

X Series ICP-MS:

Using automated collision cell ICP-MS with rapid in-sample switching to achieve ultimate performance in environmental analysis

Key Words

- Collision/reaction cell
- In-sample mode switching
- Rapid environmental analysis
- Ultimate Performance

Introduction

The entry level X Series is a standard ICP-MS instrument with no collision cell technology (CCT), designed to meet the requirements of regulatory environmental analysis. In the US, methods such as 200.8 (see AN_E0351), 6020 (see AN_E0619), or ILM05.2 (see AN_E0620) are used. In Europe, drinking water analysis must be performed in accordance with the requirements of Directive 98/83/EC and in the UK using NS30 performance testing (see AN_E0350). The Xi interface fitted as standard to the entry level X Series instrument gives a variety of benefits for this type of work, such as resistance to matrix-induced time-dependant signal drift, low and stable polyatomic ion formation (e.g. low ArO^+ , CaO^+ and ArCl^+), and an altered transmission profile that allows the determination of group I and II elements at the high mg/L level typically found in environmental samples, at the same time as ng/L determinations for species that typically occur at lower concentrations, such as cadmium (see SN_E0344).

Studying ambient concentrations of environmentally significant elements in uncontaminated waters can be more challenging as typical concentrations are often well below regulatory levels. To obtain data at these levels with confidence requires that interference contributions must be considered more carefully. Similarly, with more challenging samples such as saline waters, leachates and aqua regia digests, interferences are frequently problematic. To avoid these problems and get the ultimate performance in environmental analysis, the use of collision cell technology may be required.

The aim of a collision or reaction cell is primarily to reduce polyatomic interferences. There are a number of possible mechanisms for this to occur:

- 1) Collision induced dissociation
- 2) Chemical reaction
- 3) Charge transfer
- 4) Collisional retardation and subsequent energy filtering

The first is thought not to be a major contributor as there is generally not sufficient energy in an unreactive collision to break the chemical bonds of most prevalent polyatomic species. Possibilities 2) and 3) are the major contributors and possibility 4) can only occur to any great extent under very specific instrument conditions.

Since chemical reaction and charge transfer processes are particularly important, the effectiveness of a gas at removing a particular polyatomic species is determined by reaction kinetics. Some kinetic data are given below in Table 1.

INTERFERENT		GAS		RATE CONSTANT, k $\text{m}^3 \text{molec}^{-1} \text{s}^{-1} \times 10^{10}$
ClO^+	+	NH_3	\rightarrow	Products 6.0
ClO^+	+	H_2	\rightarrow	Products <0.01
ArAr^+	+	NH_3	\rightarrow	Products 3.1
ArAr^+	+	H_2	\rightarrow	Products 6.3

Kinetic data from <http://www.chem.yorku.ca/profs/bohme/research/research.html>

Table 1. Kinetic data for the reaction between some interferences and gases

It is seen from the examples in Table 1 that ammonia reacts faster than hydrogen with the chlorate ion, while hydrogen reacts faster with the argon dimer, i.e. different gases must be used to obtain the most effective reactive removal of different polyatomic species.

Some analytes do not commonly suffer from interference and will perform best with the cell unpressurized, e.g. Pb.

Hence for optimum data quality, a multi-element suite ideally requires several analyses under different conditions comprising:

- Standard mode
- CCT mode with our patented use of H_2 as the reagent gas*
- CCT mode with NH_3 as the reagent gas

If all three modes are required for a single batch of samples a more efficient method is to switch modes whilst continuously aspirating the sample, i.e. “in-sample” switching.

This document describes the performance of the X Series ICP-MS fitted with the Xi interface option (see SN_E0344) and CCT^{ED} (see SN_E0346) using automated “in-sample” switching for the analysis of environmental samples. Computer controlled switching between modes is provided by the PlasmaLab software. Performance figures including speed of analysis, detection limits, analytical precision, stability and accuracy are shown.

* US patent numbers 5,767,512 and 6,259,091

Analytical Considerations

A number of analytes typically of interest in environmental analysis were monitored (see Fig. 1). Over 50 analytical isotopes were used since many elements of interest have more than one 'useful' isotope for measurement.

Figure 1. Typical element suite in environmental analysis

Most analytes have few interference problems and are measured in the 'Standard' ICP-MS Mode, i.e. with high power plasma without any collision or reaction gas admitted into the cell (cell unpressurized).

