

X Series ICP-MS: Meeting UK drinking water inspectorate requirements (DWI / NS30)

Key Words

- Protocol Compliance
- DWI / NS30
- Matrix Tolerance
- Wide dynamic range (ng/L to >200mg/L)
- Drinking water analysis
- High productivity (>24 samples per hour)

Introduction

Inductively coupled plasma mass spectrometry (ICP-MS) is the method of choice for many environmental applications due to its multi-element coverage and excellent detection limits. These characteristics enable a variety of samples to be analysed for a range of elements that are impossible to measure by a single alternative technique. ICP-MS is ideally suited to the measurement of trace elements at $\mu\text{g/L}$ and ng/L levels, and has been used to replace the techniques of Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES), Graphite Furnace Atomic Absorption Spectrometry (GFAAS), hydride generation and fluorescence techniques, thus allowing all important toxic trace elements to be measured in a single analysis.

However, ICP-MS has been perceived to be inappropriate for the determination of higher levels of analytes, due to limited matrix tolerance and excessive sensitivity, thus limiting the upper calibration range. In addition, the formation of polyatomic species, can result in elevated background contribution and interfere with some analytes of interest for environmental analysis.

This paper describes how the X Series ICP-MS with Xi interface, minimizes polyatomic species in complex environmental matrices enabling detection of Fe at single figure ppb. Its unique properties effectively extend the working dynamic range of the mass spectrometer enabling the measurement of Na and other alkali metals to over 200mg/L in the same mass scan as ng/L levels of trace analytes such as Pb and Cd.

The validation of the X Series ICP-MS for the analysis of inorganic components in drinking water, where the specified analyte concentrations range from sub $\mu\text{g/L}$ (ppb) to 100's of mg/L (ppm) is described in this paper. Experiment templates in the PlasmaLab software were designed for routine "rack and run" analysis. Results are presented for the analysis of 26 trace, minor and major elements in drinking water, using the validation and quality control criteria defined in the NS30 protocol, "A manual on Analytical Quality Control for The Water Industry", by the Water Research Centre.

(1) UK Drinking Water Regulations

In the United Kingdom, the Drinking Water Inspectorate (DWI), enforce the EC Directive 98/83/EC of November 1998. These regulations list a total of 53 parameters, including colour, turbidity, organic compounds, anions

and inorganic elements, which must be monitored in drinking water. For each parameter a prescribed concentration or value is given. This relates to the maximum or minimum concentration, which must not be exceeded. The list includes 14 inorganic elements, ranging from Na, which has a maximum concentration or Prescribed Concentration Value (PCV) of 200 mg/L , to Hg, which has a PCV of 1 $\mu\text{g/L}$. The regulation requires that the detection limit (calculated from 5 x the standard deviation of the blank, run in randomised order within each batch) for each determinant must generally be less than one tenth of the PCV.

EC Directive (98/83/EC) set out new and tighter standards for the elements Cu, As, Ni, Pb, Sb and B, making these regulations even more difficult to meet with a single instrument. The most important change in the new Directive is the reduction from 50 $\mu\text{g/L}$ to 25 $\mu\text{g/L}$ (by end 2003) and 10 $\mu\text{g/L}$ (by end 2013) in the maximum permitted concentration of lead in drinking water (required LOD of Pb will be 1.0 $\mu\text{g/L}$). This change, which is in accordance with the latest guidelines of the World Health Organisation, is introduced primarily in order to protect foetuses, infants and young children from the neuro toxic effects that are known to contribute to IQ deficits, learning and behavioural problems.

Under the Directive, each laboratory is required to performance test the analytical systems for each parameter before that analytical system can be used for routine analysis of compliance samples. The design of the performance testing and calculation of the performance characteristics should be in accordance with the guidelines laid down in the publication "NS30, a manual on analytical quality control in the water industry".

(2) Requirements for Performance Testing

Following the DWI requirements and NS30 guidelines, the following protocol is typical for metals analysis:

- 1) The calibration range should be such that all results fall within the range.
- 2) The calibration must have at least 3 points plus blank, to demonstrate a linear fit.
- 3) Samples and standards must be prepared fresh, before each batch is run.
- 4) A maximum of 2 batches can be analysed on any one day, provided the instrument is switched to overnight conditions between batches.

- 5) Samples must be analysed in random order.
- 6) Samples must be analysed in replicate, in at least 5 batches. In practice, analysis of duplicate samples on 11 batches satisfies the DWI requirements on degrees of freedom.
- 7) A batch of samples must consist of the following: Blank, Standards (typically at a concentration low in the range of interest, plus one high in the range of interest), natural drinking water samples, plus the same water samples spiked with determinants.

