

Interferences in Inductively Coupled Plasma Mass Spectrometry

A Review

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Introduction

Since the appearance of the first publications describing plasma source mass spectrometry as an analytically viable technique for trace analysis¹⁻⁷ there has been a rapid increase in the number of publications detailing instrumental developments, fundamental studies and applications, which have been covered in a number of reviews,⁸⁻²² overviews²³⁻³¹ and books.³²⁻³⁴

Despite early claims that inductively coupled plasma mass spectrometry (ICP-MS) utilizing continuum sampling, was relatively free from interferences,³⁻⁵ a prominent feature in many of the 500 or so publications in the field has been the problem of interferences; either exclusively or in conjunction with a particular application. Of course, it is always the case that research papers involving a relatively new technique will include a large number devoted to potential problems and this has been so for ICP-MS. Additionally, because it is such a sensitive technique,

interferences have tended to loom larger and the applicability of the technique for rapid, multi-element analysis has meant that investigations have focused on many elements at once, thereby, further underlining the effects of interferences. However, despite these caveats, ICP-MS does suffer from several problematical interferences, particularly with regard to certain 'problem elements'.

The interferences encountered in ICP-MS can be subdivided into two categories, for convenience. Although there is considerable overlap between the two categories and they share a common cause, some of the methods used to overcome them are significantly different. Hence, the reviewers have made an attempt to cross reference applications with methodology by including applications pertaining to real samples which specifically address the problem of interferences. These are presented in Table 1 and the methods used to overcome these interferences are discussed under subheadings in the text.

Table 1 Applications to real sample analysis which have dealt at least in part with spectroscopic or non-spectroscopic interferences

Sample	Major interferences	Comments	Ref.
<i>Geological—</i>			
Silicate rocks		Analysis of SRMs	35
Rocks and iron ores	Rare earth oxides, hydroxides and doubly charged ions on REE	Interference-free isotopes for determinations of REE identified	36
Rocks	Rare earth oxides and hydroxides on REE	Optimization and interference correction procedures	37
Synthetic	$^{135}\text{Ba}^{16}\text{O}^+$ and $^{137}\text{Ba}^{16}\text{O}^+$ on Eu^+	Used Eu^{2+} to avoid BaO interferences	38
Iron ores	Iron oxides and hydroxides	Comparison of digestion procedures and analysis of SRMs	39
Various	Rare earth oxides and hydroxides on REE	Analysis of SRMs	40
Limestone and manganese nodules	Oxides, hydroxides, hydrides and argides of Mg, P, Ca, Fe, Mn on various analytes	Analysis of SRMs	41
Silicate rocks and minerals	Rare earth oxides and hydroxides on REE	Cation-exchange separation, slurry nebulization and use of doubly charged ions for determination	42
Silicate rocks	Rare earth oxides and hydroxides on REE	Optimization of conditions for slurry nebulization	43
Coal	$^{40}\text{Ar}^{36}\text{Ar}^+$ on $^{76}\text{Se}^+$; $^{40}\text{Ar}^{38}\text{Ar}^+$ on $^{78}\text{Se}^+$; $^{40}\text{Ar}^{37}\text{Cl}^+$ on $^{77}\text{Se}^+$; $^{32}\text{S}^{16}\text{O}_2^+$ on $^{64}\text{Zn}^+$	Full and semiquantitative analysis by slurry nebulization	44
Rocks, sediments, soils	Non-spectroscopic, matrix effects	Precipitation with cupferron and comparison of LiBO_2 , KHF_2 and $\text{K}_2\text{B}_4\text{O}_7$ fusions. Analysis of SRMs for Zr, Nb, Hf and Ta	45
Synthetic	Rare earth oxides and hydroxides on REE	Ion chromatographic separation	46
Rocks	Zr^{16}O^+ on $^{107}\text{Ag}^+$, $^{112}\text{Cd}^+$, $^{111}\text{Cd}^+$; $^{92}\text{Zr}^{16}\text{O}^+\text{H}^+$ on $^{109}\text{Ag}^+$	Analysis of SRMs by slurry nebulization	47
Rocks	$^{40}\text{Ar}^{61}\text{Ni}^+$ and $^{64}\text{Ni}^{37}\text{Cl}^+$ on $^{101}\text{Ru}^+$; $^{40}\text{Ar}^{63}\text{Cu}^+$ on $^{103}\text{Rh}^+$; $^{40}\text{Ar}^{65}\text{Cu}^+$ on $^{105}\text{Pd}^+$; and $^{181}\text{Ta}^{16}\text{O}^+$ on $^{197}\text{Au}^+$	NiS fire assay and Te coprecipitation of platinum group metals in geological samples	48
Rocks	—	Review of the role of slurry nebulization for the analysis of geological materials	49
Rocks	Rare earth oxides	Cation exchange and matrix separation	50
Rocks and minerals	Rare earth oxides	Normalization of $\text{MO}^+:\text{M}^+$ ratios throughout analysis using $^{232}\text{Th}^{16}\text{O}^+$; $^{232}\text{Th}^+$	51
Various	Various	Review article comparing DCP-AES, ICP-AES and ICP-MS for analysis of geological samples	52
Rocks and sediments	$^{204}\text{Pb}^+$ and $^{206}\text{Pb}^+$ on $^{203}\text{Tl}^+$ and $^{205}\text{Tl}^+$	ETV, extraction into IBMK and analysis of reference materials	53
Rocks	Non-spectroscopic, matrix effects	ETV, NiS fire assay and matrix modification with Ni	54
Silicate rocks	O, N, H and Ar containing polyatomic ions between m/z 28 and 80, and oxides and hydroxides of W	Laser ablation: 1.0 J ruby laser, Q-switched	55
Rocks	Sample ablation effects	Laser ablation: Nd:YAG laser, 0.02–1.0 J free-running or 0.02–0.12 J Q-switched, 1–10 Hz. Signal normalization with Ba^+ intensity and sample weighing	56
Limestone	Sample ablation effects	Laser ablation: Nd:YAG laser, 500 mJ fixed-Q or 250 mJ Q-switched, up to 15 Hz. Fusions and pressed pellets used as synthetic standards	57
Rocks	Polyatomic ions below m/z 80, rare earth oxides and sample ablation effects	Laser ablation: Nd:YAG laser, 500 mJ fixed-Q or 250 mJ Q-switched. Fusions used as synthetic standards	58
Rocks, fly ash	Sample ablation effects	Laser ablation: Nd:YAG laser, 500 mJ fixed-Q or 250 mJ Q-switched and simultaneous nebulization. Pressed pellets used as synthetic standards	59
Ores	O and H containing polyatomic ions	Arc ablation. Pressed pellets used as standards	60
Rocks	Non-spectroscopic, matrix effects	Internal standardization using Re–Ru to correct for suppression of Y and REE	61
Silicate rocks	Non-spectroscopic, matrix effects	ID analysis for U	62
Peridotite	Non-spectroscopic, matrix effects due to 10% dissolved solids	Flow injection analysis for the platinum group metals	63

Table 1—continued

Sample	Major interferences	Comments	Ref.
Marine sediment	$^{35}\text{Cl}^{16}\text{O}^+$ on $^{51}\text{V}^+$; $^{40}\text{Ar}^{35}\text{Cl}^+$ on $^{75}\text{As}^+$; $^{40}\text{Ar}^{16}\text{O}^+$ on $^{56}\text{Fe}^+$; TiO^+ on $^{63}\text{Cu}^+$, $^{65}\text{Cu}^+$, $^{64}\text{Zn}^+$ and $^{66}\text{Zn}^+$; FeO^+ on $^{72}\text{Ge}^+$, $^{73}\text{Ge}^+$ and $^{74}\text{Ge}^+$	Modified dissolution procedure to eliminate chloride	64
<i>Environmental—</i>			
Water	$^{36}\text{Ar}^1\text{H}^+$ on $^{37}\text{Cl}^+$	Dissolution in D_2O instead of H_2O	65
Soils and catalysts	—	Full and semiquantitative analysis by slurry nebulization	66
Sea-water	Non-spectroscopic, matrix effects	Solvent extraction and ID analysis	67
Sea-water	Non-spectroscopic, matrix effects	Solvent extraction and back extraction	68
Sea-water	Non-spectroscopic, matrix effects	Preconcentration and matrix separation using quinolin-8-ol	69
Sea-water	Non-spectroscopic, matrix effects	Preconcentration and matrix separation using quinolin-8-ol	70
Sea-water	Non-spectroscopic and $^{44}\text{Ca}^{16}\text{O}^+$ on $^{58}\text{Ni}^+$	Preconcentration and matrix separation using quinolin-8-ol, and ID analysis	71
Sediments, alloys	Oxides of Ti and Mo on Cu, Zn and Cd; non-spectroscopic interference due to U	Preconcentration and matrix separation using <i>N</i> -methylfurohydroxamic acid retained on a column of polystyrene-divinylbenzene	72
Sea-water, urine	Non-spectroscopic and $^{35}\text{Cl}^{16}\text{O}^+$ on ^{51}V ; $^{35}\text{Cl}^{16}\text{O}^1\text{H}^+$ on $^{52}\text{Cr}^+$	Preconcentration and matrix separation using bis(carboxymethyl)-dithiocarbamate	73
Sea-water	Non-spectroscopic, matrix effects	Preconcentration and matrix removal using AG 1-X2 anion-exchange resin	74
Sea-water, freshwater, hydrothermal fluids	Non-spectroscopic, matrix effects	Preconcentration and matrix removal using AG 1-X2 anion-exchange resin	75
Waste water	Non-spectroscopic; CaO^+ and CaOH^+ on ^{57}Fe , ^{59}Co , ^{60}Ni ; $^{35}\text{Cl}^{16}\text{O}^+$ on $^{51}\text{V}^+$; $^{23}\text{Na}^{40}\text{Ar}^+$ on $^{63}\text{Cu}^+$; $^{39}\text{K}^{16}\text{O}^+$ on $^{55}\text{Mn}^+$; $^{24}\text{Mg}^{24}\text{Mg}^+$ on $^{48}\text{Ti}^+$; $^{24}\text{Mg}^{35}\text{Cl}^+$ on $^{59}\text{Co}^+$	Preconcentration and matrix removal using an iminodiacetate resin	76
Sea-water	Non-spectroscopic, matrix effects	Preconcentration and matrix removal using bis(2-ethylhexyl) hydrogen phosphate and 2-ethylhexyl dihydrogen phosphate, immobilized on C_{18}	77
Acid precipitate	Non-spectroscopic, matrix effects	Preconcentration using cation-exchange resin	78
Airborne particulates	Non-spectroscopic and oxides of Hf on Pt	Preconcentration and matrix removal using cation-exchange resin for analysis of SRMs	79
Waters	Non-spectroscopic, matrix effects	Preconcentration and matrix removal using Dowex 50W-X8 cation-exchange resin	80
Groundwater	Non-spectroscopic	Preconcentration and matrix removal on cation-exchange resin	81
Synthetic	Non-spectroscopic, matrix effects due to Na and Ca	Ion pairing-LC separation and speciation	82
Fish tissue	Non-spectroscopic, matrix effects	Solvent extraction and ion pairing/exchange-LC separation of As species	83
Synthetic	—	Speciation of organotin species by supercritical fluid chromatography	84
Fly ash	Rare earth oxides on the heavier REE	Reversed phase LC separation and ID analysis	85
Water	$^{35}\text{Cl}^{16}\text{O}^+$ on $^{51}\text{V}^+$; $^{28}\text{Si}^{16}\text{O}^1\text{H}^+$ and $^{29}\text{Si}^{16}\text{O}^+$ on $^{45}\text{Sc}^+$; $^{30}\text{Si}^{16}\text{O}^1\text{H}^+$ on $^{47}\text{Ti}^+$; and $^{138}\text{Ba}^{2+}$ on $^{69}\text{Ga}^+$	Investigation of correction methods for polyatomic interferences	86
Synthetic sea-water	$^{40}\text{Ar}^{23}\text{Na}^+$ on $^{63}\text{Cu}^+$	Electrochemical separation of analyte from matrix	87
Sea-water	Non-spectroscopic and CaO^+ , ArO^+ and ArN^+ on Ni, Cr, Zn, Fe and Cu isotopes	Electrochemical separation of analyte from matrix	88
Orchard leaves, oyster tissue, blood	Non-spectroscopic, matrix effects	ETV, matrix elimination by ashing	89
Sea-water	$^{40}\text{Ar}^{16}\text{O}^+$ on $^{56}\text{Fe}^+$ and oxides and hydroxides of Ca on Fe and Ni isotopes	ETV and DPI, analysis of IBMK extracts	90
Water	$^{40}\text{Ar}^{35}\text{Cl}^+$ on $^{75}\text{As}^+$ and $^{40}\text{Ar}^{37}\text{Cl}^+$ on $^{77}\text{Se}^+$	Hydride generation with a silicone rubber gas-liquid separator	91