However, several analytes have associated interference problems due to molecular interactions between the plasma gas and/or sample matrix or sample solvent components. These can be aggravated in saline matrices or when the matrix contains organic matter. Some examples are shown in Table 2 below.

ANALYTE ISOTOPE	PRINCIPLE INTERFERENCE
²⁴ Mg	¹² C ¹² C
²⁷ Al	¹² C ¹⁴ N ¹ H
³⁹ K	³⁸ Ar ¹ H
⁴⁰ Ca	⁴⁰ Ar
⁵¹ V	³⁶ Cl ¹⁶ O
⁵² Cr	⁴⁰ Ar ¹² C, ³⁵ Cl ¹⁶ O ¹ H, ³⁶ Ar ¹⁶ O
⁵⁵ Mn	⁴⁰ Ar ¹⁴ N ¹ H, ³⁸ Ar ¹⁷ O
⁵⁶ Fe	⁴⁰ Ar ¹⁶ O, ⁴⁰ Ca ¹⁶ O
⁶⁰ Ni	⁴⁴ Ca ¹⁶ O, ²³ Na ³⁷ Cl, ⁴³ Ca ¹⁶ O ¹ H
⁶³ Cu	⁴⁰ Ar ²³ Na
⁷⁵ As	⁴⁰ Ar ³⁵ Cl
⁸⁰ Se	⁴⁰ Ar ⁴⁰ Ar

Table 2. Principle polyatomic-interferences of concern in environmental analysis

These polyatomic interferences can be removed by operating the instrument in CCT Mode, i.e. with the cell pressurized with an effective collision or reaction gas.

An illustration of how CCT can be used to overcome interferences on Cr is shown in Figures 2 and 3. Figure 2 shows that argon oxide and argon nitride polyatomic species contribute to the signals at *m/z* 52 and 54 in standard mode. These are examples of gas-based polyatomic species that produce a persistent background at these masses, reducing the detection capability and distorting the isotopic fingerprint for elements that occur at these masses. It is seen that in CCT mode (1% NH₃ in He), these gas-based species are removed. The detection limit is improved due to the enhanced signal to background ratio and the isotopic fingerprint for the analyte (in this case chromium) is no longer distorted.

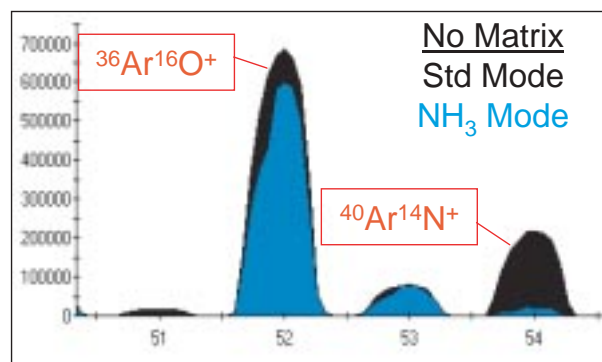


Figure 2. The use of CCT with NH₃ as the reagent gas to eliminate polyatomic interference on Cr. Spectra show 10ppb Cr in 2% HNO₃.

Figure 3 shows that in addition to persistent gas-based polyatomic species, matrix-based polyatomics can also form. In this example a chloride and carbon matrix produces the ClO and ArC polyatomic species that overlap with masses 51, 52 and 53. These are examples of interferences that vary in magnitude as a function of the concentration of the species that produces the interference, i.e. as the chloride or carbon concentration in the sample varies. This type of interference leads to inaccurate results when the sample matrix varies from that of the calibration. Isotopic fingerprints are again distorted. Once again, it is seen that CCT mode removes these interferences, allowing accurate results independent of interferent concentration and shows that the isotopic fingerprint is restored.