(3) Requirements for Statistical Validation

After acquiring the concentration data, the results must satisfy the following QC criteria:

- 1) The maximum tolerable total error of individual results should not exceed 1/10 of the PCV or 20% of the result, whichever is the greater.
- 2) The maximum tolerable total standard deviation of individual results should not exceed 1/40 of the PCV or 5% of the result, whichever is the greater.
- 3) The maximum tolerable systemic error (or bias) of individual results should not exceed 1/20 of the PCV or 10% of the result, whichever is the greater.
- 4) The estimates of total standard deviation must not be significantly greater at the 95% confidence level than the specified maximum tolerable total standard deviation at the relevant concentration.
- 5) The recovery of an added spike should not be significantly less than 95%, or significantly greater than 105%.
- 6) The limit of detection must be lower than 1/10 of the PCV. The limit of detection (LOD) implied from this specification is 5 times the within-batch standard deviation of results for blanks.

The performance testing protocol described in NS30 validates not only an analytical instrument, but also the entire laboratory protocol. If any aspect of sample or calibration standard preparation is not reproducible, then the error will be observed in the between batch variation. For this reason, it is essential that sample and standard preparation techniques are well developed and carried out reproducibly.

In a large analyte suite, there may be several issues that must be addressed regarding element stability, compatibility and cross-contamination, in addition to straightforward issues of the selection of appropriate glass/plastic ware to avoid element leaching or adsorption. In this evaluation, the internal standard (IS) mixture, which contained Be, In and Tl, was added to the standards and samples automatically by means of an on-line IS addition T-piece. As Hg was one of the required analytes, Au was added to all samples and standards at 1mg/L, and at 500ppb in the wash solution to stabilize Hg. In the absence of Au, the Hg signal is found to be unstable and exhibits extended washout times.

The X Series ICP-MS was validated for 21 controlled elements (B, Na, Mg, Al, P, K, Ca, Cr, Fe, Mn, Ni, Cu, Zn, As, Se, Ag, Cd, Sb, Ba, Hg and Pb) in drinking water, according to the NS30 protocol. At the same time, the X

Series ICP-MS was also validated for a further 5 elements (Li, V, Co, Sr and Sn). Whilst 98/83/EC lists 14 inorganic components, which must be monitored, additional elements may also be measured, provided that the NS30 protocol has been followed and validation requirements have been met. Thus, each lab can extend the validated elemental range of the technique to meet their own needs and also their customer's specific requirements.

Instrumentation

The ICP-MS instrument used was an entry level X Series ICP-MS with a Xi interface design for improved matrix tolerance, reduced polyatomic species and background contribution, in conjunction with a CETAC ASX-510 random access autosampler. Productivity was enhanced by the use of fast uptake and wash, enhanced peristaltic pump, accessory control scripts and close coupling of the autosampler, pump and spraychamber. The X Series ICP-MS, autosampler and peristaltic pump are fully automated and controlled by PlasmaLab software.

The operational criteria for ICP-MS are given in Table 1.

X SERIES ICP-MS OPERATING PARAMETERS

PARAMETER	SETTING
Forward Power	1200W
Cool Gas Flow	13.0 L/min
Aux. Gas Flow	1.0 L/min
Neb. Gas Flow	0.84 L/min
Nebuliser	Std Glass Concentric
Torch	Std 1.5mm injector torch
Spray chamber	Quartz Impact Bead
Spray chamber temp.	No Peltier
Sample uptake rate	0.8 mL/min
Interface	Xi
Detector mode	Simultaneous
No. of sweeps	135
Dwell time	2500µs
Points/mass	1
No. of replicates	3 x 20sec
ACL Script for Autosampler	Return to wash before acquisition ends
Uptake Rabbit time	20sec
Uptake Settle time	30sec
Wash Rabbit time	30sec (2% nitric acid)
Total time/sample	140sec

Table 1: X Series ICP-MS Operating Parameters.

Standard and Sample Preparation

Calibration stock solutions were prepared, each stock containing compatible groups of the analytes Ca, Na, Mg, K, Al, Fe, Cu and Zn from 10,000 mg/L single element stock solutions (e.g. Spex™). The other elements were prepared from 1,000 mg/L single element stocks (e.g. Spex™). Calibration standards were prepared in 1% nitric acid (Romil-SpA) at concentrations appropriate to the levels normally found in the sample types to be tested, as described in Table 2.

