

Rapid, simple, interference-free analysis of environmental samples using the XSERIES 2 ICP-MS with 3rd generation CCT^{ED}

- Interference-free analysis of 29 elements in environmental samples from 1 ppt to 500 ppm in less than 150 seconds

Bill Spence, Thermo Fisher Scientific, Ion Path, Road 3, Winsford, Cheshire, CW7 3GA, bill.spence@thermofisher.com

Key Words

- ICP-MS
- Collision cell
- Environmental
- Interference-free
- KED



Abstract

A Thermo Scientific XSERIES 2 ICP-MS fitted with a single collision gas produces rapid, interference-free, multi-element analysis of environmental samples.

Key Points: simpler, faster, and better environmental analysis:

- No correction equations necessary for correction of polyatomic interferences – leading to improved accuracy in real samples, lower detection limits and increased confidence in results
- Instrument is simple to set-up: a single simple gas, no element specific factors required, fully automated set up
- Provides blanket interference removal using a single set of conditions with a single gas
- Transmission of cell reaction products blocked by kinetic energy discrimination
- Cell and lens system do not need to be regularly replaced and are maintenance-free

Introduction

In environmental applications, ICP-MS has been traditionally limited by the formation of spectral interferences caused by the formation of polyatomic (molecular) ions in the plasma. These are most often formed from the combination of sample matrix components with ions at high concentrations in the plasma gas. When they have the same nominal mass-to-charge ratio as an analyte of interest, they can cause inaccuracy (bias), normally in the form of false positive results. Interference correction equations have been used to mathematically correct for the contribution of these interferences by monitoring the presence and magnitude of an interfering species at an alternative mass and deducting the relative contribution to the signal at the mass of interest. This approach has several limitations:

1) It is often complicated by the presence of additional interferences on the monitored species;

- 2) Detection limits of interference corrected analytes are degraded in the presence of the interfering species due to propagation of errors from the measurement of the monitored species;
- 3) The correction only produces reliable results at relatively low concentrations of the interfering species and/or relatively high concentrations of analyte.

For these reasons, collision/reaction cells were developed in order to provide an instrumental method of removing polyatomic interferences.

Collision/reaction cells can be used in either a reactive mode using gases such as hydrogen, ammonia, methane or oxygen, or in a passive filtering mode using an inert gas such as helium combined with kinetic energy discrimination (KED). Reactive modes tend to be somewhat element specific since a specific gas must be selected to target the removal of a specific interference without overtly affecting the transmission of the analyte. For this reason, the use of a single reactive gas is not effective for multi-element analyses and consequently multiple reactive gases are often used to obtain the best results. With helium KED mode however, the interference removal mechanism is a physical filtering effect brought about by a difference in the ionic radii of polyatomic species and atomic ions. Polyatomic species have a larger collision cross-section and therefore collide with the He collision gas more frequently as they traverse the cell, losing more kinetic energy than their counterpart atomic ions. A voltage barrier between the collision/reaction cell and the mass analyser can therefore be used to discriminate between the two types of species. This results in transmission of the analyte species to the mass analyzer and exclusion of the polyatomic. The benefit of this approach is that it is applicable to all polyatomic species, under a single set of conditions, offering interference-free multi-element analysis without the unnecessary delay incurred by switching from one cell gas to the next in reactive mode.



This note describes how a simple, yet extremely effective single gas collision cell approach removes the necessity for interference correction equations in environmental analysis, improving accuracy and detection limits with a short analysis time.

Method

Instrument Details

A Thermo Scientific XSERIES 2 ICP-MS (Thermo Fisher Scientific, Bremen, Germany) with 3rd generation collision cell technology with energy discrimination (CCT^{ED}) was used to demonstrate the effectiveness of a simple single gas collision cell approach for removing polyatomic interferences in environmental analysis. The XSERIES 2 ICP-MS collision cell technology (CCT) is described in more detail in the Collision Cell Technology technical note.