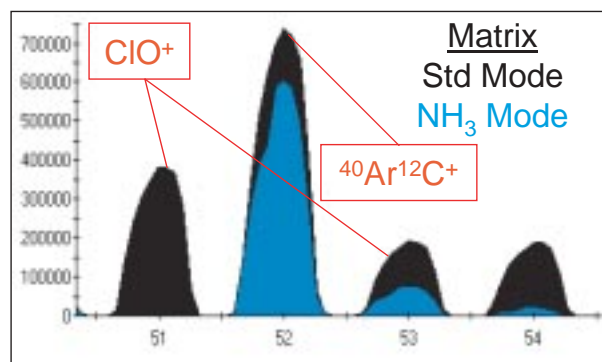


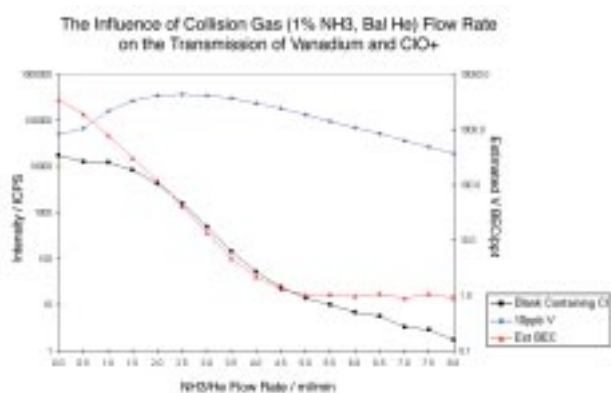
Figure 3. The use of CCT with NH₃ as the reagent gas to eliminate polyatomic interference on V and Cr. Spectra show 10ppb Cr in 2% HCl & 1% acetic acid.

Figures 2 and 3 show that some polyatomic overlaps can be eliminated using CCT with NH₃ as the reagent gas - validated by checking the isotopic fingerprint. However, NH₃ is not the ideal gas to remove all interferences and has the added disadvantage of reacting with many analyte species, bringing about a reduction in their sensitivity. Thus it is seen that a single gas cannot give the best performance for all analyte/interference combinations. Hydrogen has been found to be the most robust and generally applicable collision gas for the removal of many Ar-X polyatomics*. The cell gases used are often pre-diluted in helium. The non-reactive helium helps

* US patent numbers 5,767,512 and 6,259,091

to slow the ions passing through the cell, bringing about more reactive collisions. The mixtures used in this work were 1% NH₃ in He and 8% H₂ in He.

During method development the optimum flow rate of the reagent gas must be determined for each interfered analyte. This can be done by measuring the response of the analyte and the interferent as a function of increasing gas flow rate. The measured values are plotted on a semi-log plot of gas flow rate (x) against signal intensity (log ICPS) (y). The ideal gas flow rate is determined by extrapolating the linear portion of the interferent curve back to the x-axis or by finding the interferent/analyte signal ratio minima. An illustration is provided in Graph 1 below for the attenuation of the ³⁵Cl¹⁶O interference on ⁵¹V. In this example the ideal flow rate is around 5.5 cm³ min⁻¹.



Graph 1. Determining the optimum CCT gas flow rate for attenuation of the ClO interference on V.

Alternatively Autotune software can be used to optimise the instrument for both standard and CCT modes fully automatically. This enables unattended analysis of varying batches of samples that require differing analytical conditions for optimum performance.

When all modes of operation for the method have been selected, the stabilisation delay must be determined by monitoring analyte/interferant pairs on the PlasmaLab Real Time Display (RTD). Switching between modes is rapid requiring a stabilisation time of approximately 20-30 seconds between each mode as can be seen in Fig. 4.

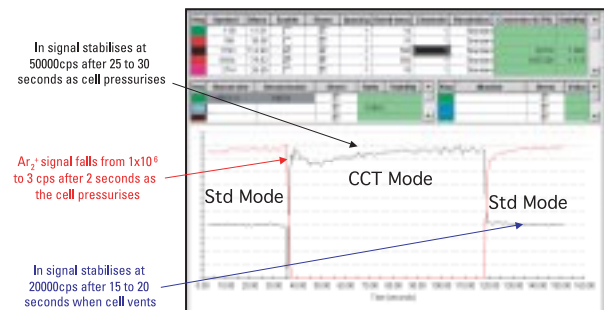


Figure 4 Rapid stabilisation when switching from Standard to CCT Mode and CCT to Standard Mode

Once optimised, the selected gas and optimum flow rate is saved along with other analytical parameters. Each settings set can be given a user definable name for easy identification. When setting up the method, the mode for measurement can be selected on an isotope-by-isotope basis (see Figure 5).