		STD 1	STD 2	STD 3	STD 4	STD 5	STOCK	AQC(L)	AQC(H)
STOCK A	Std Prep:	0.1:10	0.3:10	0.5:10	0.8:10	1:10		0.16:10	0.64:10
	Aluminium	25	75	125	200	250	2500	40	160
	Antimony	1.25	3.75	6.25	10	12.5	125	2	8
	Arsenic	6.25	18.75	31.25	50	62.5	625	10	40
	Boron	250	750	1250	2000	2500	25000	400	1600
	Cadmium	0.625	1.875	3.125	5	6.25	62.5	1	4
	Calcium	31250	93750	156250	250000	312500	3125000	50000	200000
	Chromium	6.25	18.75	31.25	50	62.5	625	10	40
	Copper	375	1125	1875	3000	3750	37500	600	2400
	Iron	25	75	125	200	250	2500	40	160
	Lead	6.25	18.75	31.25	50	62.5	625	10	40
	Magnesium	6250	18750	31250	50000	62500	625000	10000	40000
	Manganese	6.25	18.75	31.25	50	62.5	625	10	40
	Nickel	6.25	18.75	31.25	50	62.5	625	10	40
	Phosphorus	275	825	1375	2200	2750	27500	440	1760
	Potassium	150	450	750	1200	1500	15000	240	960
	Sodium	18750	56250	93750	150000	187500	1875000	30000	120000
	Zinc	625	1875	3125	5000	6250	62500	1000	4000
	Lithium	6.25	18.75	31.25	50	62.5	625	10	40
	Vanadium	6.25	18.75	31.25	50	62.5	625	10	40
	Cobalt	6.25	18.75	31.25	50	62.5	625	10	40
	Strontium	25	75	125	200	250	2500	40	160
	Tin	6.25	18.75	31.25	50	62.5	625	10	40
STOCK B	Mercury*	0.125	0.375	0.625	1	1.25	12.5	0.2	0.8
	Selenium	1.25	3.75	6.25	10	12.5	125	2	8
	Barium	125	375	625	1000	1250	12500	200	800
	Silver	1.25	3.75	6.25	10	12.5	125	2	8
					PCV level	PCV*25%			

Table 2. Calibration details used for validation, all values are in µg/L.

Interference correction samples were run after every calibration block, to determine the interference correction factor for CaO and CaOH on Fe, Co and Ni.

Each sample batch consisted of two tap waters, one river derived (soft water) and one borehole derived (hard water), these two tap waters were sub-divided and spiked at 20% and 80% of the PCV concentration, two blanks, two Analytical Quality Control (AQC) solutions and a Trace Elements in Water Reference Material (SRM 1640 diluted by a factor of 2) were prepared. The reference material was diluted to match the typical values found in drinking water, and to ensure accuracy of the standard calibrations. Following analysis of the calibration block and interference correction samples, the sample batch was analysed in random order. A different random order was used for each of the 11 batches (run over 6 days, i.e. no more than 2 batches per day), ensuring that no bias was introduced by running the samples in the same sequence.

Solution Preparation -

Std Calibration Block

Tap water

Tap water + 50ppm Ca

Tap water + 100ppm Ca

Blank 1

Blank 2

AQC 20% PCV 1

AQC 20% PCV 2

AQC 80% PCV 1

AQC 80% PCV 2

Tap water Soft 1

Tap water Soft 2

Tap water Soft + Spike Low 1

Tap water Soft + Spike Low 2

Tap water Soft + Spike High 1

Tap water Soft + Spike High 2

Tap water Hard 1

Tap water Hard 2

Tap water Hard + Spike Low 1

Tap water Hard + Spike Low 2

Tap water Hard + Spike High 1

Tap water Hard + Spike High 2

SRM 1640 1

SRM 1640 2

Run in randomised order, 2 repeats of each (i.e. a total of 40 samples in one batch).

Std Calibration Block

Tap water

Tap water + 50ppm Ca

Tap water + 100ppm Ca

All the standard and sample solutions were freshly prepared for each batch. A standard calibration block was run at the end of the randomized order of samples, and was used to perform an external drift correction.

The internal standard solution, which contained Be, In and Tl, was added to the standards and samples on-line by the means of a T-piece. After on-line dilution in the sample stream, the final concentration of the internal standards was approximately 25 µg/L, with the exception of Be, which was 10x higher to compensate for its low degree of ionization. Gold was added to every standard and sample solution at a concentration of 1mg/L, as a preservation agent for Hg. Gold was also added to the 2% nitric acid wash solution at a concentration of 500 µg/L to aid the wash out of Hg.