Configuration and Settings

A single gas collision cell mode that provides blanket interference removal was developed. This utilized pure helium as the cell gas and a kinetic energy barrier of +3 V. Table 1 shows the details of key instrument options and parameters. An autotune procedure was used to provide a completely automated setup.

Procedure

The effectiveness of helium KED mode was demonstrated by performing a typical environmental analysis. Internal standards (Li-6, Ge, Rh, and Lu) were added at a ratio of 1:1 on-line, using the integrated peristaltic pump and a mixing tee. The instrument was calibrated for 29 environmentally significant elements. No interference corrections were applied. Multiple trace nitric acid blank samples (ten replicates) were analysed to produce an instrument detection limit (3-sigma). Multiple 1 % hydrochloric acid samples (7 replicates) were analysed to

Parameter	Option or Setting
Nebulizer	Standard glass concentric
Spray chamber	Standard glass conical impact bead
Torch Option	Standard one-piece quartz torch with PlasmaScreen ^{plus}
Interface option	Xt
Cell Gas	Helium (purified with IG35-XL gas purifier, Johnson Matthey Pureguard http://www.pureguard.net)
Sample uptake rate (mL/min)	0.4 approx.
Cool Gas Flow (L/min)	13
Aux. Gas Flow (L/min)	0.7
Nebulizer Gas Flow (L/min)	0.9
Forward Power (W)	1400
Hexapole Bias (V)	-20
Quadrupole Bias (V)	-17
Cell Gas Flow Rate (mL/min)	5.5

Table 1: Key instrument options and parameters

produce a method detection limit (5-sigma) in an interfering matrix. The US EPA method 6020A ICSA solution was analysed as an interference check (comparative data in standard mode were also collected). This solution contains high concentrations of typical environmental matrix elements. Table 2 shows the constituents of the ICSA solution and lists some of the likely interferences that may arise and the elements with which they interfere.

Interferent	Conc ^a / ppm	Mg	K	Ca	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Se	Cd	Ba
C	200	CC				ArC										
Na	250										ArNa					
Mg	100											ArMg				
Al	100			AIO												
P	100										PO ₂					
S	100											SS, SO ₂				
Cl	2000				ClO	ClOH							ArCl			
K	100						KO									
Ca	300							CaO	CaO	CaO					ArCa	
Ti	2										TiO	TiO			TiO ₂	
Fe	250												FeOH			
Mo	2														MoO	ArMo
Gas-based	---		ArH	Ar		ArN		ArO						ArAr		

Table 2: ICSA solution composition and likely interferences produced.

The calibration was checked by running a quality control standard as a continuing calibration verification (CCV). The ICSA solution was analysed 10 times to represent ten

high matrix environmental samples, followed by reanalysing the CCV. This cycle was repeated 24 times, replicating a 240 unknown sample run.

Results and Discussion

Multiple Interference Removal with Helium KED Mode

Interference removal was demonstrated by producing gas flow optimization plots in 1:10 diluted seawater, which represents a worst-case environmental matrix with low concentrations of many analytes. The optimization plots are given in Figure 1. These show optimizations for chromium-52, vanadium-51, nickel-60, cobalt-59, copper-63 and arsenic-75. The optimum gas flow rate is

taken as the position at which the blank equivalent concentration (BEC) no longer decreases significantly with further increase in gas flow rate. The plots show that all interferences from the seawater matrix are eliminated with the addition of 5.5 mL/minute of helium. This produces simple optimization and operation, without the need for alternative gases and modes. Accuracy and analysis times are therefore dramatically improved.

