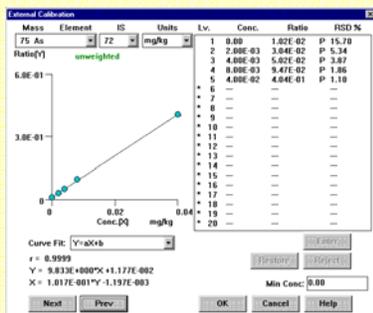


Application of Collision/Reaction Cell ICP-MS to the Analysis of Variable and Unknown Samples Without Requiring Matrix-Specific or Element-Specific Tuning and Cell Conditions

Introduction. ICP-MS is a multi-element analytical technique, which uses a high temperature plasma source to decompose, dissociate, atomise and ionise the elements of interest in a sample, providing high sensitivity, rapid analysis, low detection limits, simple spectra and routine operation. In simple solutions, few interferences obscure the measurement of the trace elements of interest; primarily the affected elements are those that are overlapped by polyatomic ions derived from the sample solvent and the plasma gas (O, H, Ar, C, N). In sample matrices of the types commonly analysed in routine laboratories, the situation with respect to interferences can be much more complicated, especially if, as is typically the case, the matrix is complex, variable and of unknown composition. Under these circumstances, it is essential that the ICP-MS is able to handle the variable sample matrices, with the minimum of information on the sample composition, in order to permit unknown samples to be analysed routinely.

Conventional ICP-MS

Numerous reports have shown that conventional ICP-MS (without collision/reaction cell) can be optimised to provide dramatic improvement in the capacity to measure "difficult" trace elements in the presence of high levels of a sample matrix, simply through the use of design and operating conditions which lead to a high and stable plasma temperature to ensure efficient sample decomposition and analyte ionisation. The calibration on the right shows As at single ng/mL levels in a matrix of 5.6% aqua regia, used for soil digestion.

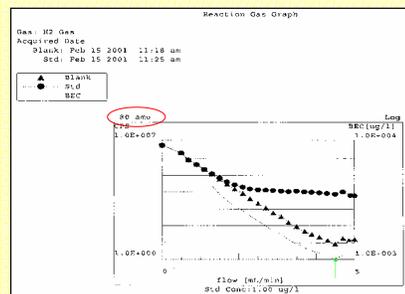


Calibration for As (2 - 40ng/mL) in 5.6% aqua regia (4.2% HCl, 1.4% HNO₃) - Agilent 7500a (non-cell instrument)