Tuning solution

This solution consisted of Li, Co, Ni, Ce, Pb, Bi and U all at a concentration of 10 µg/L in 1% nitric acid (Romil-SpA). A short-term stability was run daily to check the performance of the ICP-MS, monitoring not only the stability but also the response, oxides & doubly charged species and background at mass 5 and 220. The contribution of ArO at mass 56 was also monitored and ratioed against the equivalent counts per second of 10 µg/L of Co. Typical levels were 20ppb equivalent.

The Xi interface response gives at least a factor of 10 lower sensitivity than can be achieved using a standard

interface, the ICP-MS was not de-tuned to achieve this sensitivity (which can lead to instability). With a standard interface the higher-level analytes such as Na, Ca and K would be above the maximum measurable concentration of the instrument. Other benefits of the Xi interface are low ArO contribution on mass 56, and low background levels at mass 5 and 220 (up to 10 times lower than the standard interface) showing that the signal to noise ratio of most elements remains unchanged compared with the standard interface, and the 56Fe signal to noise was much improved (by a factor of 4).

Analogue detector optimization solution

This solution consisted of a multi-element mixed standard (Spex, CLMS-2) at a concentration to give acceptable count rates in both detector modes (pulse count/analog) i.e. 1,500,000cps for most elements. A solution of 500 µg/L in 1% nitric acid was used for the automatic setup of the pulse count/analog cross calibration factor of the detector.

Results and Discussion

The results of all the individual batch analyses were manually ordered into sample type per batch and a statistical processing, defined by NS30, was carried out. Tables 3 and 4 show the calculated results of two elements found in tap water, one at high concentration and one at low concentration.

Na(23)	BLANK	AQC LSPK	AQC HSPK	TAP SOFT(1)	(1)+LSPK	(1)+HSPK	TAP HARD(2)	(2)+LSPK	(2)+HSPK
Overall Mean	28	28225	116394	8650	35240	119803	23907	51121	133553
M0	343	503998	9174882	35524	673427	208041008	142671	1251134	59849372
M1	6449	136490336	1689025792	9240188	121460696	1474254848	64708096	240566576	1214781440
F-Value	19	271	184	260	180	7	454	192	20
Significance	***	***	***	***	***	***	***	***	***
*** Significant at the 0.0001 level									
Sw	18.52	709.93	3029.01	188.48	820.63	14423.63	377.72	1118.54	7736.24
Sb	39.07	5830.66	20492.99	1516.96	5495.16	17791.95	4017.63	7734.91	16992.15
St	43.24	5873.72	20715.64	1528.62	5556.10	22904.03	4035.35	7815.37	18670.36
F 0.05	1.72	1.83	1.83	1.83	1.83	1.58	1.83	1.83	1.72
F-Value	57.67	1.08	0.79	0.78	0.62	0.91	0.71	0.58	0.49
Estimated D.F.	13	10	10	10	10	19	10	10	13
OK?		PASS	PASS	PASS	PASS	PASS	PASS	PASS	PASS
Recovery		100.1	96.97		96.79	101.32		99.09	98.96
Recovery OK?		PASS	PASS		PASS	PASS		PASS	PASS
LOD	186.7 µg/L								
1/10th PCV	20000 µg/L								
LOD OK?	PASS								

Table 3. NS30 Performance Test Results for Na

Pb(208)	BLANK	AQC LSPK	AQC HSPK	TAP SOFT(1)	(1)+LSPK	(1)+HSPK	TAP HARD(2)	(2)+LSPK	(2)+HSPK
Mean	0.02	10.09	38.90	0.49	10.07	39.06	0.36	10.24	38.49
M0	0.00	0.02	0.74	0.00	0.03	0.36	0.00	0.03	0.78
M1	0.01	8.83	100.88	0.19	7.12	78.60	0.02	6.87	72.35
F-Value	11.79	414.39	136.52	60.85	244.34	220.86	5.89	203.75	93.23
Significance	***	***	***	***	***	***	***	***	***
*** Significant at the 0.0001 level									
Sw	0.04	0.15	0.86	0.06	0.17	0.60	0.05	0.18	0.88
Sb	0.06	1.48	5.00	0.21	1.33	4.42	0.06	1.31	4.23
St	0.07	1.49	5.08	0.22	1.34	4.46	0.08	1.32	4.32
F 0.05	1.67	1.83	1.83	1.79	1.83	1.83	1.57	1.83	1.79
F-Value	1.83	0.55	0.43	1.07	0.44	0.33	1.29	0.42	0.32
Estimated D.F.	15	10	10	11	10	10	21	10	11
OK?	PASS	PASS	PASS	PASS	PASS	PASS	PASS	PASS	PASS
Recovery		100.8	97.2		95.9	96.5		98.9	95.4
Recovery OK?		PASS	PASS		PASS	PASS		PASS	PASS
LOD	0.17 µg/L								
1/10th PCV	1.0 µg/L								
LOD OK?	PASS								