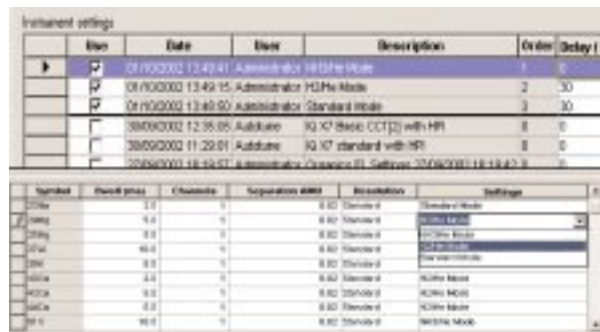


Figure 5. Selecting saved settings in an analytical method

In addition the software groups elements together according to the measurement mode selected such that all elements in Standard Mode are measured together, sequentially, with similar groupings for H₂ Mode and NH₃ Mode. The analytical profile for this study was as shown in Figure 6.

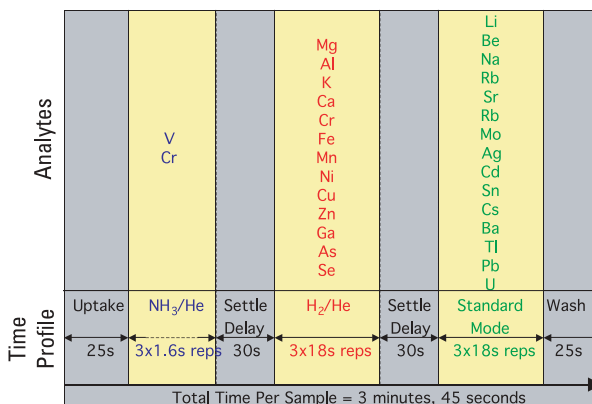


Figure 6. Analytical profile for a typical environmental element suite, 30 elements / 55 isotopes

The in-sample switching with rapid stabilisation between measurement modes combined with the intelligent sequencing ensures that the X Series ICP-MS provides the fastest possible sample throughput. The total time per sample for this analysis was 3 minutes and 45 seconds.

Experimental

Analysis of Four Certified Reference Samples

In order to evaluate the applicability and performance of the X Series with CCT^{ED} with in-sample switching, 4 certified reference waters were analysed repeatedly over a period of 12 hours. The autosampler was set up with the following standards and samples. Twelve replicate analyses were performed, recalibrating at the beginning of each cycle.

Calibration

Blank

1 ppb multi-element standard

10 ppb multi-element standard

Samples

River water reference samples were prepared as follows:

NIST 1640 diluted 1+9 and spiked to 2% HCl

CNRC SLRS-2 spiked to 2% HCl

CNRC SLRS-3 spiked to 2% HCl

CNRC SLRS-4 diluted 1+1 and spiked to 2% HCl

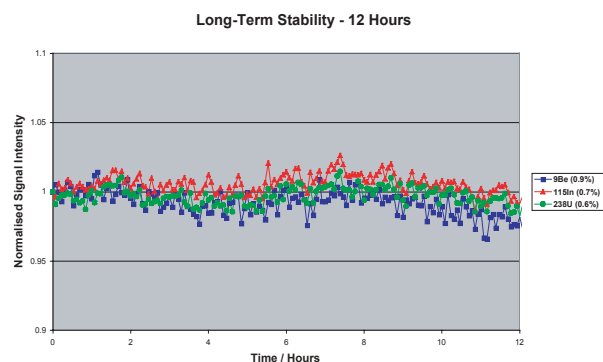
NIST 1640 and SLRS-4 samples were diluted to reduce the analyte concentrations, providing a greater analytical challenge. All samples were spiked with UPA hydrochloric acid (Romil, Cambridge, UK) to 2% to increase the presence of chloride-based interferences.

Results and Discussion

1. Long term stability was evaluated for the different modes of operation
2. Method Detection Limits were calculated after running 10-replicate blank samples 12 times against 12 different calibrations, i.e. prior to each calibration block, the autosampler probe was driven from the wash station to the blank 10-times and blank levels for all analytes recorded. All other samples and standards were measured once during each cycle.
3. Analytical accuracy was evaluated by comparing the results for the reference samples with the certified values

Long Term Stability

During the 12-hour measurement period the instrument was automatically switching 'in-sample' to measure analytes in NH₃ Mode, H₂ Mode and Standard Mode. Results for the long-term stability of selected elements in the 10ppb standard, measured in Standard Mode, are shown in Graph 2. The elements Be, In and U (being representative of the low, mid and high mass ranges) are shown measured in Standard Mode and show stabilities without reference to any internal standard of 0.9, 0.7 and 0.6% RSD respectively over the 12-hour period. Drift over this period is much less than 5% relative to the initial measured signal intensity.