Table 1—continued

Sample	Major interferences	Comments	Ref.
Corn stalk, kale, rice flour, citrus leaves, bovine liver etc.	$^{40}\text{Ar}^{37}\text{Cl}^+$ on $^{77}\text{Se}^+$	Hydride generation and determination of Se by ID analysis	92
Pesticides	$^{14}\text{N}^{16}\text{O}^1\text{H}^+$ on $^{31}\text{P}^+$ and $^{16}\text{O}_2^+$ on $^{32}\text{S}^+$	Low pressure MIP-MS with GC for determination of P- and S-containing pesticides	93
Lobster	$^{35}\text{Cl}^{16}\text{O}^+$ on $^{51}\text{V}^+$ and $^{40}\text{Ar}^{35}\text{Cl}^+$ on $^{75}\text{As}^+$	Interference correction using elemental equations	94
Agricultural crops	Non-spectroscopic due to Na, Mg, P, K, Ca and dissolved solids	Drift correction by multiple standardization	95
Marine sediment	Non-spectroscopic, matrix effects	Internal standardization using $^{40}\text{Ar}^{40}\text{Ar}^+$ and ID analysis	96
Marine sediments	Non-spectroscopic, matrix effects	ID analysis	97
Dogfish liver, dogfish muscle	Non-spectroscopic, matrix effects	ID analysis	98
Sea-water	Non-spectroscopic, matrix effects	ID analysis for Ba	99
Sediment pore water	Non-spectroscopic, matrix effects	ID analysis for U	100
Dogfish muscle, lobster hepatopancreas	Non-spectroscopic, matrix effects due to 4% Na	Flow injection and ID analysis after solvent extraction	101
<i>Biological—</i>			
Faeces	$^{70}\text{Ge}^+$ on $^{70}\text{Zn}^+$ and $^{58}\text{Ni}^+$ on $^{58}\text{Fe}^+$	Precipitation of analytes with ammonium pyrrolidin-l-ylidithioformate	102
Protein	$^{40}\text{Ar}^{35}\text{Cl}^+$ on $^{75}\text{As}^+$	Precipitation of chloride with silver	103
Bovine liver, serum, milk	$^{35}\text{Cl}^{35}\text{Cl}^+$ on $^{70}\text{Zn}^+$ and $^{35}\text{Cl}^{16}\text{O}^{16}\text{O}^+$ on $^{67}\text{Zn}^+$	Solvent extraction of Zn in diethylammonium diethyldithiocarbamate and ID analysis	104
Serum	$^{40}\text{Ar}^{37}\text{Cl}^+$ on $^{77}\text{Se}^+$; $^{40}\text{Ar}^{35}\text{Cl}^+$ on $^{75}\text{As}^+$; $^{35}\text{Cl}^{16}\text{O}^+$ on $^{51}\text{V}^+$; and $^{35}\text{Cl}^{16}\text{O}^1\text{H}^+$ on $^{52}\text{Cr}^+$	Separation of matrix using gel filtration	105
Urine	$^{40}\text{Ar}^{35}\text{Cl}^+$ on $^{75}\text{As}^+$	Anion exchange-LC separation of As species	106
Urine	$^{40}\text{As}^{35}\text{Cl}^+$ on $^{75}\text{As}^+$	Anion exchange-LC separation of As species	107
Serum	$^{40}\text{Ar}^{23}\text{Na}^+$ and $^{31}\text{P}^{16}\text{O}^{16}\text{O}^+$ on $^{63}\text{Cu}^+$	Size exclusion separation and determination of ^{63}Cu : ^{65}Cu isotope ratios	108
Serum	Oxides and hydroxides of Na, Cl, S and Ca on Fe, Co, Cu and Zn	Interference correction by subtraction of a synthetic blank containing the matrix elements	109
Oyster tissue, bovine liver, kale	Polyatomic ions due to HNO_3 , HCl , H_2SO_4 , H_3PO_4 , H_2O_2 and NH_3 . $^{35}\text{Cl}^{16}\text{O}^+$ on $^{51}\text{V}^+$ and $^{40}\text{Ar}^{35}\text{Cl}^+$ on $^{75}\text{As}^+$	Interference correction by mathematical calculation	110
Orchard leaves, bovine liver, oyster tissue, fly ash, zircalloys	Various polyatomic interferences due to plasma gases and acids used for dissolution	Comparison of detection limits with ICP-AES	111
Plasma, urine, bovine liver	$^{37}\text{Cl}^{37}\text{Cl}^+$ on $^{74}\text{Se}^+$ and $^{40}\text{Ar}^{37}\text{Cl}^+$ on $^{77}\text{Se}^+$	Hydride generation and determination of Se isotope ratios	112
Urine	$^{40}\text{Ar}^{35}\text{Cl}^+$ on $^{75}\text{As}^+$	N_2 addition to attenuate polyatomic ions	113
Urine	Oxides and hydroxides of Ca on Ni; $^{23}\text{Na}^{39}\text{K}^+$ on $^{62}\text{Ni}^+$; and $^{23}\text{Na}^{35}\text{Cl}^+$ on $^{58}\text{Ni}^+$	Principal component analysis used for interference correction	114
Cod liver, shellfish	Non-spectroscopic, matrix effects	Internal standardization with $^{40}\text{Ar}^{40}\text{Ar}^+$ and isotope dilution analysis	115
Bovine liver, orchard leaves, human lung etc.	Non-spectroscopic, matrix effects	Internal standardization with Bi and Ti for U determination	116
Oyster tissue, bovine liver, tomato leaves, blood plasma	Non-spectroscopic; $^{35}\text{Cl}^{16}\text{O}^{16}\text{O}^+$ and $^{33}\text{S}^{34}\text{S}^+$ on $^{67}\text{Zn}^+$	Flow injection, ID and external calibration compared	117
Urine, synthetic ocean water	Non-spectroscopic, matrix effects	Hildebrand grid nebulizer for samples with high salt content	118
Urine	$^{40}\text{Ar}^{35}\text{Cl}^+$ on $^{75}\text{As}^+$, $^{40}\text{Ar}^{37}\text{Cl}^+$ on $^{77}\text{Se}^+$, and $^{35}\text{Cl}^{16}\text{O}^+$ on $^{51}\text{V}^+$	N_2 addition to inner, intermediate and outer gas to alleviate polyatomic ion interferences	119
Fish tissue	Non-spectroscopic, matrix effects	ID analysis for Sn	120

