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High resolution sector field ICP-MS and multicollector ICP-MS as tools for trace metal speciation in environmental studies: a review†

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Metal speciation provides improved information on the fate, uptake, beneficial or toxic aspects and, finally, translocation of metal between the different compartments of the environment. Speciation has therefore become an important topic of present-day analytical research. Inductively coupled plasma mass spectrometry (ICP–MS) is the detection technique of choice for different separation modes, and their hyphenation allows the performance of metal speciation on a routine basis. Sector field inductively coupled plasma mass spectrometry (ICP–SFMS) presents good detection capability and resolving power which results in important features for challenging applications, such as speciation analysis. Further, isotope ratio precision at the molecular level will certainly promote new information both with regard to chemical reactivity and traceability of reaction pathways. Multicollector inductively coupled plasma mass spectrometry (MC-ICP-MS) now offers such potential, and hence allows new scientific grounds to be investigated. An overview of the new directions that speciation should take and the potential and limits of ICP-SFMS and MC-ICP-MS in this domain will be discussed.

Introduction

Metal speciation has become an indispensable tool for studying the biogeochemistry and beneficial or toxic aspects of trace metals. The uptake, accumulation, transport, and interaction of the different metals and metalloids in nature are strongly influenced by their specific elemental form. It has generally been accepted for several years that the determination of total concentrations of elements in environmental samples does not give an accurate estimation of their potential environmental and biological impact, and therefore a complete characterization of a metal in a biogeochemical system requires the elucidation of properties such as its oxidation state, associated organic ligands and/or complexed forms.[1] The main analytical challenges for trace element speciation are the identification and the quantification of the chemical forms in which the element is present in the sample. Moreover, these requirements are hampered due to the very low concentrations of the analytes and the complexity of the sample matrix.

The International Union of Pure and Applied Chemistry (IUPAC) has defined *speciation* as "the specific form of a chemical element defined according to its molecular, complex, electronic or nuclear structure".[2] Therefore, *speciation analysis* is the process leading to the identification and determination of the different chemical and physical forms of an element existing in a sample. Although this definition tends to restrict the term speciation to the state of distribution of an element among different chemical species in a sample, in practice the use of the term is much wider, specifying either the transformation and/or the distribution of species or the analytical activity to identify chemical species and measure their distribution.

The increasing concern for the monitoring of chemical species in various fields, either for research or regulatory purposes, has led to the development of hyphenated techniques that involve the coupling of a selective separation with sensitive and element specific detection. Thermally stable and volatile species, and those which can be converted into such, are preferably separated by gas chromatography (GC). Species not amenable to GC are separated by liquid chromatography (LC) or capillary electrophoresis (CE). Inductively coupled plasma mass spectrometry (ICP-MS) is now by far the most widely used detection technique for speciation purposes due to its selectivity, sensitivity and multi-element/multi-isotope capabilities.[3]

The relative polarity, solubility, and molecular weight of the species of interest determine the type of liquid chromatography to be used for a specific application. The various modes of LC include reversed phase, reversed phased ion-paired, micellar, ion exchange, size exclusion, and chiral liquid chromatography. The coupling of LC with ICP-MS has the advantage of the compatibility of the chromatographic eluent flow rate and the uptake flow rate required for stable pneumatic nebulization. Furthermore, LC operates at room temperature, and for this reason interfacing the two techniques is straightforward. Regarding the possible mobile phases, only buffers with low salt concentration may be used, and the use of organic solvents in the mobile phase should be reduced or eliminated, if possible. Several reviews can be found in the literature regarding the use of LC coupled with ICP-MS.[4,5]

Capillary electrophoresis has the capacity to separate a wide range of analytes, from large biomolecules to small inorganic ions. It can separate positive, neutral, and negative ions in a single run with high separation efficiencies. Other advantages in comparison to liquid chromatography are nanoliter sample volumes, small amounts of reagents and low costs of capillary columns. On the other hand, as only very small sample volumes are introduced into CE it is generally difficult to obtain satisfactory limits of detection in terms of concentration for most species. It could also be mentioned that CE is extremely dependent on sample clean-up. The CE-ICP-MS coupling was discussed in detail by Olesik *et al.*[6] and the recent developments in its application for speciation analysis were recently reviewed.[7–8]

GC-ICP-MS has the advantage of enhanced sensitivity relative to LC-ICP-MS since samples are introduced to the plasma in gaseous form. Nearly 100% sample transport efficiency can be achieved with GC-ICP-MS, resulting in lower detection