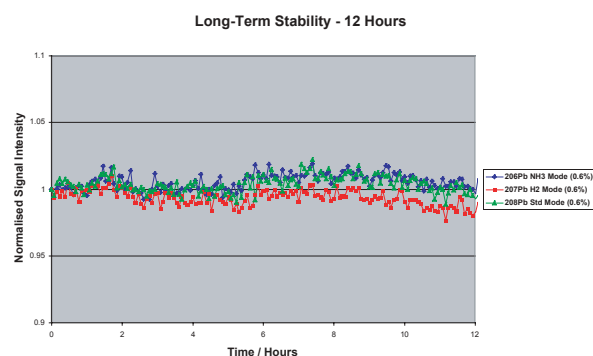


Graph 2. Stability of the 10 ppb standard measured in standard mode over the 12-hour period without the use of internal standards

In order to compare the relative stabilities and highlight any drift in each mode, three Pb isotopes were analysed in different modes during each analytical cycle – ²⁰⁸Pb in Standard Mode, ²⁰⁷Pb in H₂ Mode and ²⁰⁶Pb in NH₃ Mode.

Graph 3 shows that excellent stability (0.6% RSD) for each of the Pb isotopes was achieved without reference to any internal standard over the 12-hour period. Drift over this period is much less than 5% relative to the initial measured signal intensity.

The precision and stability are shown to be independent of the measurement mode required to achieve optimum detection limits and no hysteresis effects are observed when switching modes.

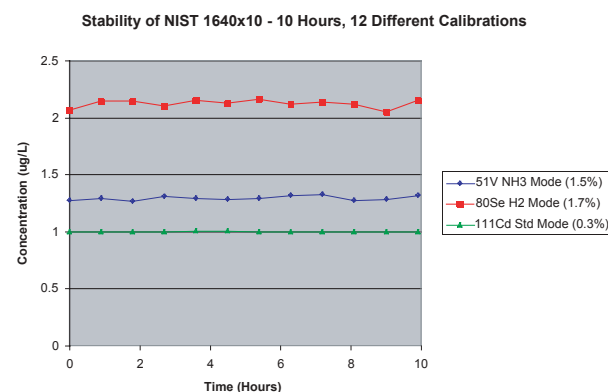


Graph 3. Stability of Pb isotopes in the 10 ppb Calibration Standard in different measurement modes over the 12-hour period without the use of internal standards

Data acquired during the repeat analysis of the NIST CRM was used to evaluate the stability in the various measurement modes.

Stability was evaluated for Cd, measured in Standard Mode, Se measured in H₂ Mode and V measured in NH₃ Mode for the NIST 1640 reference material (diluted 1+9 and spiked to 2% HCl) over a 10-hour period.

Data shown in Graph 4 without reference to any internal standard over a 10-hour period confirms that excellent repeatability is obtained and that there is no degradation in data quality due to the continual switching between different measurement modes.



Graph 4. Stability of V, Se and Cd in NIST 1640 in different measurement modes over a 10-hour period without the use of internal standards

Method Detection Limits

Method detection limits were determined by taking 10 2% HCl measurements prior to each calibration block. The autosampler probe was returned to the rinse position between each blank analysis.

⁷ Li	0.01	⁵⁵ Mn	0.01	⁷⁷ Se	0.1	¹¹⁴ Cd	0.003
⁹ Be	0.003	⁵⁶ Fe	0.06	⁷⁸ Se	0.03	¹¹⁸ Sn	0.1
²³ Na	2	⁵⁸ Ni	0.02	⁸⁰ Se	0.03	¹²⁰ Sn	0.009
²⁴ Mg	0.1	⁵⁸ Co	0.005	⁸² Se	0.1	¹³³ Cs	<0.001
²⁵ Mg	0.3	⁶⁸ Ni	0.03	⁸⁶ Rb	0.004	¹³⁸ Ba	0.007
²⁷ Al	0.2	⁶³ Cu	0.02	⁸⁷ Rb	0.008	¹⁴⁰ Ce	<0.001
⁴⁰ Ca	3	⁶⁴ Zn	0.05	⁸⁸ Sr	0.005	²⁰³ Tl	0.002
⁴⁴ Ca	1	⁶⁵ Cu	0.02	⁹⁸ Mo	0.007	²⁰⁵ Tl	0.001
⁵¹ V	0.01	⁶⁶ Zn	0.05	⁹⁸ Mo	0.005	²⁰⁶ Pb	0.01
⁵² Cr	0.2	⁶⁸ Ga	0.02	¹⁰⁷ Ag	0.009	²⁰⁷ Pb	0.01
⁵³ Cr	0.05	⁷¹ Ga	0.005	¹⁰⁸ Ag	0.009	²⁰⁸ Pb	0.009
⁵⁴ Fe	1	⁷⁵ As	0.01	¹¹¹ Cd	0.002	²³⁸ U	<0.001