Table 1—continued

Sample	Major interferences	Comments	Ref.
<i>Metals—</i>			
Uranium	Non-spectroscopic, matrix effects	Solvent extraction of uranium matrix with <i>N,N</i> -diethylacetamide in toluene	121
Aluminium	Not specifically addressed	Solvent extraction and separation of Ga from Al	122
Aluminium	Not specifically addressed	Solvent extraction and separation of U and Th from Al	123
Nickel alloys	$^{59}\text{Co}^{16}\text{O}^+$ on $^{75}\text{As}^+$ and oxides of Mo on Cd	Analysis of reference materials	124
Steels	Oxides and hydroxides of Fe on $^{70}\text{Zn}^+$, $^{70}\text{Ge}^+$, $^{72}\text{Ge}^+$, $^{73}\text{Ge}^+$, $^{74}\text{Ge}^+$, $^{71}\text{Ga}^+$, and $^{75}\text{As}^+$; and non-spectroscopic interferences	Analysis of SRMs and investigation of interference effects	125
Steels	O-, N-, H- and Ar-containing polyatomic ions	Laser ablation: 160 mJ Nd:YAG, 1–20 Hz, free-running or Q-switched	126
Steels	O- and H-containing polyatomic ions	Spark ablation	127
Steels	O- and H-containing polyatomic ions	Arc ablation. Pressed pellets used as standards	128
Copper	Non-spectroscopic, matrix effects	ID analysis for Ag and Sb	129
Aluminium chip	Non-spectroscopic, high dissolved solids	Flow injection for analysis of samples with 2% dissolved solids	130
Nickel alloy	Non-spectroscopic, matrix effects	Flow injection analysis for samples of up to 0.75% dissolved solids	131
<i>Organics—</i>			
Polymers	Sample ablation effects	Laser ablation: 0.2 J Nd:YAG, Q-switched. $^{13}\text{C}^+$ used as internal standard	132
Methacrylic acid	Non-spectroscopic, matrix effects	Optimization of plasma conditions and ion optics to reduce interferences	133
Fuel oil	Argides, oxides, nitrides of C and other C-containing polyatomic ions between <i>m/z</i> 24 and 53	Introduction of oxygen to prevent C build-up on the cones	134
Fuel oil	Argides, oxides, nitrides of C and S and other C-containing polyatomic ions	Introduction of oxygen to prevent C build-up on the cones	135
<i>Miscellaneous—</i>			
Al_2O_3	$^{40}\text{Ar}^{12}\text{C}^+$ on $^{52}\text{Cr}^+$ and $^{40}\text{Ar}^{16}\text{O}^+$ on $^{56}\text{Fe}^+$	Dry powder aerosol introduction	136
Na_2CO_3 fusions	Non-spectroscopic, matrix effects	Flow injection, ion-lens tuning and internal standardization used to correct for interferences	137
Catalysts	Non-spectroscopic, matrix effects	ID and comparison to wet chemical analysis	138
Various biological, environmental, geological	Non-spectroscopic, matrix effects	ID, on-line flow injection analysis	139
Phosphoric acid and ammonium nitrate	Non-spectroscopic, matrix effects due to $2.5 \text{ mol l}^{-1} \text{ H}_3\text{PO}_4$ and $1.5 \text{ mol l}^{-1} \text{ NH}_4\text{NO}_3$	Flow injection analysis for Ge, Pd and Pt	140

Spectroscopic Interferences

This category of interferences probably forms the largest and most intractable in ICP-MS. Spectroscopic interferences are caused by atomic or molecular ions having the same nominal mass as the analyte of interest, thereby interfering with the analysis by causing an erroneously large signal at the *m/z* of interest. Such interferences can be conveniently divided into two categories, depending on the origin of the interference.

Firstly, there are interferences caused by overlapping isotopes of different elements. These interferences are easy to predict and well documented, so they can be easily overcome by utilizing alternative isotopes or elemental equations for analysis. The second category is that of molecular or polyatomic-ion interferences caused by polyatomic ions formed from precursors in the plasma gas, entrained atmospheric gases, water, acids used for dissolution and the sample matrix. The polyatomic ions so formed,

may then result in interferences on analytes with the same nominal *m/z*.

Fundamental Studies

Interferences caused solely by the plasma gas, entrained atmospheric gases and water are present regardless of whether a sample is being analysed.^{1–7, 36, 37, 141–154} There is considerable debate as to the origin of polyatomic ions. Several possibilities exist depending on the type of polyatomic ion under discussion and whether continuum or boundary layer sampling has been utilized. As the most recent generation of ICP-MS instruments exclusively make use of continuum sampling, the contribution from the boundary layer might be considered to be small. However, Vaughan and Horlick¹⁵¹ have postulated that the boundary layer around the edges of the sampling orifice may still contribute polyatomic oxides and that from a consideration

of the plasma temperature calculated by using the dissociation constants of the oxides, it is unlikely that metal oxides are formed in the bulk plasma.

The most likely sources of polyatomic ions are as follows. (i) Condensation reactions in the expansion region in accordance with molecular beam theory.¹⁵⁴⁻¹⁵⁶ However, Douglas and French¹⁵⁷ have calculated that for a typical ICP-MS sampling interface, the degree of ionization in the expansion region is frozen at that of the source and that little ion-molecule chemistry occurs. This would tend to discount the possibility of condensation reactions. (ii) Collisional reactions in the boundary layer around the outside surface of the sampler.^{4,151} (iii) Survival through the plasma itself, particularly with respect to refractory metal oxide ions.¹⁵⁶

The design and geometry of the interface can also be an important factor. For instance, Lam and Horlick¹⁵² have studied the effect of the spacing between the sampler and skimmer on polyatomic ions. They found that Cu^+ , ArO^+ , Ar_2^+ , Ar_2H^+ and CeO^+ signals decreased as spacing increased, while ArN^+ increased and ArOH^+ was anomalous. They speculated that ArN^+ arose primarily owing to air entrainment, so it behaved differently compared with ions that came from the central channel of the plasma.

Several groups of workers have shown that it is possible to arrive at a compromise set of operating conditions, which yield low levels of oxides and doubly charged ions for the two main commercially available instruments, namely the SCIEX Elan^{36,141,142} and the VG PlasmaQuad^{143,145,146,153,154} and also for other configurations.¹⁴⁸⁻¹⁵⁰ It is generally agreed that conditions that result in the lowest levels of refractory oxides are low nebulizer gas flow, high power and a greater spacing between the load coil and sampler. It has been noted¹⁴³ that there are substantial differences between the operating conditions that yield low levels of doubly charged ions, depending on the make of instrument. This is not surprising because there are substantial differences between the design of the load coil in the SCIEX and VG instruments. The SCIEX Elan has a centre tapped load coil,¹⁵⁸ which results in a relatively low plasma potential of from +0.5 to -3.5 V.¹⁵⁹ With this design the proportion of doubly charged ions is greatest at high power and low nebulizer gas flow rate.¹⁴²

The VG PlasmaQuad has an asymmetrically grounded load coil, which can result in a plasma potential anywhere between +5 and +20 V, which increases in conjunction with increasing nebulizer gas flow rate.¹⁶⁰ It has been postulated that this causes an increase in the proportion of doubly charged ions, which is greatest at high nebulizer gas flow rate and low power. Other load coil configurations have been tested¹⁶¹ which result in no apparent relationship between ion energy and doubly charged ions. However, Ross *et al.*,¹⁶² have compared centre-tapped and inverted load coil geometries on the same instrument, and found that the main difference between them was that they required individually optimized sampling depth, nebulizer gas flow rate and extraction voltage. This confirmed that the influence of operating conditions on doubly charged ions was dependent on the load coil configuration.

The situation becomes more unpredictable when constituents in the sample matrix and acids used for dissolution also contribute to polyatomic ion formation. It is futile to compile an exhaustive list of such interferences, since their magnitude will depend on a number of factors, including instrument design, the nature of the sample and operating conditions. In any case, several groups of workers have sought to document the more commonly occurring interferences likely to be caused by acids or well characterized samples.^{142,144,163,164} In general, however, when the sample to be analysed has a complex or unknown matrix, experience on the part of the analyst is still essential to

anticipate and recognize potential interferences. Hence, the problems caused by polyatomic interferences depend to a great extent on the nature of the sample and the level at which a determination must be made. In order to examine more closely particular interferences that occur most frequently, the reviewers have decided to categorize and document the methods that have been developed to mitigate or overcome them. In addition to this, Table 1 contains a list of applications categorized with respect to the type of sample analysed, to serve as a cross reference for applications to real sample analysis.

Methods to Overcome Spectroscopic Interferences

Alternative sample preparation methods

Sample dissolution procedures. The most obvious way to avoid interferences caused by acids used for digestion is to use alternative acids. Hence, if vanadium or arsenic is to be determined then hydrochloric acid must be avoided, because of the occurrence of $^{35}\text{Cl}^{16}\text{O}^+$ at m/z 51 and $^{40}\text{Ar}^{35}\text{Cl}^+$ at m/z 75. The commonly occurring interferences caused by water and acids have been documented.^{142,144}

The use of nitric acid for the digestion of biological and food samples has been widely favoured,^{109,110} because it contains only the species H, O and N, which are present in the plasma and entrained gases in any case. The use of sulfuric and phosphoric acids has generally been avoided owing to the propensity for a large number of S- and P-containing polyatomic ions to form. For more intractable samples such as rocks and minerals, where acids such as hydrofluoric, hydrochloric and perchloric acids are commonly used, the analyst should be aware of and compensate for the polyatomic interferences caused by these acids. However, even for these samples, dissolution procedures can often be modified to avoid the use of one or other of these acids altogether.^{64,165,166}

The dissolution of geological samples has received considerable attention,¹⁶⁷ owing to the intractable nature of such samples. A useful review by Jarvis and Jarvis⁵² puts the problems of interference correction, internal standardization and sample dissolution in context with the more established techniques of ICP atomic emission spectrometry (AES) and direct current plasma (DCP)-AES.

An alternative approach investigated by Ebdon *et al.*,⁴⁴ Williams *et al.*,⁶⁶ Mochizuki *et al.*⁴³ and Jarvis *et al.*,^{47,49} has been to prepare samples by grinding them and forming a fine suspension of slurry in a suitable dispersant. The slurried samples were then nebulized in an identical manner to that for solutions, by means of a Babington-type nebulizer. This technique has the advantage that the sample digestion step can be omitted altogether, thereby avoiding the necessity of using acids for dissolution and facilitating the analysis of refractory compounds which are difficult to solubilize. However, some of the drawbacks include the possibility of contamination during the grinding process and difficulty in obtaining a sufficiently fine suspension unless a suitable surfactant is used for a particular sample type. Similarly, Pfannerstill *et al.*¹³⁶ used a PCW-powder disperser to introduce powdered samples. This method required only that the samples be ground to a fine powder, with no other reagents used for sample preparation whatsoever. This resulted in a completely dry plasma with a consequent reduction in the $^{40}\text{Ar}^{16}\text{O}^+$ interference on $^{56}\text{Fe}^+$. The drawback of these methods has been the difficulty in achieving a finely divided suspension, with a particle size of ideally less than 2 μm . However, solid sample analysis offers a number of advantages including speed and lack of complexity in sample preparation for many matrix types.