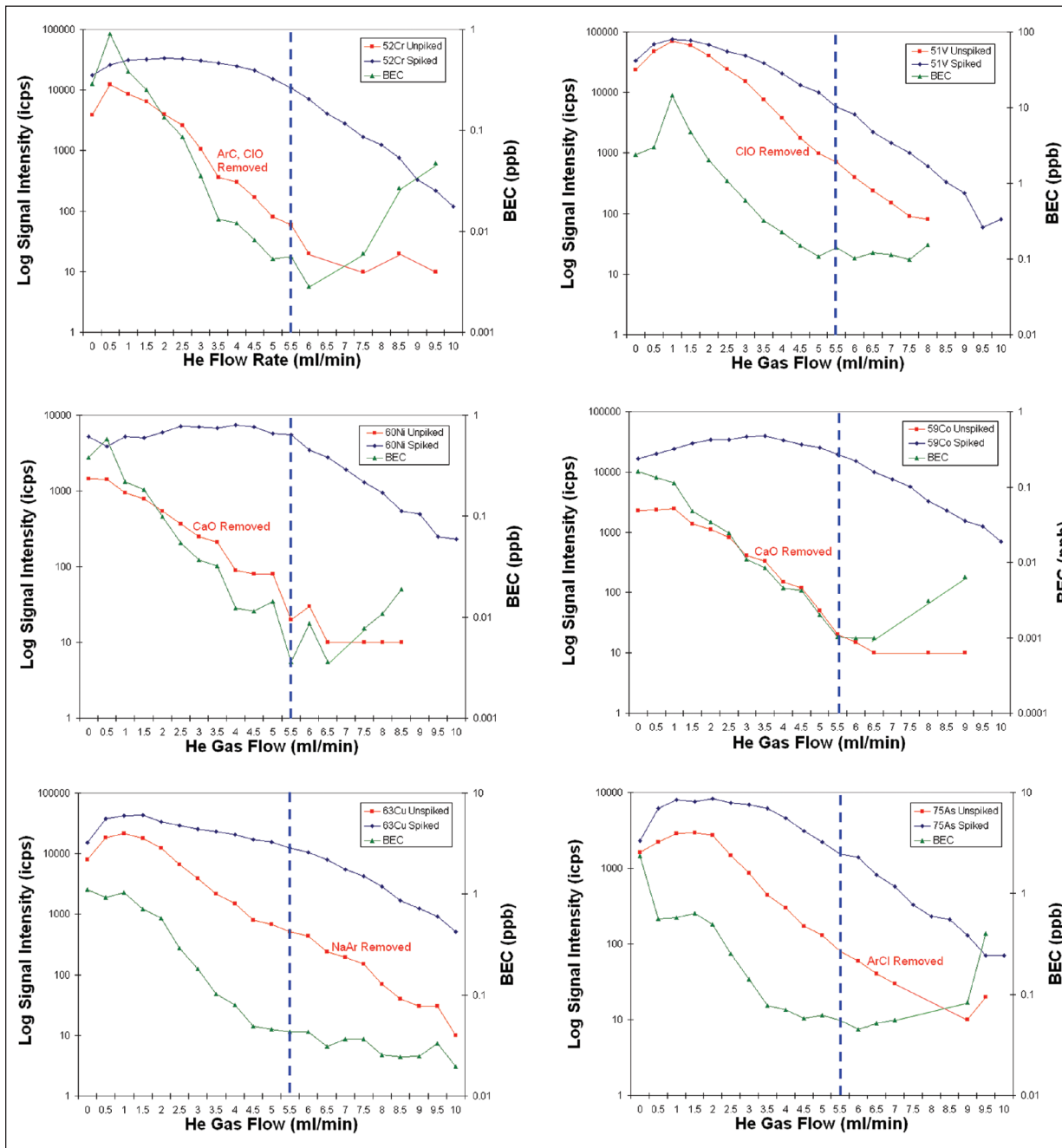


Figure 1: Gas optimization plots in 1:10 diluted seawater

Simultaneous multiple interference removal was further demonstrated by the analysis of the ICSA solution. Figure 2 graphically compares the measured results for the ICSA solution for selected interfered elements in helium KED cell mode and standard mode. No correction equations were used in either case. The expected value for all indicated elements is zero. The standard mode results show the presence of matrix-based polyatomic interference in many cases. Without interference correction this results in positively biased data. The cell mode results show virtually no interference on the majority of elements. In fact, the presence of trace contamination in the ICSA solution was confirmed in this mode by performing multiple isotope scans. Good elemental isotopic fit was obtained for elements showing some residual contribution, such as copper, zinc, and lead, confirming the presence of contamination. Figure 3 shows the scan confirming the presence of lead contamination.