H₂/He Mode
 NH₃/He Mode
 Standard Mode

Table 3. Estimated 3-sigma MDLs (ppb) obtained over the 10-hour analysis

The mean 3-sigma DLs obtained from 12 such data blocks over the 10-hour analysis period are shown in Table 3. MDLs in the ppt to sub-ppt range are obtained for almost all elements and all are well below current regulatory requirements.

Analytical Accuracy

Accuracy is reported in Tables 4 and 5 below where the measured and certified values for the certified reference standards are reported together with a % Recovery value.

% Recovery = (Measured concentration/Certified concentration) x 100.

1640X10	7Li	9Be	24Mg	51V	52Cr	55Mn	59Co	60Ni	65Cu
Measured	4.96±0.03	3.40±0.02	579±4	1.30±0.02	3.58±0.05	11.89±0.09	2.02±0.02	2.67±0.02	8.39±0.07
Reference	5.07	3.49	582	1.3	3.86	12.19	2.03	2.74	8.52
Recovery %	98	97	100	100	93	98	99	97	99

1640X10	66Zn	75As	80Se	85Rb	88Sr	107Ag	111Cd	138Ba	208Pb
Measured	5.11±0.05	2.61±0.02	2.12±0.04	0.192±0.004	12.0±0.1	0.75±0.03	2.21±0.02	14.2±0.1	2.65±0.03
Reference	5.32	2.66	2.2	0.200	12.4	0.762	2.28	14.8	2.79
Recovery %	96	98	97	96	97	98	97	96	95

SLRS-2	27Al	40Ca	51V	55Mn	56Fe	60Ni
Measured	87±3	5500±300	0.248±0.007	10.1±0.2	127±2	1.01±0.03
Reference	84	5700	0.25	10.1	129	1.03
Recovery %	104	97	99	100	98	98

SLRS-2	65Cu	66Zn	75As	88Sr	138Ba	238U
Measured	2.96±0.05	3.42±0.06	0.78±0.03	28.1±0.4	13.5±0.1	0.0464±0.0005
Reference	2.76	3.33	0.77	27	13.80	0.049
Recovery %	107	103	101	103	98	95

H₂/He Mode
 NH₃/He Mode
 Standard Mode

All concentrations in µg/L n=12

Table 4. Results for NIST 1640x10 and SLRS-2

SLRS-3	27Al	40Ca	51V	52Cr	53Cr	55Mn	56Fe
Measured	32.2±0.6	5900±300	0.299±0.006	0.28±0.09	0.28±0.01	3.85±0.04	98±1
Reference	31	6000	0.3	0.30	0.30	3.9	100
Recovery %	104	96	100	92	93	99	98

SLRS-3	63Cu	65Cu	75As	95Mo	98Mo	111Cd	138Ba	238U
Measured	1.37±0.02	1.39±0.02	0.73±0.01	0.192±0.005	0.193±0.005	0.012±0.001	13.2±0.1	0.0416±0.0005
Reference	1.35	1.35	0.72	0.19	0.19	0.013	13.4	0.045
Recovery %	102	103	101	101	102	96	98	92

SLRS-4x2	9Be	24Mg	27Al	40Ca	51V	52Cr	55Mn	56Fe
Measured	0.004±0.001	794±5	27.7±0.3	3000±200	0.165±0.006	0.16±0.08	1.69±0.02	51.4±0.4
Reference	0.0035	800	27	3100	0.160	0.165	1.69	51.5
Recovery %	105	99	103	98	103	95	100	100

SLRS-4x2	59Co	60Ni	65Cu	75As	88Sr	111Cd	138Ba	238U
Measured	0.0194±0.0009	0.31±0.01	0.86±0.02	0.36±0.01	14.0±0.1	0.0066±0.0008	6.22±0.05	0.0237±0.0003
Reference	0.0165	0.335	0.905	0.34	13.15	0.006	6.1	0.025
Recovery %	117	93	95	107	106	100	102	95