A particularly novel method for avoiding spectral interferences was that adopted by Smith and Houk,⁶⁵ who used

D₂O rather than H₂O for dissolution, thereby attenuating the interference due to ³⁶Ar¹H⁺ at *m/z* 37 and allowing the determination of ³⁷Cl⁺:³⁵Cl⁺ isotope ratios.

Precipitation and solvent extraction. While it is possible to avoid potential interferences due to acids used for dissolution, if the sample matrix itself contains the interfering species then it is often necessary to separate the analyte completely from the interfering matrix component. Coprecipitation can be a convenient method of achieving this.^{45,48,102,103,168-170} Lyon *et al.*¹⁰³ determined a number of trace elements in clinical samples and found that polyatomic interferences caused high recoveries for several elements. They reduced the interference due to ⁴⁰Ar³⁵Cl⁺ on ⁷⁵As⁺ by precipitation of the chloride with silver and also postulated that the method could effectively reduce other chloride based interferences such as ¹²C³⁵Cl₂⁺ on ⁸²Se⁺, ⁴⁰Ar³⁷Cl⁺ on ⁷⁷Se⁺ and ³⁵Cl¹⁶O⁺ on ⁵¹V⁺. Ting and Janghorbani¹⁰² adopted a similar approach, although they separated the analytes of interest by precipitation with ammonium pyrrolidin-1-ylidithioformate, hence avoiding the spectral interferences caused by ⁷⁰Ge⁺ on ⁷⁰Zn⁺ and ⁵⁸Ni⁺ on ⁵⁸Fe⁺, for the determination of these elements in faecal matter. Hall *et al.*⁴⁵ precipitated Zr, Nb, Hf and Ta with cupferron, although they concentrated on the removal of non-spectroscopic, rather than spectroscopic interferences. Jackson *et al.*⁴⁸ utilized Te coprecipitation after a NiS fire assay of geological materials in order to improve recoveries for the platinum group metals. This technique also had the added benefit that it separated the analyte from the bulk of the matrix, thereby avoiding potential interferences, although the coprecipitation of Cu from some samples still caused interferences due to ⁴⁰Ar⁶³Cu⁺ on ¹⁰³Rh⁺ and ⁴⁰Ar⁶⁵Cu⁺ on ¹⁰⁵Pd⁺.

Solvent extraction methods have also been investigated by several workers as a means of separating the analyte from the matrix.^{67,68,104,121-123, 171} Palmieri *et al.*¹²¹ successfully extracted uranium from an aqueous phase and determined 30 elements at concentrations of between 10 and 100 µg l⁻¹. Other workers have similarly extracted trace elements from sea-water.^{67,68}

Solvent extraction methods have been well characterized for many elements and matrices with regard to flame atomic absorption spectrometry and ICP-AES, although the high sensitivity of ICP-MS requires that particular attention be paid to the purity of reagents. The advent of more rapid ion-exchange and on-line separation techniques has reduced the popularity of solvent extraction for total trace element determinations. However, the resurgence of solvent extraction methodology is sure to occur as more emphasis is being placed upon element speciation studies, where the integrity of the organometallic complex can only be guaranteed by using an appropriate solvent extraction procedure.

While precipitation or solvent extraction of the analyte or potential interfering element provides an effective way of reducing interferences, the methods have generally been performed only in batch mode and precipitation methods always present the danger of coprecipitation of trace analytes with the matrix element. Additionally, there is the possibility of substantially increasing blank levels owing to impurities in the organic solvents or complexing agents necessary for extraction.

On-line separation methods. A more elegant and rapid method of analyte separation is that of preconcentration or matrix removal using chelating resins,^{69,70-77,105} ion exchange^{46,50,78,79,172-176,81} or chromatographic methods,^{82-85, 106-108, 177-193}, which ultimately allow such procedures to be used on-line.

McLaren *et al.*⁶⁹ and Beauchemin and co-workers^{70,71} have successfully utilized silica-immobilized quinolin-8-ol to preconcentrate trace metals from sea-water, thereby

removing interferences in the matrix and improving detection limits by up to 7-fold for several elements. Lyon *et al.*¹⁰⁵ used gel filtration to de-salt protein samples and remove chloride, thereby allowing the determination of ⁷⁷Se⁺, which normally suffers from an interference due to ⁴⁰Ar³⁷Cl⁺. However, they also noted low recoveries for Zn and Cu which were also retained by the gel. Jiang *et al.*⁷² used *N*-methylfurohydroxamic acid to complex Mo^{VI}, Ti^{IV} and U^{VI} and retained the metal complexes on a column packed with polystyrene-divinylbenzene. Thus, they removed spectral interferences caused by the oxides of Ti and Mo on determinations of Cu, Zn, and Cd, and non-spectroscopic interferences caused by U. Using similar methods of metal complexation and separation, Plantz *et al.*⁷³ separated the alkaline and alkaline earth elements from trace analytes. In addition, Bakowska *et al.*⁷⁴ and Falkner and Edmond⁷⁵ preconcentrated gold from sea-water.

Cation-exchange resins have been used by several groups of workers to remove matrix elements and preconcentrate trace analytes. Of particular interest is the work of Mukai *et al.*,⁷⁹ who determined Pt in airborne particulate matter after separation of Hf, the oxides of which interfere with the major isotopes of Pt at *m/z* 194, 195 and 196. Along similar lines, Kawabata *et al.*⁴⁶ developed an extremely effective and elegant ion-exchange chromatographic method for the separation and determination of the rare earth elements (REE).

The distinction between the use of separation science for matrix removal and for element speciation is often blurred, since by definition the utilization of a chromatographic technique almost always involves separation of the analyte from the matrix. However, the use of liquid chromatography can result in problems when organic mobile phases or those with a high salt content are used, owing to analyte suppression or salt build-up on the cones. Thompson and Houk⁸² evaluated reversed-phase, ion-pairing chromatography for 30 elements and demonstrated the speciation of various forms of As and Se. They also noted that the separation of matrix elements such as Na and Ca was possible. Beauchemin *et al.*^{83,181} have investigated the speciation of arsenic in a number of real samples, utilizing solvent extraction in the sample preparation step. Ironically, they found that despite the separation powers of the chromatographic step, the presence of a matrix element had a deleterious effect on peak resolution in ion-pairing chromatography; while anion and cation exchange were more tolerant of a high matrix concentration, but caused salt build-up on the cones. Heitkemper *et al.*,¹⁰⁶ separated arsenic species using anion-exchange chromatography. They observed an interference on As^{III} due to co-elution of chloride, which forms ⁴⁰Ar³⁵Cl⁺ in the plasma, though the other arsenic species were well separated and not affected. Subsequent work by Sheppard *et al.*¹⁰⁷ further refined the separation to resolve the chloride peak. Lyon and Fell¹⁰⁸ applied size exclusion chromatography to separate sodium and phosphate and allow the determination of copper isotope ratios in serum, which would ordinarily suffer from a polyatomic interference at *m/z* 63 due to ⁴⁰Ar³³Na⁺. Studies by Caruso's group^{84,194} demonstrated the applicability of coupling supercritical fluid chromatography to ICP-MS for the speciation of organotin. The advantages of this technique are low blank levels in the mobile phase and the possibility of using supercritical fluid extraction, on-line, for separation of organometallic trace analytes from the matrix. Braverman⁸⁵ has demonstrated that the REE can be separated by reversed-phase high-performance liquid chromatography (HPLC), thereby avoiding potential oxide interferences due to the light REE on the heavier ones.

A different approach to matrix separation has been investigated by Pretty *et al.*,⁸⁷ who used an on-line electrochemical method to selectively preconcentrate Cd and Cu

from concentrated solutions of U and Na. This successfully eliminated the interference due to $^{40}\text{Ar}^{23}\text{Na}^+$ on $^{63}\text{Cu}^+$. Similarly, Chong *et al.*⁸⁸ electrochemically preconcentrated trace elements from sea-water on a niobium wire, in batch mode.

Alternative sample introduction methods

Desolvation. An extremely simple method to reduce oxides and hydroxides is to cool the spray chamber, thereby condensing some of the water vapour.^{195,196} Similarly, more efficient solvent removal can be achieved by the use of more complex arrangements such as Peltier effect coolers,¹⁹⁷ membrane interfaces^{198,199} and heater/condensers.^{200–204} The results of studies involving spray chamber cooling and desolvation have indicated that the analyte signal can be increased and the signal due to doubly charged ions, oxide and hydroxide ions can be reduced^{195,196} by as much as an order of magnitude.^{200,201} However, Hutton and Eaton¹⁹⁵ also observed a decrease in the level of ArAr^+ ions, while Jakubowski *et al.*²⁰¹ observed an increase in polyatomic ions such as ArAr^+ and ArN^+ , though the latter group used a 40 MHz ICP while the former operated the plasma at 27 MHz. Likewise, Tsukahara and Kubota²⁰⁰ found that the effect of desolvation on analyte signal intensity was highly dependent on the nebulizer gas flow rate and to some extent on the mass of the analyte. This illustrates the danger of making comparisons between different instruments and different sets of operating conditions, because of the highly interactive nature of the variables.

Alves *et al.*²⁰⁴ have recently described a cryogenic desolvation device with multiple desolvation steps that removed almost all of the solvent from the aerosol. Using this method they reduced metal oxide to metal ion ratios for Ca, Mo and La to between 0.02 and 0.05% and also attenuated polyatomic ion interferences due to ArO^+ , ClO^+ and ArCl^+ by several orders of magnitude. They also reported a reduction in $\text{UO}^+:\text{U}^+$ to 0.06% using cryogenic desolvation in combination with adding acetylene to the central channel.