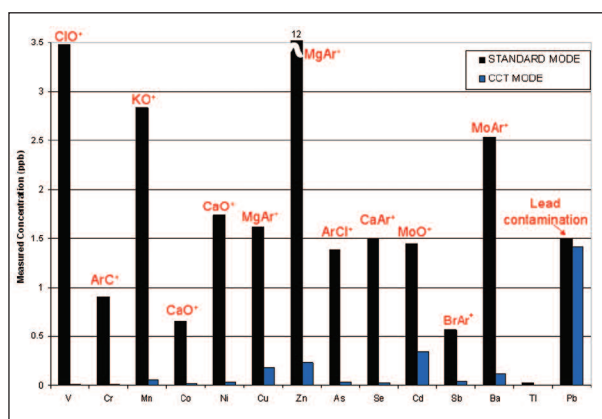


Figure 2: A comparison of results of analysis of the 6020A ICSA solution in standard mode and helium KED cell mode for selected interfered elements

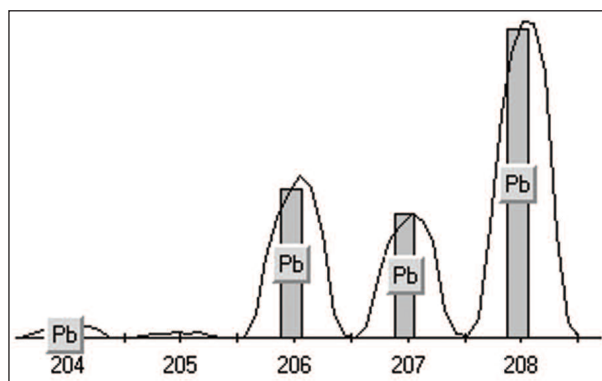


Figure 3: Confirmation of the presence of lead contamination by isotopic pattern fitting

Detection Limits and Dynamic Range

Table 3 shows the results of the calculated detection limits in both trace nitric acid and 1 % hydrochloric acid (HCl). Instrument detection limits at or below the single figure part per trillion (ppt) level were obtained for the majority of elements in this mode. The robust method detection limits in hydrochloric acid, which was used to provide an interfering matrix, are typically at the tens of ppt level for the majority of elements, even in the presence of interference. The method detection limits may be adversely affected due to the presence of some contamination in the hydrochloric acid.

Lower mass elements exhibit reduced sensitivity in this mode yielding improved dynamic range for group I and II elements that are typically present at high part per million (ppm) levels in typical environmental samples. Linear dynamic ranges (LDRs) of at least tens to hundreds of ppm are obtainable in this mode, allowing simultaneous measurement of typical environmental levels of high concentration elements and ultratrace elements.

m/z	Element	3-s IDL in tr. HNO3 (ppb)	MDL in 1 % HCl (ppb)	LDR Tested (ppb)
9	Be	0.05	0.1	1000
23	Na	0.5	5	500000
24	Mg	0.2	1	100000
27	Al	0.1	0.5	100000
39	K	5	20	500000
44	Ca	3	10	500000
51	V	0.002	0.03	10000
52	Cr	0.0005	0.02	10000
55	Mn	0.0005	0.02	10000
56	Fe	0.02	0.05	500000
59	Co	0.0005	0.01	10000
60	Ni	0.001	0.02	10000
65	Cu	0.001	0.01	10000
66	Zn	0.003	0.02	10000
75	As	0.005	0.02	10000
78	Se	0.01	0.1	10000
88	Sr	0.0001	0.01	1000
90	Zr	0.0001	0.02	1000
98	Mo	0.0001	0.01	10000
107	Ag	0.003	0.01	10000
111	Cd	0.0003	0.005	10000
118	Sn	0.002	0.02	10000
121	Sb	0.001	0.02	10000
137	Ba	0.001	0.02	10000
202	Hg	0.01	0.05	10000
205	Tl	0.00005	0.002	10000
208	Pb	0.0005	0.01	10000
232	Th	0.0001	0.001	10000
238	U	0.0001	0.001	10000

