3	0.35
Pb	1.5	1.2
Sb	1.5	0.2
Se	1.5	0.2
Sn	1.5	0.2
Sr	0.03	0.04
Ti	0.15	0.2
Zn	0.15	0.2

This accessory will be especially useful in the future as the US EPA makes further plans for drinking water analysis. For instance, Arsenic will drop from 50 to 10 ppb in 2006[2].

Table 4: Analysis time and description of instruments

	ULTIMA 2	ULTIMA 2CE
Number of elements	22	22
Cycle time[1]	<7 minutes	<4 minutes
Number of replicates	3	3
Integration time	5 seconds	5 seconds on mono 5 seconds on poly
Optic Sequential	1 m, Czerny-Turner Ion-etched 110 x 110 mm original holographic grating 2400 gr/mm, double order	1 m, Czerny-Turner Ion-etched 110 x 110 mm original holographic grating 2400 gr/mm double order
Optic Simultaneous	None	0.5 m, Paschen-Runge Ion-etched holographic grating 3600 gr/mm double order

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Table 4: Analysis time and description of instruments, continued

	ULTIMA 2	ULTIMA 2CE
Practical resolution Sequential	<0.005 nm	<0.005 nm
Practical resolution Simultaneous	None	<0.020 nm
Spectral range	165-800 nm with far UV option to 120 nm	165-800 nm
Purge for UV	Nitrogen/Argon	Nitrogen/Argon

Table 5: Conditions of analysis for compliant analysis

Parameter	Condition
RF Generator	1000 W
Plasma gas	12 L/min
Sheath gas	0.15 L/min
Auxiliary gas	0 L/min
Nebulizer gas	0.45 L/min, concentric pneumatic
Spray chamber	Cyclonic
Sample flow rate	1 ml/min
Optical purge for analysis < 190 nm	Nitrogen, 3 L/min
Integration time	5 s seq, 5 s sim (on ULTIMA 2CE)

4 Method detection limits

Method detection limits are calculated on three standard deviations of 8 analyses of a sample at 6 times the maximum MDL level. Results for the MDLs are shown in Table 5. The MDL results shown were measured using the analysis conditions in Table 4 in one run with three replicates each for the 8 analyses. When the ULTIMA 2CE is used, the trace metal elements are analyzed on the sequential portion of the instrument in order to maintain the highest level of performance for the low detection limits required.

Table 6: Required and achieved MDL

Sequential			Simultaneous		
Element	Required (ppb)	Achieved (ppb)	Element	Required (ppb)	Achieved (ppb)
Sb	30	5	Ba	100	10.9
A	5	1.8	Be	2.5	0.2
Cd	2.5	0.9	C	5	1.3
Pb	1.5	0.9	Co	25	3.5
Se	2.5	2.0	Cu	12.5	1.1
Ag	5	0.9	Mn	7.5	0.5
Tl	5	2.1	Ni	20	4.2
			V	25	1.0
			Zn	10	1.9

The increased control limits to 70-130% are demonstrated on the CRQL sample in Table 6. These limits are increased compared to ILM04 but can still be difficult due to the decreased MDL in ILM05.

Table 7: Recovery on CRQL

Sequential				Simultaneous			
Element	Actual (ppb)	Measured (ppb)	% Recovery	Element	Actual (ppb)	Measured (ppb)	%
Sb	60	48.1	80	Ba	200	196	98
As	10	8.5	85	Be	5	4.9	99
Cd	5	4.4	88	Cr	10	10.7	107
Pb	3	2.3	76	Co	50	51.1	102
Se	5	5.2	105	Cu	25	22	88
Ag	5	3.9	80	Mn	15	14.5	97
Tl	10	9.5	95	Ni	40	38.9	97
				V	50	47.6	95
				Zn	20	24.1	120

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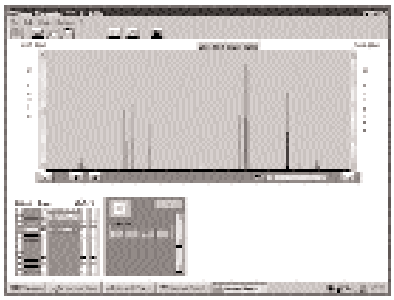

Figure 2: Win-IMAGE full spectrum scan.

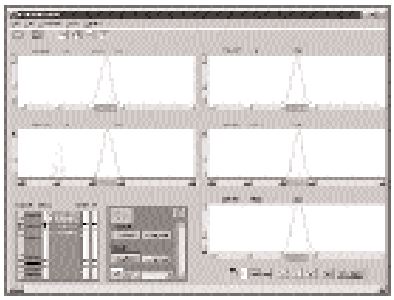

Figure 3: Win-IMAGE five line display.

The ULTIMA 2 is operated from the powerful Analyst™ Windows 95/98/2000/NT software. The software offers complete templates for environmental QC as required by ILM05, with easy-to-use tasks, QC functions, and data transfer and storage. In addition,Analyst software provides complete FDA regulatory formatting and audit trails required for 21 CFR Part 11. The complete analysis of a sample is important to the environmental laboratory for many reasons. Simplified method development for any sample is possible when all constituents are known. Through the use of optional Win-IMAGE the analysis of 125,000 emission lines in less than 2 minutes can be made for each sample. This offers the laboratory an archived file for future retrospective analysis. In addition, this file can be used for future defense of an analysis if necessary, even if the element was not originally analyzed.

The Win-IMAGE spectrum can be viewed at 5 lines simultaneously, allowing user's to select the most appropriate line for analysis. Actual analysis can occur from one to five lines at a time at the user's choice. Analytical results for a defined suite of elements are displayed at each line selected for analysis.

Figure 4: Win-IMAGE element selection (background) and analytical result (foreground) display.

5 Conclusion

Environmental laboratories will face many challenges as they prepare for the requirements of ILM05. A fast full performance ICP AES system will be required to meet these challenges. The ULTIMA 2 and ULTIMA 2CE meet and exceed all requirements of the ILM05 to provide accurate, precise, reliable analysis for today's laboratories.

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