Thermal vaporization. Thermal vaporization as a method of sample introduction into ICP-MS has received considerable attention, utilizing electrothermal vaporization (ETV),^{53,54,89,90,205–221} and direct sample insertion (DSI).^{222–226}

Park *et al.*⁸⁹ studied the effects of 1 μg of Na, Ca, Cr, Ni and Se on analyte signal and found that the effect of the matrix on analyte vaporization from the graphite tube was minimal, but that there was considerable analyte suppression due to easily ionizable matrix elements. They also showed that it is possible to include chemical modification and an ashing stage in order to eliminate anions in an acid matrix, or organic constituents. Park and Hall⁵³ found it necessary to separate Tl from Pb by solvent extraction into isobutyl methyl ketone (IBMK) because of spectral interferences of the latter on the determination of the former. Hall *et al.*,⁹⁰ have compared ETV with DSI and found that the inclusion of drying and ashing stages made it possible to analyse IBMK extracts without the problems normally associated with organic sample introduction. In addition, oxide and hydroxide interferences were reduced. Similarly, several groups of workers^{212,215,216} have reduced the $^{40}\text{Ar}^{16}\text{O}^+$ interference on $^{56}\text{Fe}^+$ by including a drying stage and Shibata *et al.*²¹³ reduced rare earth oxide interferences by up to three orders of magnitude by a combination of hydrogen addition and drying the sample.

Karanassios and Horlick²²⁴ have investigated a DSI device and found that the elimination of water from the plasma reduced background spectral interferences by a considerable amount. The same workers²²⁵ also found that interferences due to light rare earth oxides on the heavier

REE and other oxide interferences could be reduced. Also, it was possible to eliminate the matrix suppression due to U on Zn by vaporizing Zn at a lower temperature than U.

Despite the effectiveness of ETV or DSI for removing solvent from the sample it is evident that the increased transport efficiency of thermal vaporization methods can also contribute to, rather than reduce, interferences, especially if a chemical modifier is used.^{54,89,90} Memory effects for refractory analytes can also occur, necessitating the use of Freon²⁰⁵ or NaF^{225} to improve volatilization. It has even been suggested that the use of a chemical modifier may be a necessity,²²¹ to ensure that analyte transport for samples and standards is the same.

Laser ablation. The introduction of samples by means of laser or arc ablation of a solid has offered considerable potential, in conjunction with ICP-MS, for the rapid semi-quantitative analysis of solids.^{55–59,126,132,227–241} This has been reviewed by Denoyer *et al.*²⁴² Papers dealing with interferences have concentrated on the advantages of using a dry plasma, in much the same way as for thermal vaporization. Arrowsmith¹²⁶ noted a 1–2 order of magnitude decrease in O-, H-, and N-containing species including CeO^+ , in the dry plasma, compared with pneumatic nebulization. Mochizuki *et al.*⁵⁵ also compared background spectra for solution nebulization and laser ablation. They noted decreases in intensity of up to 2 orders of magnitude for a variety of O-, N-, H- and Ar-containing species over the mass range m/z 28–80 and also a 1000-fold decrease in WO^+ intensity.

Despite the reduction of some interferences, laser ablation still has some way to go before it is accepted as a routine, quantitative technique. The main problem is the paucity of suitable solid certified reference materials to use as standards and the necessity of matrix matching standards and samples. Some workers have used synthetic standards,^{57–59} in the form of fusions and pressed pellets, with some success; however, such a technique can cause an increase in blank levels and polyatomic ions due to the flux or binder. If one of the sample constituents (matrix or analyte) is of known concentration, it can be used as an internal standard,¹³² though this is rarely the case and it is often necessary to fall back on theoretically or empirically derived response factors.²³² Pang *et al.*²³⁴ have utilized the novel method of acoustic wave normalization to improve precision and similar approaches could possibly be extended to correct for differing rates of ablation.

In a related area of application Jiang and Houk^{60,128} have investigated the technique of arc ablation and observed lower signals due to O- and H-containing species and metal oxides, compared with a wet plasma. Jakubowski *et al.*¹²⁷ have reported similar reductions using spark ablation.

Hydride/vapour generation. Hydride generation provides an elegant means of sample introduction for the hydride forming elements As, Se, Sn, Sb, Ge, Te, Pb, Bi and elemental Hg. It has the advantages of highly efficient sample transport, approaching 100% and separation of the analyte from the matrix. Hydride generation has been coupled to ICP-MS,^{91,92,112,243–250} primarily to increase sensitivity and avoid certain spectral interferences such as $^{40}\text{Ar}^{35}\text{Cl}^+$ on $^{75}\text{As}^+$, $^{37}\text{Cl}^{37}\text{Cl}^+$ on $^{74}\text{Se}^+$ and $^{40}\text{Ar}^{37}\text{Cl}^+$ on $^{77}\text{Se}^+$.

Janghorbani and Ting²⁴⁶ found that even a 10% solution of HCl gave rise to very little interference on $^{74}\text{Se}^+$ and $^{77}\text{Se}^+$, while Branch *et al.*⁹¹ avoided the spectral interferences due to $^{40}\text{Ar}^{35}\text{Cl}^+$ on $^{75}\text{As}^+$ and $^{40}\text{Ar}^{37}\text{Cl}^+$ on $^{77}\text{Se}^+$ using a silicone gas-liquid separator to completely separate the reagents from the analyte; thereby eliminating any carry over of HCl or NaCl, which is likely with a conventional gas-liquid separator.⁹² However, despite the suitability of the technique for overcoming the interferences mentioned, the hydride generation step itself is prone to chemical

interferences by the first row transition metals, which can be preferentially reduced unless the reaction conditions are carefully optimized.

Another method of vapour generation is to generate volatile oxides, and this has been applied to the determination of Re^{251} and $\text{Os}^{211,252,253}$ after generation of Re_2O_7 and OsO_4 as volatile oxides. The technique has been used to increase sensitivity, but it has the added advantage that separation of the analyte from the matrix is also achieved.

Instrumental and other methods

Alternative gas and mixed gas plasmas. Two papers^{254,255} have documented investigations into He ICPs as sources for ICP-MS. The advantages of a He compared with an Ar plasma are the greater degree of ionization achieved in the He plasma for elements with a high first ionization potential and the absence of major interfering species due to the Ar isotopes, such as $^{40}\text{Ar}^{35}\text{Cl}^+$. However, owing to the resistivity and high thermal conductivity of He compared with Ar, the generation of a stable discharge has proved difficult and He ICPs have found limited application as sources for ICP-MS.

Mixed-gas plasmas have been investigated by several groups, using N_2 ,^{152,199,203,113,119,256-261} He,^{262,263} Xe²⁶⁴ and H_2 .^{265,266} Evans and Ebdon^{257,258} introduced less than 5% of N_2 into the central channel, or spiked samples with 10% isopropanol, and attenuated the signal due to ArCl^+ by three orders of magnitude and substantially reduced interferences due to other polyatomic ions such as ClCl^+ and ArAr^+ . They proposed that competitive formation of nitrides or carbides helped to reduce the levels of Ar- and Cl-containing polyatomic ions. In a follow-up study¹¹³ the method was successfully applied to the determination of As in urine. Similarly, Lam and co-workers^{152,199,203,259} have investigated the addition of N_2 to the outer gas and central gas and observed decreases in polyatomic ions such as ArCl^+ , ClO^+ , ArO^+ and metal oxide ions. They also found that analyte-ion signals were increased with the addition of 5% N_2 to the other gas and proposed that charge transfer between NO^+ and analyte atoms could be the cause. Wang *et al.*¹¹⁹ have recently compared the effect of N_2 addition to the various gas flows of the ICP and found that 1% N_2 addition to the outer gas flow, or 3% N_2 addition to the inner gas flow, caused a reduction in interferences caused by $^{40}\text{Ar}^{35}\text{Cl}^+$ and $^{35}\text{Cl}^{16}\text{O}^+$ on $^{75}\text{As}^+$ and $^{51}\text{V}^+$. However, they observed no effect on TiO^+ , CeO^+ or UO^+ species.

Houk *et al.*²⁵⁶ have found that the ionization temperature (T_{ion}) measured by MS in the axial channel is reduced by the inclusion of N_2 in the outer gas. This may account for the large reduction in intensities for many polyatomic ions, which require more energy for ionization compared with atomic analytes. In a similar vein Smith *et al.*²⁶⁴ have introduced Xe into the central channel at 10 or 37 ml min^{-1} and observed substantial reductions in many polyatomic ions. They considered that the lower excitation and ionization energy of Xe compared with Ar might be the reason for the reduction in polyatomic ions.

Shibata *et al.*²⁶⁶ investigated the introduction of H_2 into the central channel and observed an increase in the intensity of analyte ions and the ions Ar^+ , ArH^+ , N^+ , O^+ and OH^+ . By using an optical fibre they were able to observe the region between the sampler and skimmer cones and found that the addition of hydrogen to the central gas increased the excitation temperature and electron number density and also increased the concentration and kinetic energy of species such as ArH^+ and Ar^+ . Hence, they proposed that collisional or charge transfer ionization within the interface region might play a greater role when H_2 was added to the plasma.

Using a different approach Rowan and Houk²⁶⁷ have

investigated collision-induced dissociation (CID) of polyatomic ions using ICP-MS. They found that ArN^+ , ArAr^+ and ArO^+ ions were substantially attenuated by using a bath gas of Xe or CH_4 . In future, such methods may form the basis for reducing polyatomic ions in ICP-MS, especially with the advent of low cost ion traps used in tandem with a quadrupole.

Alternative plasma sources. The source that has gained considerable attention as an alternative to the ICP is the microwave induced plasma (MIP), initially investigated by Douglas and French^{268,269} and subsequently, mainly by Caruso's group, in conjunction with gas chromatography,²⁷⁰⁻²⁷³ pneumatic nebulization²⁷⁴⁻²⁸¹ and electrothermal vaporization²⁸²⁻²⁸⁴ sample introduction.