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limits. Atomization and ionization efficiencies of the analytes are higher since energy from the plasma is not required for desolvation and volatilization. GC is more difficult to couple to ICP-MS than LC, but it is achieved by the use of a transfer line which connects the outlet of the GC to the base of the torch. GC-ICP-MS coupling has been also reviewed in the literature.[9,10]

The majority of ICP-MS instruments used for elemental speciation and trace elemental analysis have been quadrupole mass analyzers. The mass resolution offered by quadrupole ICP-MS (Q-ICP-MS) has proved to be inadequate for many elements that are prone to spectroscopic interferences.[11] Spectroscopic interferences can be attributed to the presence of isobaric and/or polyatomic interferences of various origin. Many of these interferences can be decreased or overcome today by the use of cold plasma conditions,[12,13] aerosol desolvation,[14] multiple collision cell,[15] dynamic reaction cell[16] and high resolution sector field ICP-MS (ICP-SFMS).[17] Sector field ICP-MS instruments, which were first commercialized in the late 1980s, offer resolving power as high as 10 000 that is sufficient to overcome the large majority of spectral interferences. The only drawback of this approach is the substantial loss in ion transmission efficiency observed on increasing mass resolution.

In recent years, the development of multicollector ICP-MS (MC-ICP-MS) has resulted in an important tool for highly precise isotope ratio measurements and thus an opening of new horizons in environmental research. MC-ICP-MS is also based on the magnetic field design, but uses multiple detectors instead of a single one. Therefore, MC-ICP-MS offers the capability of detecting and measuring multiple isotopes at exactly the same time. As a result of this approach, they are recognized as producing the ultimate in isotope ratio precision.[18]

The aim of this paper is to highlight the major areas of environmental research where the on-line coupling of separation techniques to ICP-SFMS and MC-ICP-MS can provide an important contribution in environmental trace metal speciation.

Sector field inductively coupled plasma mass spectrometry

Although quadrupole mass analyzers represent the highest percentage of all inductively coupled plasma mass spectrometers installed worldwide, limitations in their mass resolution have led to the development of high resolution mass spectrometers. These instruments, known as high resolution ICP-MS (HR-ICP-MS), sector field ICP-MS or double focusing ICP-MS (DF-ICP-MS), are based on the magnetic field approach.

The entrance slit, the magnetic field and electrostatic analyser, and the exit slit could be considered as the main components of double focusing ICP-MS instruments. Traditionally, the electrostatic analyzer is placed before the magnetic field, but nowadays the so-called "reverse geometry" with the electrostatic analyzer behind the magnetic field is considered to be more advantageous since the mass analysis reduces the high ion currents from the source, and only ions of the selected mass are subjected to the subsequent energy analysis. Consequently, an improvement in the sensitivity as well as a reduction of the noise level could be achieved. A diagram of a reverse geometry spectrometer is shown in Fig. 1. Varying resolution is achieved by scanning the magnetic field under different entrance and exit slit width conditions. The lowest practical resolution achievable, using the widest entrance and exit slits, is approximately 300–400, whereas the highest practical resolution, using the narrowest entrance and exit slits, is approximately 10 000. It should be pointed out that as the resolution increases, the transmission of the ions decreases, and therefore although extremely high resolution is available, detection limits will be compromised under these situations.[17]

Besides high resolving power, another attractive feature of sector field instruments is their very high sensitivity combined with extremely low background (<0.2 ions s^{-1}). The higher sensitivity and the lower background gives better detection limits, typically in the pg L^{-1} range, although some limitations should be expected depending on the blank signal for the element(s).[19] In addition to the good detection capability, another benefit of magnetic-sector instruments is their ability to measure quantitatively with excellent precision. The flat-topped peaks, typical of a sector field ICP-MS operated at low mass resolution, translate into high-precision data and as a result, in the low resolution mode, relative standard deviation (RSD) values are in the range 0.1–0.5%.[20] Therefore, sector field ICP-MS operating at low resolution mode results in an improvement in isotope ratio precision measurements when compared with quadrupole ICP-MS. Although precision usually decreases as resolution is increased, since the peak shape gets worse, modern instruments with high-speed electronics and low mass bias are still capable of precision values of $<0.1\%$ RSD in medium or high resolution mode.[21]

Metal speciation and ICP-SFMS

The release of trace metals into the environment arises from natural sources (crustal, marine, biogenic or volcanic) or from