Table 4. NS30 Performance Test Results for Pb

An example of the overall drift of the ICP-MS is shown in Figure 1. This illustrates that the overall internal standard drift over a 2.5 hour run which followed the DWI / NS30 protocol of randomized sample runs and included the heavy matrix tap water (borehole derived), showed less than 5% drift. Any variation in response due to matrix changes in the samples, were easily corrected with the internal standard.

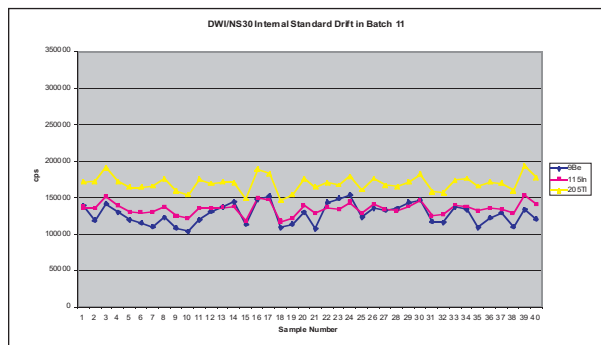


Figure 1. Internal Standard Drift in samples during a 2.5 hour DWI / NS30 protocol run.

The results from the NS30 statistical evaluation for detection limits are shown in Table 5, calculated from the randomized ordered blanks within all the 11 batches.

ELEMENTS *NEW PCV	ISOTOPE	PCV/10 µg/L	LOD µg/L
Li	7		0.03
B*	11	100	17.7
Na*	23	20000	186.7
Mg	25	5000	11.5
Mg	26	5000	31.6
Al	27	20	3.8
P	31	220	12.9
K	39	120	27.5
Ca	44	25000	133.2
V	51		1.9
Cr	52	5	0.14
Fe	54	20	6.21
Mn	55	5	0.26
Fe	56	20	9.83
Co	59		0.02
Ni*	60	2	0.13
Cu*	65	200	0.93
Zn	66	500	1.84
As*	75	1	0.18
Se	82	1	0.37
Sr	88		0.61
Ag	109	1	0.15
Cd	111	0.5	0.02
Sn	120		0.12
Sb*	121	0.5	0.07
Ba	135	100	8.84
Hg	200	0.1	0.10
Pb*	208	1	0.17

Table 5. NS30 Performance Test Results for LOD's.

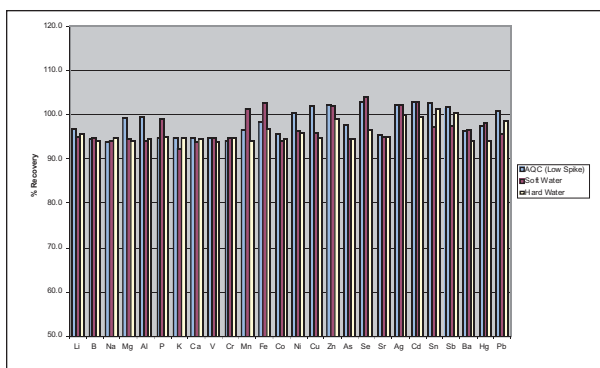


Table 6. NS30 Performance Test Results for Recoveries in Low Spiked AQC and Tap water samples.

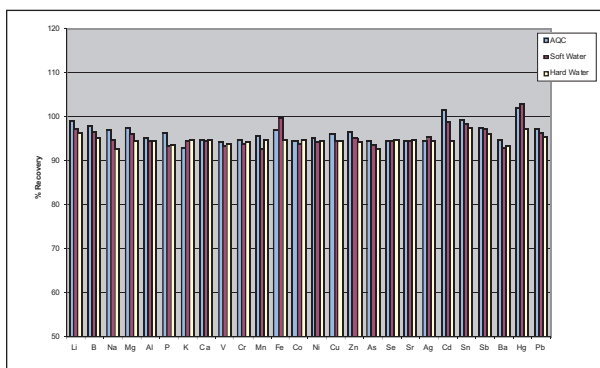


Table 7. NS30 Performance Test Results for Recoveries in High Spiked AQC and Tap water samples.