The potential advantage of the MIP is the ease with which plasmas can be formed in a number of gases, particularly helium, which eliminates interferences due to the three isotopes of argon ^{36}Ar , ^{38}Ar and ^{40}Ar . This allows the determination of $^{39}\text{K}^+$ and $^{40}\text{Ca}^+$ and the consequent elimination of polyatomic ions such as ArAr^+ , ArO^+ , ArN^+ , ArC^+ and ArCl^+ which should facilitate the determination of $^{77}\text{Se}^+$, $^{78}\text{Se}^+$, $^{80}\text{Se}^+$, $^{56}\text{Fe}^+$, $^{52}\text{Cr}^+$ and $^{75}\text{As}^+$. Additionally, He has a higher ionization potential (IP) than argon (IP=24.59 V for He compared with 15.76 for Ar) which facilitates more efficient ionization of I (IP=10.45 V), Br (IP=11.84 V), Cl (IP=12.97 V), P (IP=10.49 V) and S (IP=10.36 V). Background studies with the He MIP^{270,274,277} have indeed indicated that the mass spectrum is cleaner above m/z 40. However, Ar contamination in the He still caused some interferences and signals due to Xe^+ and Kr^+ were present. Also, ions such as N^+ , O^+ , N_2^+ , O_2^+ , OH^+ , NH^+ and NO^+ may even be more abundant than in the Ar ICP owing to the greater degree of ionization possible with a He plasma and also the greater degree of air entrainment that occurs with a low power, low flow MIP.

Chambers *et al.*²⁸⁵ have measured ion kinetic energies with a He MIP source and related these observations to theoretical considerations of the design of a sampling interface. They reached similar conclusions to previous workers, namely that a 0.4 mm orifice sampler was the best compromise between minimizing orifice clogging and air entrainment and that much greater pumping speeds were necessary in the first stage in order to pump He effectively.

Another alternative to Ar that has been investigated is the N_2 MIP,^{275,278,279} which also allows the interference-free determination of $^{77}\text{Se}^+$, $^{78}\text{Se}^+$, $^{80}\text{Se}^+$, $^{52}\text{Cr}^+$ and $^{75}\text{As}^+$, although the presence of $^{14}\text{N}_4^+$ precluded the determination of $^{56}\text{Fe}^+$. Wilson *et al.*²⁷⁵ have observed that the levels of metal oxides and hydroxides were higher, probably owing to the lower temperature of the N_2 MIP, greater air entrainment through the sampling orifice and the presence of O_2 in the N_2 supply.

An alternative to the generation of plasmas at atmospheric pressure is to generate them at low pressure. In this way air can be excluded, the gas flow much reduced, considerably lower power used to sustain the plasma and plasmas can be generated using He, O_2 , N_2 and other gases with much greater ease. Low pressure MIPs have been investigated for MS.^{93,286-288} The application of a low-pressure plasma in MS is particularly attractive since the exclusion of air and consequent reduction in interferences due to $^{16}\text{O}_2^+$ on $^{32}\text{S}^+$ and $^{14}\text{N}^{16}\text{O}^+\text{H}^+$ on $^{31}\text{P}^+$ would make it a highly sensitive and selective gas chromatographic detector for these elements. Story *et al.*⁹³ have investigated low pressure He and N_2 MIPs for the determination of P and S by gas chromatography (GC). They found that it was possible to obtain much lower background at m/z 31 and 32, provided the gas supply was relatively uncontaminated and there were no leaks in the low pressure system.

The main advantages of the MIP over the ICP as a source for MS are the ability to form plasmas in a number of gases

at atmospheric pressure, which may form the basis for a low cost, plasma MS instrument operating with air or N₂ and the relatively uncomplicated nature of the MIP generator and matching network compared with that of the ICP, although higher power MIPs up to 1000 W would probably start to rival the ICP in size and complexity. On the negative side, the MIP can be difficult to tune at higher powers and the introduction of a central gas flow can be difficult when gases such as He are used. Other problems associated with He include the necessity for a much greater first stage pumping capacity in order to ensure that skimming occurs at the optimal position and a 0.4 mm orifice sampler, to minimize air entrainment, which will also increase the propensity for the orifice to clog. Because of these drawbacks the MIP may only become a complementary technique to the ICP, with respect to aqueous solution introduction, for specific applications. However, it does show considerable promise as a source for GC detection and it is in this area that it is most likely to become widely accepted.

High resolution instruments. One of the most effective methods of overcoming spectral interferences is to use a mass spectrometer with sufficient resolution to resolve between species that have similar m/z . Hence, Bradshaw *et al.*²⁸⁹ have used a double focusing magnetic sector mass spectrometer that was capable of achieving a resolution of 50 000. However, a resolution of 30 000 was sufficient to resolve OCl⁺ at m/z 50.964 from V⁺ at m/z 50.944 and ArO⁺ at m/z 55.957 from Fe⁺ at m/z 55.935. Similarly, Morita *et al.*²⁹⁰ have resolved SO⁺ at m/z 47.967 from Ti⁺ at m/z 47.948 and others have undertaken similar studies.²⁹¹⁻²⁹³ A high resolution (HR)-ICP-MS instrument is now available commercially, and a recent report²⁹⁴ indicates that higher sensitivity and lower background is possible compared with quadrupole based instruments. However, it is likely that a trade-off in sensitivity will result if an extremely high degree of resolution is required.

The main drawback to using an HR instrument is the expense and added complexity compared with a quadrupole ICP mass spectrometer. However, HR-ICP-MS is certainly the technique of choice if polyatomic interferences must be overcome, and improvements in magnetic sector technology will undoubtedly bring this technique within the budget of many laboratories.

Multivariate correction methods. Perhaps one of the simplest methods to correct for spectroscopic interferences is the use of elemental equations or multivariate correction methods.^{86,94,110,114,295-297} For example,¹¹⁰ the interference caused by ⁴⁰Ar³⁵Cl⁺ on ⁷⁵As⁺ can be corrected for by measuring the ⁴⁰Ar³⁷Cl⁺ signal at m/z 77 and back-calculating the contribution from ⁴⁰Ar³⁵Cl⁺ at m/z 75, assuming that the sample does not contain ⁷⁷Se⁺.

Ketterer *et al.*²⁹⁵ have extended this approach, and used multiple linear regression and principal component analysis techniques to correct for MoO⁺, ZrO⁺ and RuO⁺ on Cd⁺, In⁺ and Sn⁺, respectively. Likewise, Vaughan and co-workers^{114,296} have used principal component analysis to correct interferences caused by light rare earth oxides on heavier REE and by oxides and hydroxides of Ca and polyatomic ions due to Na, K and Cl in urine, in determinations of Ni.

Such approaches to interference correction do not entail any considerable expense for additional hardware, but do require a thorough knowledge of the interferences that are likely to be encountered with any particular matrix. Hence, a flexible and user-friendly software package and a comprehensive database that can be continually updated is essential if the method is to become widely accepted. However, if many samples with similar matrices are to be analysed, then such an approach, even in its simplest form, would prove invaluable.

Other methods. Several workers have investigated negative-ion mode ICP-MS for the determination of the halogens.²⁹⁸⁻³⁰⁰ The advantage of this approach is that the spectrum is much simpler, owing to the absence of positive ions such as Ar⁺, although the baseline noise is considerably higher. Unfortunately, the only elements that can be detected with any degree of sensitivity are the halogens.

Inductively coupled plasmas with a frequency of 40 MHz have been evaluated³⁰¹⁻³⁰³ and found to offer no particular advantage over 27 MHz instruments, although it is easier to maintain a discharge to which an alternative gas such as He or N₂ has been added. Additionally, an orifice-linked discharge has been found to increase the proportion of doubly charged ions.

Non-spectroscopic Interferences

Non-spectroscopic interferences form the second major group of interferences associated with ICP-MS. Unlike a spectroscopic interference, where the analytical signal is enhanced by another element or polyatomic species with the same nominal mass, a non-spectroscopic interference is characterized by a reduction or enhancement in analyte signal due to factors exerting an influence on sample transport, ionization in the plasma, ion extraction, or ion throughput in the resultant ion beam. Furthermore, the nature and concentration of the sample matrix has a direct bearing on the severity of these effects.

The influence of the matrix on sample transport and ionization has been well characterized for ICP-AES. However, suppression or enhancement effects caused by a highly concentrated matrix have tended to be more severe in ICP-MS, probably owing to the predominant influence of ion extraction and focusing in the mass spectrometer. Hence, matrix effects will be discussed as they apply to ICP-MS, since the consensus in the literature at this time points to the overriding influence of processes occurring during ion extraction and focusing. Consequently, to avoid the trap of enlarging the scope of the review considerably, sample transport and ionization effects will be discussed in less detail, since these topics have already received considerable attention with respect to ICP-AES and the main emphasis will be placed on investigations into non-spectroscopic interferences in ICP-MS.

Fundamental Studies

Sample introduction and transport

A comprehensive review of the processes that influence sample nebulization and transport through the spray chamber, has been published by Sharp³⁰⁴ and other relevant discussions can be found in books by Boumans³⁰⁵ and Montaser and Golightly,³⁰⁶ so a detailed survey of the literature will not be presented here. Much of the work on nebulization and sample transport has been undertaken by Browner's group,³⁰⁷⁻³¹⁷ Maessen and co-workers³¹⁸⁻³²² and Boumans and co-workers.³²³⁻³²⁶ Without exception, these studies have been undertaken with respect to sample introduction systems for ICP-AES, although the principles remain the same for ICP-MS, since the same methods of sample introduction are utilized in both techniques and have been summarized by Browner and Zhu.³²⁷

Much of the aforementioned work on sample nebulization and transport has involved the study of organic solvents, both from the point of view of the analysis of such samples in practical terms, but also because they provide a convenient way of comparing solvents with a wide variety of physical properties. It is evident from the literature pertaining to ICP-AES that the factors that affect nebulization and sample transport are the design of the nebulizer

and nebulizer gas flow and the viscosity, surface tension, density, evaporation rate and vapour pressure of the sample. Hence, the primary droplet size distribution will be influenced by the design of the nebulizer, the nebulizer gas flow rate and the viscosity and surface tension of the solvent, so that solvents with lower surface tension will result in smaller droplets. The amount of gravitational settling that occurs as the droplets pass through the spray chamber will depend on the solvent density, and in combination with the evaporation rate and vapour pressure of a particular solvent, will determine the tertiary droplet size distribution. One of the main consequences of this is the necessity to matrix match samples and standards with respect to the solvent, in order to ensure similar nebulization and transport characteristics. Additionally, Winge *et al.*,³²⁸ and Olesik and co-workers,^{329,330} have shown that the behaviour of individual droplets in the plasma can be a source of considerable signal fluctuation. In the latter study, which is most pertinent to this review, the vaporization of solute droplets in the plasma was found to cause extreme local variations in plasma temperature and hence in analyte ionization, illustrating the influence that even very small aerosol droplets can have on a highly energetic source such as the ICP. More work in this area may well elucidate the origins of polyatomic ions, especially metal oxides.