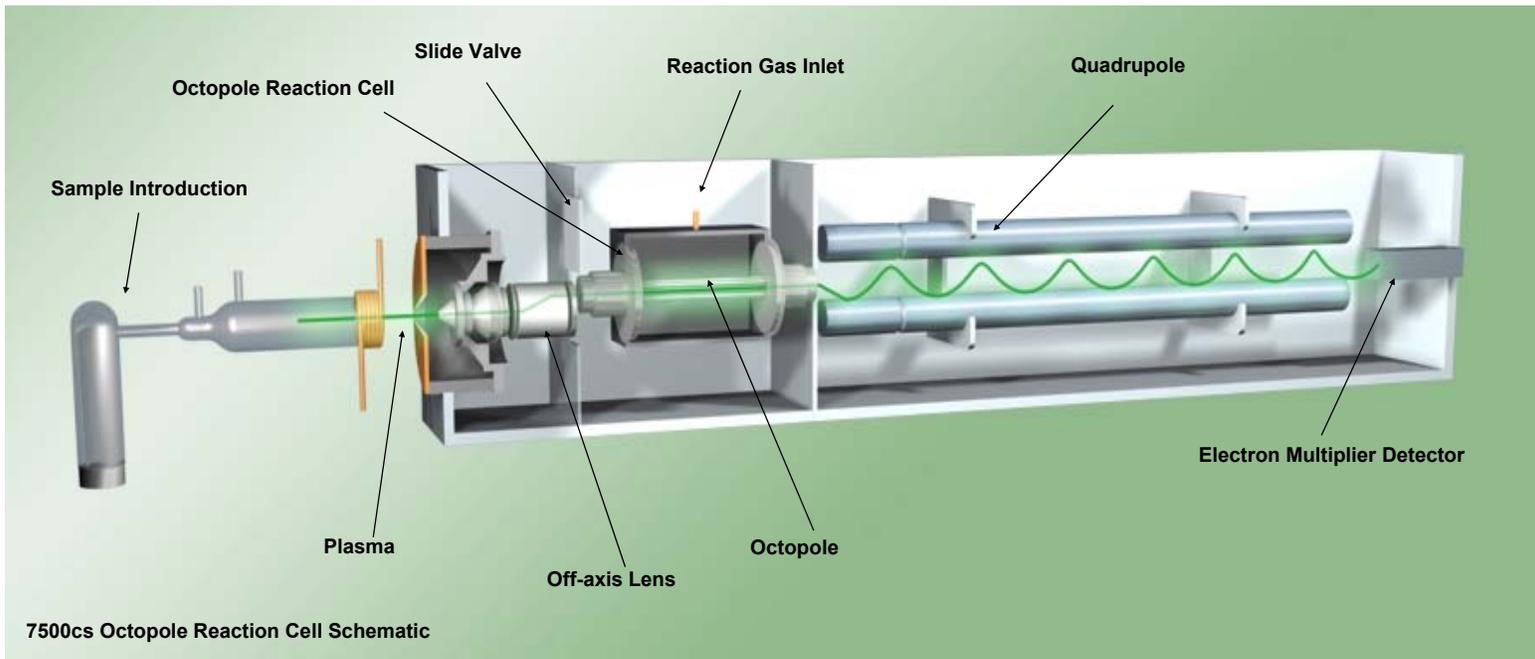
Collision/Reaction Cell ICP-MS

The collision/reaction cell provides the analyst with an additional method for reducing or removing interfering species from the mass spectrum. In **reaction mode** (shown here), specific target interferences are removed from specific analyte masses, using well-defined reaction pathways. **Collision mode** (using pure He cell gas) is non-specific: it attenuates ALL polyatomic species using a single set of cell conditions.

In collision mode, the larger polyatomic (interferer) species undergo more collisions (and so lose more energy) than the smaller, monatomic (analyte) species. Interference removal occurs by energy discrimination and is therefore non-specific, but relies on a very small ion energy spread of all ions entering the cell



H₂ cell gas optimisation plot for ⁸⁰Se



7500cs Octopole Reaction Cell Schematic

Reported limitations of Cell-based ICP-MS Utilising Highly Reactive Gases Include:

- Loss of sensitivity (due to reaction) for some required analyte elements; may require several sets of gas conditions for full analysis, so increasing method development
- Inability of a single reaction gas to remove multiple interfering species on a single analyte (e.g. ⁸⁰Se in a complex matrix).
- Appearance of new interfering species (eg cluster ions); requires each matrix to be evaluated individually for new interfering species, before cell conditions for each analyte isotope can be determined – makes cell conditions matrix specific
- Multiple anomalous peaks due to traces of residual gas/matrix contamination in cell (providing reactive analyte loss and cluster ion formation, even in non-gas mode)
- Residual or new (cell-formed) interferences, leading to a requirement to utilise multiple, matrix-dependent interference correction equations
- Cell-formed interferences can interfere with internal standard - incorrect quantification

Due to the above limitations, the operating conditions required for accurate analysis of complex, high matrix samples are highly analyte and matrix dependent, effectively preventing the reliable analysis of unknown sample types in cell mode with a reactive gas.

Cell Operation with an Inert Cell Gas

Using an inert cell gas and efficient energy discrimination (ED) removes all of these reported problems, since the cell is operating as a non-reactive environment. The use of an inert gas allows ED to be used as the primary interference removal process, which eliminates the method development inherent in the use of reactive cell gases. This means that the analysis conditions are independent of the analyte being measured (and of the interferences being removed), multi-element analysis is possible and the operating conditions do not have to be optimised for each matrix type.

A further benefit of collision mode is that no interference correction equations are necessary. Use of ED depends on the use of a high purity inert cell gas, which is free from organic contaminants and water vapour, so plumbing of the gas supply requires care. A light collision gas (He) is preferred, since less analyte ion scattering occurs.