Table 3: Detection limits and linear dynamic range (LDR) in helium KED mode

Accuracy

To assess the accuracy of the method a reference water sample, NIST 1640, was analysed after spiking to 1 % with hydrochloric acid to provide additional interference. Excellent agreement with all certified values was achieved, with recoveries between 95 and 105 %. Table 4 shows the results of this analysis.

m/z	Element	NIST 1640 + 1 % HCl (ppb)	NIST 1640 Cert. (ppb)	Recovery %
9	Be	35.9	34.9	103
23	Na	28461	29350	97
24	Mg	5620	5819	97
27	Al	53.5	52	103
39	K	1046	994	105
44	Ca	6982	7045	99
51	V	13.2	13.0	102
52	Cr	36.8	38.6	95
55	Mn	120	122	99
56	Fe	35.1	34.3	102
59	Co	20.1	20.3	99
60	Ni	27.6	27.4	101
65	Cu	88.3	85.2	104
66	Zn	51.9	53.2	98
75	As	26.3	26.7	99
78	Se	21.4	22.0	98
88	Sr	128.0	124.2	103
98	Mo	46.7	46.8	100
107	Ag	8.1	7.7	105
111	Cd	23.1	22.8	101
121	Sb	13.6	13.8	99
137	Ba	148	148	100
208	Pb	27.5	27.9	99

Table 4: Results of analysis of reference sample NIST 1640

Stability

To demonstrate the stability of the analysis, the results of the CCV sample analysed after every 10 samples of high matrix ICSA solution are plotted in Figure 3. US EPA methods such as 200.8 and 6020A suggest a control limit of 100±10 %. Figure 3 shows that all CCV measurements during the 240 high matrix sample run remained within the control limits, demonstrating the superior stability of the instrument when analyzing high matrix samples, in this case over nearly 13 hours.

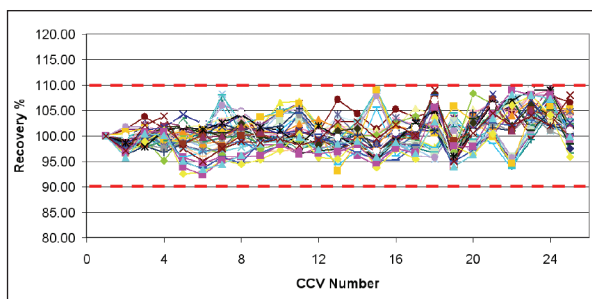


Figure 3: CCV results during the analysis of 310 samples, including 240 measurements of the ICSA solution analyzed to represent high matrix unknown samples

Conclusions

This note has demonstrated that a simple single-gas collision cell mode for multi-element environmental analysis simultaneously eliminates all polyatomic interferences of concern in the analysis of environmental samples. Consequently, interference correction equations are no longer required. The removal of interferences results in better accuracy in real samples and lower detection limits when interfering species are present. This leads to increased confidence in data quality.

This mode produces lower sensitivity for very low mass elements and selenium. This is advantageous for the extended range analysis of typically high concentration group I and II elements and linearity can be obtained up to at least 500 ppm for elements such as sodium, potassium, and calcium. If improved detection limits are required for selenium, hydrogen mode can be used (see the accompanying application note).

The helium KED mode is simple to set-up, requiring only a single gas and no optimisation of complex interference-specific filtering settings. The set-up can be fully automated with an autotune sequence. Since only one gas mode is used, the long stabilization delays typically associated with multiple mode analyses are not required. This dramatically improves the speed of analysis, allowing the measurement of a typical 29 element environmental method in just 2 1/2 minutes per sample, or 24 samples per hour. This is the fastest interference-free analysis available.

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