Effects on ionization in the plasma

In addition to influencing nebulization and transport properties, the sample matrix can have a profound effect on the temperature in the plasma and hence the atomization, excitation and ionization characteristics of the discharge. In particular, the effects of organic solvents and an excess of easily ionizable elements have received considerable attention with respect to ICP-AES.

The introduction of organic solvents into the ICP has been shown to decrease the excitation temperature^{322,331} and electron density,³³¹ due to the increased solvent load and energy required to dissociate molecular species such as C_2 . Such phenomena have caused severe matrix effects in ICP-AES when organic samples have been analysed,³³²⁻³³⁴ requiring matrix matching or dilution with a common solvent.³³⁵ The analysis of organic solvents or petroleum-based samples, by ICP-MS, has received comparatively little attention *per se*,^{133-135,336-339} although the coupling of liquid chromatography necessarily involves the introduction of organic mobile phases in many cases. The introduction of organic solvents in ICP-MS is subject to the same strictures that apply to ICP-AES in terms of sample introduction, the maintenance of a stable plasma and the effect on plasma temperature, hence it would be reasonable to suppose that this would result in similar matrix effects. Longerich³³⁶ has observed signal suppression and enhancement compared with 1% nitric acid, depending on whether solutions of 1% acetic acid, 1% ethanol, 12% acetic acid or 12% ethanol were aspirated. It was not determined whether sample nebulization and transport, the effect of the solvent on the ionization temperature in the plasma or mass discrimination in the ion beam (or a combination of all four) was the cause. Similar effects were observed by Marshall and Franks¹³³ on the introduction of methacrylic acid, which they found to be highly dependent on operating conditions. Interestingly, Allain *et al.*³³⁷ found that the introduction of glycerol, glucose or methane caused substantial signal enhancements for Hg, As, Au, Se and Te, but relatively little change for elements with lower first IPs, using a 56 MHz ICP. They speculated that the introduction of the organic compounds improved the ionization efficiency in the plasma and hence improved sensitivity for those elements with high IPs. They pointed out that, in such a situation, an internal standard should be chosen primarily

with respect to IP. Measurements of T_{ion} made by mass spectrometric means^{4,340-342} have indicated that T_{ion} in the plasma is dependent on operating conditions. Wilson *et al.*³⁴¹ found that 2 mmol l⁻¹ NaCl had no effect on T_{ion} , whereas desolvation caused T_{ion} to drop 500 K. In order to determine conditions in the extracted gases, Houk's group have made measurements of the electron temperature (T_e), electron density (n_e) and floating potential (V_f) in the expansion stage^{343,344} and behind the skimmer.³⁴⁵ They found that T_e in the expansion stage increased upon the addition of water to the plasma, but decreased when 0.14 mol l⁻¹ KNO₃ or CsNO₃ was added, whereas n_e was not greatly affected. Behind the skimmer, the introduction of water caused an increase in T_e but a decrease in n_e . The addition of 0.14 mol l⁻¹ Li, Na and Rb caused T_e to decrease slightly whereas Co and U caused an increase. The effect of matrix elements on n_e was variable depending on the position behind the skimmer and the mass of analyte, however, n_e was more likely to be elevated with a heavier matrix to the greatest extent furthest behind the skimmer. It was noted that these effects do not necessarily reflect those that occur in the ICP central channel and Lepla *et al.*³⁴⁶ have made simultaneous atomic emission and mass spectrometric measurements of the ICP showing that matrix effects are quite different, with ICP-MS suffering from more severe analyte suppression effects than ICP-AES.

It is evident from the foregoing that the effect of organic solvents on the behaviour of the analyte in the plasma may result in the different effects on analyte signal in ICP-MS compared with ICP-AES. This is hardly surprising since the former technique involves the invasive mass spectral sampling of ions, whereas the latter technique involves non-invasive optical sampling of excited state atoms and ions. Hence, more work needs to be done to elucidate the exact effect of the solvent on ionization conditions within the plasma as it affects ICP-MS.

Salt build-up on the cones

Suppression of analyte signal can be caused, to a great extent, by deposition of salt on the sampler and skimmer cones,^{347,348} thereby clogging the orifices and substantially affecting the sampling process. While flow injection can alleviate the worst effects of orifice clogging,^{117,130} it may actually be better in some circumstances to allow the sampling orifice to partially clog, thereby achieving a pseudo steady-state situation where the rate of deposition is equalled by the rate of dissociation.

Matrix induced suppression in the ion beam

Investigations into the influence of matrix elements on the analytical signal in ICP-MS have generated many conflicting reports and theories.^{1-5,263,95,118,349-360} The initial investigations^{1,2} dealt with boundary layer sampling conditions and so bear limited relevance to later investigations which were all performed on instruments utilizing continuum sampling. Boundary layer sampling was particularly prone to both spectroscopic and non-spectroscopic interferences. Differences between instrumental configurations and operating conditions might be the cause of the different trends observed by various workers. However, in general the most serious matrix effects are those caused by an excess of a heavy, easily ionizable element or elements in the matrix, which cause suppression of analyte signal, or in some cases an enhancement. For instance, Tan and Horlick³⁵³ studied the effects of the matrix elements Na, Cs, Zn, K, Rh, In, Cd, Sn and Sb on the analytical signals for a range of analytes with different masses and first IPs. They observed suppression of analyte signal, in the presence of a high concentration of matrix, at low nebulizer gas flow rates, but

enhancements at higher flow rates. In similar studies, Gregoire^{351,352} observed only suppression, while Beauchemin *et al.*³⁵⁰ observed enhancements in analyte signal due to Na, K, Cs, Mg and Ca, suppression due to B, Al and U and no effect for Li. Several important points can be identified from the conflicting information.

(i) Heavy matrix elements with low IPs cause the most severe effects. (ii) Light analyte elements with high IPs are most severely affected. (iii) Plasma operating conditions have a great influence on the magnitude of these effects. (iv) The matrix effect is dependent on the absolute amount of matrix element rather than on the molar ratio of matrix element to analyte, hence the effects can be reduced by dilution of the sample.

The theories that have been put forward indicate that processes occurring in the plasma, and/or extracted gases, account for these effects. One theory is that of ionization suppression in the plasma,³⁴⁹ whereby the large excess of a matrix element with a low first IP results in a large excess of electrons and positive ions after ionization. This excess forces the equilibrium for the analyte towards atom formation, resulting in a suppression of analyte ion formation. However, this theory lacks credibility considering that the proportion of ions and electrons contributed by even a large amount of matrix will be small compared with the vast excess contributed by Ar and nebulized water molecules in the plasma, and this alone cannot explain the severity of the matrix effects observed in ICP-MS. Indeed, this mechanism has largely been discounted as the explanation for matrix effects in ICP-AES.³⁶¹⁻³⁶³

Gregoire³⁵² has proposed that 'ambipolar diffusion' may be a possible explanation. The mechanism is such that the presence of a large excess of a high mass easily ionizable element in the plasma gives rise to an electric field caused by the diffusion of electrons, at a greater rate than ions, out of the central channel. The electric field results in the diffusion of lighter analyte ions towards the annular region of the plasma, thereby giving rise to a drop in the number of ions that can be sampled from the central channel. Recent results by Hobbs and Olesik,³⁶⁴ utilizing laser-excited fluorescence to radially resolve the analyte distribution in the plasma, suggest that this phenomenon does indeed occur in the plasma. However, the extent to which this may cause matrix-induced suppression in ICP-MS is debateable, since Douglas and French¹⁵⁷ have calculated that the sampled portion of the ICP can be up to eight orifice diameters wide.

Tan and Horlick³⁵³ have suggested that mass separation effects, in the expansion region and subsequently in the ion beam, may play a role. They mention two effects, namely pressure diffusion and Mach-number focusing, whereby the heavier ions are focused towards the axis of the beam and the lighter ions diffuse away to a greater extent, although the theories were originally developed for neutral molecular beams. Similarly, Kawaguchi and co-workers^{355,360} have proposed that lighter analyte ions are subject to collisional scattering in the presence of heavier matrix ions.

Gillson *et al.*³⁵⁶ have suggested that space charge effects in the ion beam play a major role. This is caused by the loss of electrons from the ion beam due to the nature of the ion optics, which focus only positively charged species, and results in coulombic repulsion between ions. In the presence of an excess of relatively heavy matrix ions, which have greater translational energy, the lighter analyte ions are repelled from the ion beam to the greatest extent. It has been postulated that mass separation effects are particularly critical in the expansion region since the skimmer cone samples from only a relatively narrow portion of the expansion gases around the axis behind the sampling orifice, and indeed, matrix effects have been shown to be

less severe when a skimmer with a larger orifice than normal was used.³⁵⁷

Recently, Hieftje's group³⁶⁵⁻³⁶⁹ have reported the results of a systematic investigation of mass-bias effects and matrix-induced interferences in ICP-MS. Their conclusions indicate that gas dynamic theory developed for neutral beams is inadequate for the development of ion sampling interfaces and ion focusing in ICP-MS, owing to the existence of space charge effects in the focused ion beam. Their arguments can be summarized as follows.

(i) Measurements of space and floating potentials behind the skimmer using a Langmuir probe³⁶⁵ indicated the existence of considerable charge separation in the extracted plasma gas, due to the greater collisional frequency of electrons with the metal sampling plate. This resulted in an electron-poor ion beam, in which coulombic repulsion between positive ions caused them to be scattered off-axis.