Mode of Operation

The operation of a cell in collision mode, using ED as the method of interference removal, requires strict control of ion energy entering the cell. This is achieved using a shielded torch configuration, which provides much smaller ion energy spread than end-grounded or centre-grounded unshielded torch configurations. The control of ion energy is essential for effective interference removal by ED, since it is the small difference in ion energy that results from the larger number of collisions that a polyatomic ion suffers, compared to a monatomic ion, which is used to distinguish between the analyte and interferant species at the cell exit. For this discrimination to be possible, the analyte and interferant ions must enter the cell with essentially the same energy.

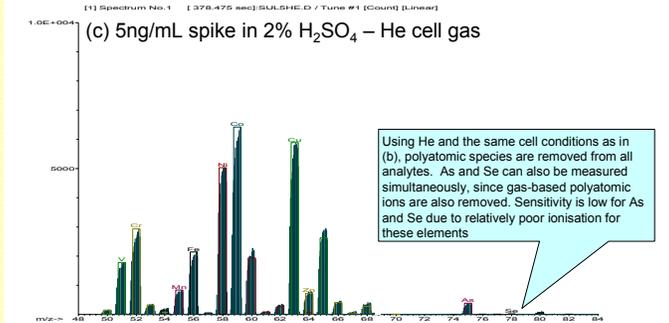
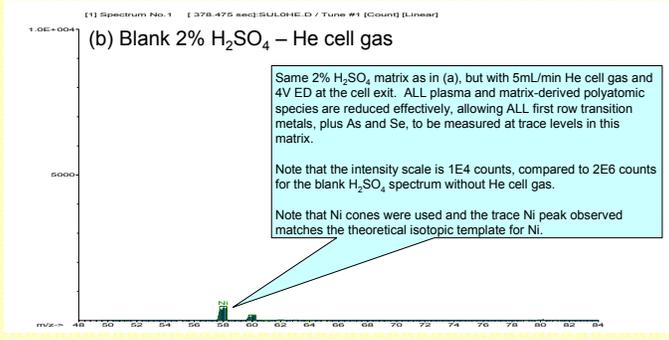
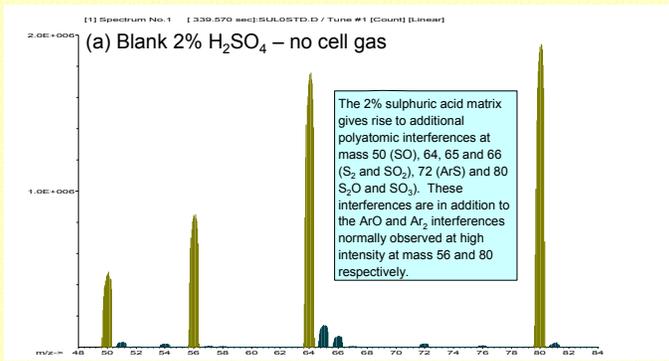
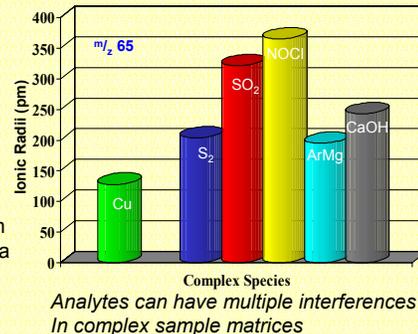
Multi-element Analysis in Single Component Matrix

The spectra below show the ability of collision mode to remove multiple polyatomic ion species in a matrix of 2% H₂SO₄. In addition to the normal ArO and Ar₂ background species, SO, S₂, SO₂, ArS, S₂O and SO₃ interferences interfere with the 1st row transition elements, As and Se. Efficient removal of all S-based species is not possible in reaction mode. One reported approach for reaction mode proposed to measure analytes indirectly via the formation of cluster ions with NH₃ reaction gas. This approach is inherently unreliable in unknown complex matrices: He collision mode is with ED is the only reliable method for the measurement of Zn in a sulphate-containing matrix.

Capacity to Remove Multiple Interferences from Multiple Analytes

It is the ion filtering effect of the inert cell gas, combined with a small ion energy spread, which enables the removal of ANY polyatomic ion from the ion beam. This is because ALL polyatomic ions have substantially larger ionic cross-sections than a monatomic (analyte) ions.