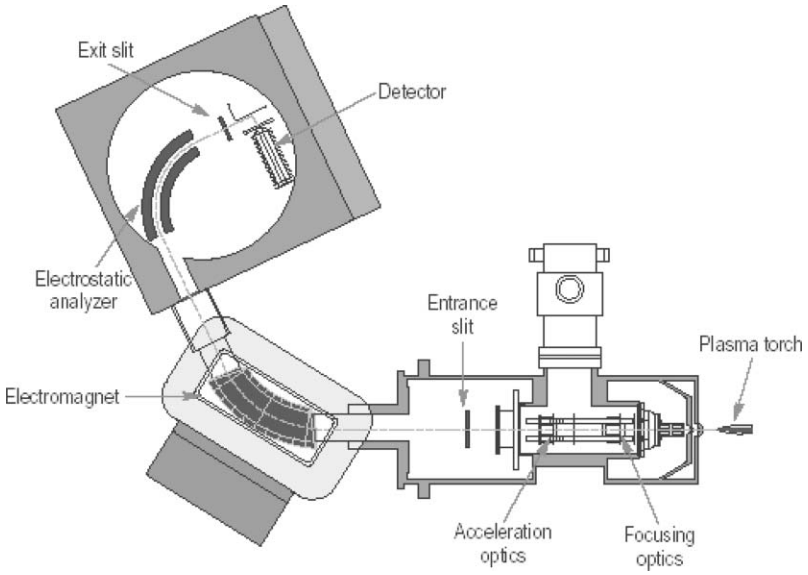

Fig. 1 Scheme of a reverse geometry double-focusing magnetic-sector mass spectrometer.

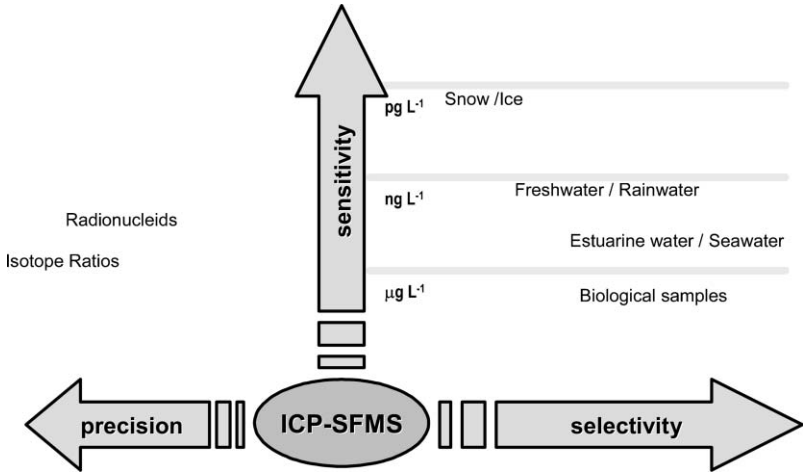

Fig. 2 Potential features of sector field ICP-MS for trace metal analysis of relevant environmental samples.

anthropogenic emissions (liquid wastes, industrial gases and aerosols or fossil-fuel combustion). Therefore, metals and metalloids are present in all compartments of the environment, and knowledge of their environmental pathway is of high importance in order to assess their global impact. Nowadays, there is a great interest in the determination of trace metal concentrations in pristine and remote areas in order to have a better understanding of the long-range transport of metals from the different natural and anthropogenic sources. The low detection limits of ICP-SFMS, down to the pg L^{-1} range when used at low resolution, in combination with the high resolving power, prove to be an important feature for many environmental applications. As a result, during the last decade, sector field ICP-MS has been revealed as an important tool for the analysis of total trace metal concentration at very low level in rainwater,[22] surface water,[23] estuarine and sea-water,[24] and snow and ice cores.[25–27] Fig. 2 shows the relation between the potential features of sector field ICP-MS in conjunction with trace metal analysis of relevant environmental samples.

Chromatographic methods generate transient signals, and therefore these require the ability to acquire signal *versus* time data. The measurement of isotopes in the same *m*/*z* range does not require a change in the settings of the magnetic field, and therefore the scan speed could be comparable of the one of quadrupole instruments. However, when the *m*/*z* range increases, the magnetic field setting changes, and longer time is needed. Nowadays, the scanning speed of modern ICP-SFMS instruments is sufficiently high to measure fast and transient signals, as produced by chromatographic columns used in on-line speciation studies.

Recently, Houk[28] described the use of high resolution mass spectrometers with an ICP source in a book,[29] and special attention was paid to their use for speciation purposes. Table 1 illustrates the main applications of sector field ICP-MS to the speciation analysis of environmental samples using liquid chromatography, capillary electrophoresis and gas chromatography as separation techniques. Within the next sections, these applications will be discussed in detail.