(ii) Ion kinetic energies were measured by retarding plate analysis³⁶⁶ and it was concluded that the optimal skimming position predicted by gas dynamic theory results in an ion flux in which coulombic repulsion caused considerable scattering of analyte ions in the second and third vacuum stages, exacerbated when the ions were focused using ion optics. Ironically, they found that if the extracted gases were skimmed closer to the mach disc, the resultant ion flux was less, but ultimately resulted in a much greater on-axis ion flux in the second and third stages, with consequently greater ion throughput and a reduction in matrix effects.

In related studies Vaughan and Horlick³⁷⁰ have used a computer model to predict the effect of ion lens potentials on ion transport and found that the optimal lens conditions are dependent on the ion kinetic energies even without the contribution from space charge effects. Tanner³⁷¹ has developed a procedure to calculate the effect of space charge on ion trajectories which confirms its role in matrix-induced suppression. He suggested that increasing the ion energies (but maintaining a narrow spread in energies), by accelerating the ions after the skimmer, alleviated suppression; but also pointed out that the necessity to decelerate them before the quadrupole would once again result in space charge effects. Ross and Hieftje³⁷² applied the results of their fundamental studies and demonstrated that matrix effects could be eliminated by removal of the photon stop and second stage ion optics, without any other degradation in analytical performance.

(iii) The parameters that affect ion-beam dispersion to the greatest extent were found to be the solvent load, inner gas flow rate, first stage pressure and the geometry of the interface and ion lenses. These factors combined to influence the ion kinetic energies and space charge in the ion beam.

Such conclusions would seem to indicate that the performance of the present generation of quadrupole ICP-MS instruments could easily be improved by modifications to the interface and lens stack, thereby eliminating the most severe effects of space charge in the ion beam.

Methods to Overcome Matrix Induced Suppression in ICP-MS

Internal standardization

Internal standardization has been proposed as a possible remedy for matrix effects and instrumental drift. Beauchemin *et al.*³⁵⁰ investigated the background species $^{12}\text{C}^+$ and $^{40}\text{Ar}^{40}\text{Ar}^+$ as internal standards to correct for matrix effects and found some improvement in precision for those elements reasonably close in m/z . They subsequently used $^{40}\text{Ar}^{40}\text{Ar}^+$ as an internal standard for the analysis of real samples with some success,^{96,115} however, this approach should be treated with caution because it is quite likely that

the mechanism of formation of $^{40}\text{Ar}^{40}\text{Ar}^+$ is different to that of the analyte ions, with a different distribution in the plasma. Thompson and Houk³⁵⁴ have suggested that the internal standard should be close in atomic mass and have a similar first IP to the analyte, if correction for matrix effects is to be successful. Several workers^{137,358,359} have found that In used as an internal standard corrects adequately for a variety of elements in the presence of a large excess of matrix present as a dissolved salt. However, Marshall and Franks¹³³ have found that analyte suppression caused by samples of 5% methacrylic acid could not be corrected for by using only Rh as an internal standard and Igarashi *et al.*¹¹⁶ achieved much better recoveries for Th and U when Bi or Tl were used as internal standards rather than In. Vanhaecke *et al.*³⁷³ have found that an internal standard should be chosen that is as close as possible in m/z to the analyte. Doherty⁶¹ utilized Re and Ru to correct for non-spectroscopic interferences on the determination of Y and the REE, by calculating a linear function based on the recoveries for Re and Ru, which was then applied to the masses in between.

Internal standardization has been shown to be an extremely effective means of compensating for matrix induced suppression, providing that an internal standard of similar mass and ionization energy to the analyte is chosen. Furthermore, the routine use of an internal standard is recommended for even the simplest matrices in order to compensate for instrumental drift. The effectiveness of internal standardization in ICP-MS is due to the rapid scanning capability of the quadrupole (unlike a sequential monochromator) thereby eliminating the effects of short term signal drift. However, the high frequency signal fluctuations observed by Hobbs and Olesik³³⁰ would still be a source of considerable imprecision unless a truly simultaneous instrument could be devised.

Isotope dilution

Isotope dilution (ID) analysis is capable of a high degree of accuracy and provides a means whereby the analyte in question serves as its own *de facto* internal standard. For these reasons the technique has proved very popular for elemental analysis by ICP-MS^{62,97-100,120,129,138,139,374-376} and the principles and practice of IDMS for elemental analysis have been summarized by Fasset and Paulsen.³⁷⁷ Lásztity *et al.*¹³⁹ have investigated an on-line ID method, with greatly simplified sample preparation and analysis. Ward and Bell³⁷⁴ have compared ID for the determination of Rb by ICP-MS and thermal ionization MS, achieving a three fold improvement in precision with the former over the latter.

While ID can be a highly accurate and precise method of analysis, allowances must be made for possible mass discrimination effects and spectroscopic interferences. Hence, the measurement of natural isotopic abundances for an unspiked sample is necessary to confirm the absence of spectroscopic interferences, and an isotopic standard of known composition should be analysed to normalize the possible effects of mass discrimination.

Separation methods

Methods used to separate the matrix from the analyte in order to avoid non-spectroscopic interferences are identical to those discussed under Precipitation and solvent extraction and On-line separation methods for spectroscopic interferences. Indeed, a considerable number of these applications have specifically addressed the problems of non-spectroscopic interferences. Hall *et al.*⁴⁵ utilized precipitation with cupferron to separate Zr, Nb, Hf and Ta from a matrix containing U and Al thereby removing the non-spectroscopic interferences. Jackson *et al.*⁴⁸ used Te

coprecipitation after a NiS fire assay of geological materials, which conveniently separated the analyte from the bulk of the matrix, thereby avoiding potential interferences.

Palmieri *et al.*¹²¹ have used solvent extraction to separate the REE from U, while others have similarly extracted trace elements from sea-water.^{67,68}

Matrix removal using chelating resins or ion-exchange has proved popular because of the on-line nature of the technique. McLaren *et al.*⁶⁹ and Beauchemin and co-workers^{70,71} have successfully utilized silica-immobilized quinolin-8-ol to preconcentrate trace metals from sea-water and Jiang *et al.*⁷² used *N*-methylfurohydroxamic acid to complex and retain Mo^{VI} , Ti^{IV} and U^{VI} on a column packed with polystyrene-divinylbenzene, thereby achieving separation from U. Plantz *et al.*⁷³ and Heithmar *et al.*⁷⁶ have also separated the alkali and alkaline earth elements.

Cation-exchange resins have been used by Mukai *et al.*⁷⁹ to separate Pt from a Hf matrix and by Gregoire¹⁷² for the determination of B, which, being an element with low mass, is particularly prone to matrix-induced suppression. Ketterer⁸¹ utilized a cation-exchange membrane to separate Re (as the perrhenate ion) from Na, Mg, Al, K and Ca in groundwater samples.

Thompson and Houk⁸² evaluated reversed-phase, ion-pairing chromatography for 30 elements and demonstrated the speciation of various forms of As and Se. They also noted that the separation of matrix elements such as Na and Ca was possible.

Flow injection

Flow injection methods fall into two categories: flow injection in combination with other methods such as on-line matrix separation or chromatography, which have been discussed already, and flow injection for its own sake where the sample is injected into a simple aqueous carrier stream. This section deals with the latter of the two methods which has found considerable application for ICP-MS,^{63,101,117,130,131,137,140,359,378-383} because of the high sample throughput of which it is capable and the possibility for on-line sample manipulation. Flow injection has the added advantage that it presents the sampling cone with much less of the sample matrix than continuous nebulization, so the sampling orifice is less likely to clog.^{117,130}

Another way in which flow injection may help to reduce matrix-induced suppression has been demonstrated by Vickers *et al.*,³⁷⁹ who found that signal suppression due to a $1 \times 10^{-2} \text{ mol l}^{-1}$ U matrix was only 15% when dispersion of the flow injected sample was 25.2, as opposed to 95% for continuous nebulization, with only a 40% reduction in sensitivity. Similarly, Eaton *et al.*⁶³ demonstrated a similar reduction in the suppression caused by 27% NaCl on In. Presumably the dispersion of the sample had the same effect as dilution. Flow injection also provides a convenient method for on-line dilution³⁸² and ID analysis.³⁸⁰

Other methods

Aside from major modifications to instrumental hardware discussed under Salt build-up on the cones and other readily identifiable methods of minimizing matrix-induced suppression discussed above, miscellaneous other methods have been investigated.

Several workers have found that compromise ion-lens settings can be achieved (usually lens settings that are optimal for the sample matrix) so that suppression effects are substantially reduced.^{133,137,359} This approach was investigated in detail by Evans and Caruso,³⁸⁴ who used simplex optimization to determine ion-lens conditions which yielded zero analyte suppression due to $10\,000 \mu\text{g g}^{-1}$ of U on ^{115}In . They found that the extraction-lens voltage was the

most critical factor and also that a 0.4 mm sampling orifice resulted in very little suppression, although this size orifice also caused a large reduction in sensitivity.

Beauchemin and Craig²⁶⁰ have studied the effect of the addition of N₂ to the outer gas flow and found that matrix-induced suppression was much reduced in the mixed-gas plasma.

Conclusions

The most widely used methods to overcome both spectroscopic and non-spectroscopic interferences in ICP-MS involve a sample pre-treatment step to separate the analyte from the matrix. On-line column separation methods have been at the forefront of developments in this field and will continue to play a role in the development of chromatographic methods for speciation studies.

The development of HR-ICP-MS is expected to continue and should eventually lead to a low-cost instrument to replace the current generation of quadrupole instruments. Such high resolution instruments could be based on a magnetic sector or ion trap, although as yet only magnetic sector instruments have been produced commercially.

Fundamental studies into the causes of matrix-induced suppression in the ion beam have led to a greater understanding of these phenomena and have highlighted certain aspects of current instruments which require redesign, in particular, the interface geometry and ion lenses.

It is evident that ICP-MS is now entering into a new phase of development. If the next generation of instruments address the problems discussed in this review, a mature analytical technique will emerge that is capable of robust analyses of the most difficult samples.

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