Since the number of collisions that an ion suffers will be dependent on its ionic cross-section (assuming equal ion energy at the cell entrance), ALL polyatomic ions will collide more frequently than monatomic analyte ions and so will suffer greater collisional deceleration, allowing them to be rejected from the ion beam through the use of a positive voltage step (ED) at the cell exit. The identify of the polyatomic ion is irrelevant.



While 2% H₂SO₄ is a single-component matrix, this illustrates that He collision mode with ED removes multiple interferences using a single set of operating conditions, demonstrating its applicability to unknown, complex samples.

Reliable Semi-quantitative Analysis is dependent on the maintenance of a predictable relationship between counts vs concentration for each analyte isotope. Using a simple, non-specific calibration based on the stored or measured mass/response curve for the instrument and using only constant corrections for isotopic abundance and degree of ionisation, semi-quantitative analysis can produce usable concentrations for many elements, based on calibrations that contain only a few reference elements

Element Mass	NIST 1640 Traces in Water		SLRS-4 River Water		LGC 6010 Hard Drinking Water		LGC 6177 Landfill Leachate	
	SQ Conc.	Ref	SQ Conc.	Ref	SQ Conc.	Ref	SQ Conc.	Ref
Li 7	IS Element	50.7	IS Element	N/A	IS Element	N/A	IS Element	N/A
Be 9	35	34.94	0.25	0.607	<2.220E-3	N/A	<2.400	N/A
B 10	290	301.1	6	N/A	63	N/A	6,700	8,900
Na 23	30,000	29,350	2,400	2,400	20,000	21,900	1,500,000	1,750,000
Mg 24	5,700	5,819	1,600	1,600	3,700	4,200	62,000	73,500
Al 27	54	52	66	54	160	208	110	N/A
Si 28	4,800	4,730	1,900	N/A	4,300	N/A	22,000	N/A
P 31	35	N/A	41	N/A	670	N/A	12,000	11,600
S 34	110	N/A	110	N/A	470	N/A	1,600	N/A
K 39	1,000	994	730	680	5,100	5,100	810,000	780,000
Ca 44	9,300	7,045	5,900	6,200	73,000	83,200	77,000	74,800
Sc 45	<5.800E-3	N/A	<6.800E-3	N/A	0.0065	N/A	0.21	N/A
Ti 49	0.089	N/A	0.11	N/A	0.11	N/A	18	N/A
V 51	13	12.90	0.28	0.32	0.32	N/A	63	N/A
Cr 52	37	38.6	6	5.33	51	48	160	180
Mn 55	120	121.5	3.5	3.37	45	48	130	140
Fe 56	29	34.3	120	163	240	236	3,300	3,800
Co 59	19	20.28	0.045	0.033	0.12	N/A	40	N/A
Ni 60	26	27.4	1	0.67	42	48	170	210
Cu 63	87	86.2	2.2	1.81	75	N/A	41	N/A
Zn 66	56	53.2	1.3	0.93	540	542	250	260
Ga 69	32	N/A	2.8	N/A	21	N/A	130	N/A
Ge 72	IS Element	N/A	IS Element	N/A	IS Element	N/A	IS Element	N/A
As 75	24	26.67	0.71	0.68	49	55	66	N/A
Se 78	21	21.96	<1.400	N/A	13	9.5	<15.00	N/A
Br 79	<0.1600	N/A	8.9	N/A	17	N/A	6,900	N/A
Rb 85	1.8	2	1.2	N/A	2.4	N/A	400	N/A