H₂/He Mode
 NH₃/He Mode
 Standard Mode

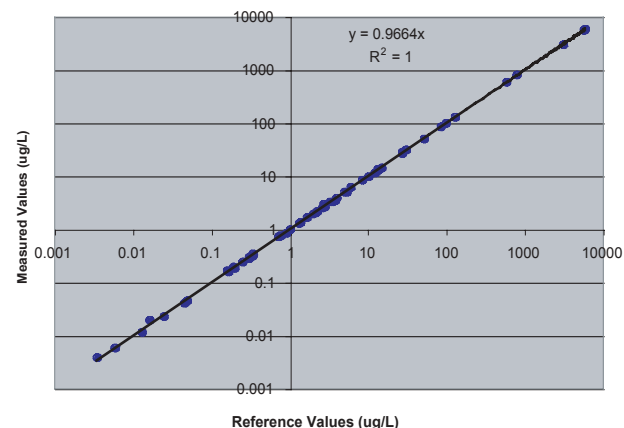
All concentrations in µg/L n=12

Table 5. Results for SLRS-3 and SLRS-4

The collision cell performance for removal of matrix-based interferences is proven for analytes such as vanadium and arsenic, where accurate data were obtained at the ppt level in the presence of high chloride levels without the use of any interference correction equations. Similarly, the collision cell allows the measurement of isotopes that normally suffer from persistent gas-based interference, such as iron-56 (ArO), calcium-40 (Ar) and selenium-80 (Ar₂). At the same time, standard mode analysis can be used with the detection limit enhancement offered by the PlasmaScreen Plus option, achieving excellent accuracy at the single and double figure ppt level for analytes such as beryllium, cadmium and uranium.

Graph 5 shows that that excellent accuracy was achieved across the range of single units of ppt through to tens of ppm and was independent of detector mode (analog or pulse counting), and measurement mode (Standard Mode or CCT Mode).

Accuracy of Analysis Summary Plot



Graph 5. Accuracy summarised as a linear log-log plot of measured versus certified concentration

Conclusion

The entry level X Series ICP-MS is designed to meet the legislated requirements of US EPA and European protocols such as EPA 6020, 6020A, ILM05.2D, European Council Directive 98/83EC etc. If your analytical needs are met by such legislation then Collision Cell Technology is not required.

If your analytical requirements become more demanding, the X Series uniquely provides the flexibility to upgrade to Collision Cell Technology with a simple < 1-day in-the-field installation without affecting the Standard Mode performance of the spectrometer, hence futureproofing your investment against ever decreasing MDL requirements.

With performance enhancing options such as CCT^{ED}, the X Series ICP-MS combines research performance with routine operation.

Confident low-level analysis of challenging, high matrix samples can be analysed with optimised CCT settings and rapid switching between settings yielding the ultimate performance. Two different cell modes, including the use of hydrogen, can be combined with standard mode analysis in a single sample acquisition to provide a rapid best-of-all-worlds approach.

The typical sample analysis duration is < 4 minutes for up to 55 isotopes, hence the sample throughput is excellent for a high performance analysis.

Excellent stability is obtained independent of the measurement mode with RSDs <1% over a 12-hour period and it is seen that switching modes within each sample causes no stability degradation or hysteresis effects.

In-sample mode switching allows the optimum conditions for each analyte to be used, resulting in the ultimate analytical performance without the need to re-run samples. This leads to detection limits in the ppt to sub-ppt range for the majority of elements. Detection limits are significantly improved for species normally affected by gas-based polyatomics, such as ArO and remain excellent in Standard Mode due to the high signal to noise ratio of the X Series.

Excellent accuracy is demonstrated, even at sub- $\mu\text{g/L}$ levels in the presence of matrix-based interferents such as chloride. In this study, accuracy to within +/-5% for the vast majority of analytes was achieved without the use of interference correction equations, even after spiking to 2% HCl.

References

Thermo Electron Application Notes:

- AN_E0351 US EPA 200.8 Using the X Series ICP-MS
- AN_E0619 US EPA SW-846 Method 6020A Using the X Series ICP-MS
- AN_E0620 US EPA Method ILM05.2D Using the X Series ICP-MS
- AN_E0350 Routine Trace Metals Analysis Using the X Series ICP-MS, Meeting UK Drinking Water Inspectorate Requirements (DWI / NS30)
- SN_E0344 Xi Interface for the X Series ICP-MS
- SN_E0346 Collision Cell Technology with Energy Discrimination - Unsurpassed Interference Elimination

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