The results for the low spike and high spike recoveries are shown in Tables 6 and 7. All of the statistical evaluations indicate that the entry level X Series ICP-MS gave acceptable results under the requirements of the protocol defined in NS30.

The results shown in Table 8 show the accuracy and recovery of the Trace Elements in Water Reference Material SRM 1640, which was run as one of the randomized samples in the validation, showing that accurate results were obtained for low levels of analytes.

ELEMENTS	ISOTOPE	SRM 1640 REF VALUE µg/L	SRM 1640 OVERALL MEAN µg/L	RECOVERY %
Li	7	50.7	53.30	105.1
B	11	301.1	313.96	104.3
Na	23	29350	28037.09	95.5
Mg	26	5819	5866.15	100.8
Al	27	52	51.05	98.2
P	31		0.00	
K	39	994	949.99	95.6
Ca	44	7045	6825.48	96.9
V	51	12.99	12.37	95.3
Cr	52	38.6	37.21	96.4
Mn	55	121.5	127.92	105.3
Fe	56	34.3	33.30	97.1
Co	59	20.28	20.71	102.1
Ni	60	27.4	27.95	102.0
Cu	65	85.2	83.24	97.7
Zn	66	53.2	54.87	103.1
As	75	26.67	27.60	103.5

Se	82	21.96	22.73	103.5
Sr	88	124.2	131.11	105.5
Ag	109	7.62	7.41	97.2
Cd	111	22.79	23.97	105.2
Sn	118		0.73	
Sb	121	13.79	14.50	105.2
Ba	135	148	148.27	100.2
Hg	200		0.07	
Pb	208	27.89	27.46	98.5

Table 8. Accuracy and recovery of Trace Elements in Natural Water (SRM 1640).

Conclusion

This work demonstrates that 26 elements can be determined to DWI requirements, following NS30 analytical guidelines, using a single analytical technique. Using the X Series ICP-MS with the Xi interface allowed linear calibrations to be obtained for high concentration elements, such as Na up to 200ppm, as well as easily meeting the required detection limits for the trace elements such as Pb. A LOD for Pb of 0.17 µg/L will also easily fulfil future legislation of <1 µg/L LOD.

This system was proven to be matrix tolerant, with a long-term drift of typically < 5% when running high matrix samples such as borehole tap waters for 2.5 hours. The reduction in polyatomic species and reduced background levels (<0.05 cps) afforded by the Xi interface gave good detection limits for elements that typically suffer from interferences in heavy matrices (i.e. borehole tap waters) such as Fe, Co and Ni which have interferences of $^{40}\text{Ca}^{16}\text{O}$, $^{40}\text{Ca}^{18}\text{OH}/^{42}\text{Ca}^{16}\text{OH}/^{40}\text{Ca}^{16}\text{OH}_3$ and $^{44}\text{Ca}^{16}\text{O}$ respectively. The method detection limits for these problematic elements easily met the DWI criteria; the LOD's for Fe were 9.8 µg/L, Co 0.02 µg/L and Ni 0.13 µg/L.

The high productivity of the X Series ICP-MS was demonstrated enabling sample acquisitions of < 2.5 minutes/sample with protocol compliance.

In addition to these offices, Thermo Electron Corporation maintains a network of representative organizations throughout the world.

Australia

+61 2 9898 1244

Austria

+43 1 333 50340

Belgium

+32 2 482 30 30

Canada

+1 800 532 4752

China

+86 10 5850 3588

France

+33 1 60 92 48 00

Germany

+49 6103 4080

Italy

+39 02 950 591

Japan

+81 45 453 9100

Netherlands

+31 76 587 98 88

Nordic

+46 8 556 468 00

South Africa

+27 11 570 1840

Spain

+34 91 657 4930

Switzerland

+41 61 48784 00

UK

+44 1442 233555

USA

+1 800 532 4752

www.thermo.com



Thermo Electron Limited, Winstanley, UK is ISO certified.

©2003 Thermo Electron Corporation. All rights reserved. All trademarks are the property of Thermo Electron Corporation and its subsidiaries.

Specifications, terms and pricing are subject to change. Not all products are available in all countries. Please consult your local sales representative for details.

AN40350_E 12/03C

Thermo
ELECTRON CORPORATION