Sr 88	120	124.2	26	26.3	250	N/A	980	N/A
Y 89	0.011	N/A	0.04	N/A	0.011	N/A	0.28	N/A
Zr 90	0.091	N/A	0.057	N/A	0.047	N/A	49	N/A
Nb 93	0.0035	N/A	<1.200E-3	N/A	<1.300E-3	N/A	1.4	N/A
Mo 95	16	45.75	0.3	0.21	1.3	N/A	5.6	N/A
Ru 101	<3.400E-3	N/A	<3.500E-3	N/A	<3.800E-3	N/A	<0.04200	N/A
Rh 103	IS Element	N/A	IS Element	N/A	IS Element	N/A	IS Element	N/A
Pd 105	<2.900E-3	N/A	<2.900E-3	N/A	<3.200E-3	N/A	<0.03500	N/A
Ag 107	7.7	7.62	0.011	N/A	4.3	5.2	1.8	N/A
Cd 114	22	22.79	0.011	0.012	0.012	N/A	0.94	N/A
In 115	0.0046	N/A	<1.500E-3	N/A	<1.700E-3	N/A	0.18	N/A
Sn 118	2.1	N/A	0.042	N/A	0.054	N/A	48	N/A
Sb 121	15	13.79	0.011	N/A	13	11.9	5.4	N/A
Te 125	<0.1200	N/A	<0.1200	N/A	0.13	N/A	3	N/A
I 127	0.17	N/A	0.93	N/A	2.4	N/A	1,200	N/A
Cs 133	0.078	N/A	0.014	N/A	0.052	N/A	3.5	N/A
Ba 137	140	148	12	12.2	110	116	770	N/A
La 139	0.42	N/A	0.35	N/A	0.0017	N/A	0.24	N/A
Ce 140	0.52	N/A	0.48	N/A	<1.400E-3	N/A	0.7	N/A
Pr 141	0.076	N/A	0.062	N/A	<1.000E-3	N/A	<1.000E-2	N/A
Nd 146	0.35	N/A	0.15	N/A	<4.800E-3	N/A	0.2	N/A
Sm 147	0.072	N/A	0.027	N/A	<4.700E-3	N/A	<0.05000	N/A
Eu 153	0.0098	N/A	0.0065	N/A	0.0022	N/A	<0.09000	N/A
Gd 157	0.005	N/A	0.0032	N/A	<3.400E-3	N/A	0.036	N/A
Tb 159	0.0017	N/A	0.0017	N/A	9.30E-04	N/A	0.0098	N/A
Dy 163	0.021	N/A	0.013	N/A	<1.700E-3	N/A	0.14	N/A
Ho 165	0.006	N/A	0.0024	N/A	4.10E-04	N/A	0.061	N/A
Er 168	0.016	N/A	0.0084	N/A	0.0034	N/A	0.052	N/A
Tm 169	<3.600E-4	N/A	0.001	N/A	<3.700E-4	N/A	0.011	N/A
Yb 172	0.0082	N/A	0.0054	N/A	0.0042	N/A	0.044	N/A
Lu 175	6.50E-04	N/A	3.20E-04	N/A	9.90E-04	N/A	0.011	N/A
Hf 178	<1.400E-3	N/A	0.0014	N/A	<1.500E-3	N/A	0.44	N/A
Ta 181	3.10E-04	N/A	3.10E-04	N/A	3.10E-04	N/A	0.0066	N/A
W 182	0.017	N/A	0.0058	N/A	0.12	N/A	58	N/A
Rf 185	0.0087	N/A	0.011	N/A	0.025	N/A	0.061	N/A
Cs 189	<1.600E-3	N/A	0.0033	N/A	0.0034	N/A	<0.01700	N/A
Ir 193	IS Element	N/A	IS Element	N/A	IS Element	N/A	IS Element	N/A
Pt 195	<1.300E-3	N/A	<1.300E-3	N/A	0.0053	N/A	<0.01300	N/A
Au 197	0.006	N/A	<1.000E-3	N/A	0.051	N/A	5.4	N/A
Hg 202	0.012	N/A	0.065	N/A	0.003	N/A	0.28	N/A
Tl 205	0.035	N/A	0.045	N/A	<7.400E-4	N/A	<7.600E-3	N/A
Pb 208	27	27.89	0.16	0.086	92	95	17	N/A
Bi 209	0.015	N/A	0.001	N/A	0.02	N/A	2.4	N/A
Th 232	0.16	N/A	0.065	N/A	0.022	N/A	0.1	N/A
U 238	0.85	N/A	0.09	0.05	0.46	N/A	0.35	N/A

Analysis using Agilent 7500C in He Mode
 All Elements under same analysis conditions
 All Elements in ug/L

The table above shows the accurate determination of multiple elements in a variety of reference material matrices, using only a single set of He cell gas conditions for ALL elements in ALL samples. No interference correction equations were used.