Liquid chromatography coupled to ICP-SFMS

The first paper on the use of high resolution ICP-MS as a detector for liquid chromatography was published by Rottmann and Heumann[30] in 1994. This work shows the potential of a high performance liquid chromatography (HPLC) system using size exclusion chromatography with a sector field ICP-MS (Element, Finnigan MAT, Bremen, Germany) for the on-line speciation of Fe complexes in humic substances. Working at resolution 3000, the separation of $^{56}Fe^{+}$ from the $^{40}Ar^{16}O^{+}$ spectroscopic interference was achieved. Therefore, for the first time, it was possible to determine an element like iron, which is not measurable in Q-ICP-MS due to spectroscopic interferences, when applying a coupling technique.

The speciation of selenocompounds in environmental samples requires very high sensitivity (due to the low concentration level of the different species in the samples) and high

Table 1 Specific applications of separation techniques coupled to ICP–SFMS

Element	Studied species	Matrix	Separation	Instrument	Resolution	Reference
Fe	Fe–DOM complexes	River water	LC	Element	3000	30
Se	SeCys, selenocystamine, SeMet, SeEt	Standards	LC	Element prototype	300, 1400	31,32
Se	SeCys, selenocystamine, SeMet, SeEt	Herring gull eggs	LC	Element prototype	1400	33
As	As^{III}, As^{V}, MMA, DMA, TMAO, tetra, AB, AC	Water, sediments, emergent/ subemergent freshwater plants	LC	Element2	300, 4000	35
As	As^{III}, As^{V}, MMA, DMA, TMAO, tetra, AB, AC	Freshwater fish	LC	Element2	300	36
As	As^{III}, As^{V}, MMA, DMA, AB	Pore water and soil water extracts	LC	Element1	300	37
Pt	Pt–glutathione, Pt–cysteine and Pt–methionine complexes	Grass (*Lollium multiflorum*) cultivated in Pt-contaminated and non-contaminated soil	LC	Element prototype	300	38
Pt, Pd, Rh	Pt, Pd and Rh phytochelatins and carbohydrates	Grass (*Lollium multiflorum*) cultivated hydroponically	LC	Element2	300, 4000	39
Cr	Cr^{III}, Cr^{VI}	Industrial process solution	LC	Element	3000	40
As	As^{III}, As^{V}, MMA, DMA, AB, AC	Pore water and soil water extracts	CE	Element1	300	37
Hg	Hg^{2+}, CH_3Hg^{+}, $CH_3CH_2Hg^{+}$	Standards	CE	Element	300	41
Sn, Hg, Pb	—	Standards	GC	—	—	42
Sn	DBT, TBT	PACS-2 (marine sediments)	GC	Element2	300	43

resolution power (in order to avoid the spectroscopic interferences that affect all Se isotopes). Feldmann *et al.*[31,32] describe the speciation optimization of four organic selenium compounds (selenocysteine, selenocystamine, selenomethionine and selenoethionine) by coupling HPLC to ICP-SFMS (Element prototype, Finnigan MAT, Bremen, Germany) with hydraulic high pressure nebulization (HHPN) for sample introduction. In order to optimize the chromatographic separation of the selenium compounds, measurements at different mass resolutions ($R = 300$ and $R = 1400$) were performed. Reversed-phase chromatography (column Nucleosil 120 Å, C18, 5 μm) was applied for the separation using a methanol–water mixture (5 + 95, v/v) as eluent. ^{82}Se was chosen as the working isotope since it showed a higher signal-to-background ratio in comparison with ^{77}Se. The methanol induced spectroscopic interferences ($^{12}C_4{}^1H_2{}^{16}O_2{}^+$, $^{12}C_5{}^1H_6{}^{16}O^+$ and $^{12}C_6{}^1H_{10}{}^+$) on the working isotope ^{82}Se were resolved by application of a mass resolution of $R = 1400$. An increase of the mass resolution, if only moderate, led to an improvement of the limit of detection (LOD) by a factor of 4 for selenocysteine, selenomethionine, and selenoethionine owing to the lower spectroscopic background. For selenocystamine there was no relevant improvement of the LOD. Table 2 shows the limits of detection obtained for both mass resolutions. The same research group applied the optimized procedure described above to the speciation of Se compounds in herring gull eggs[33] as a biomonitor to trace the heavy metal level of a polluted marine ecosystem within the German Environmental Specimen Bank. Within this project, herring gull eggs were collected from mud flats of the North Sea, and unexpectedly high total Se levels (mg kg^{-1} range) were observed in the eggs.[34] The isotopes ^{34}S, ^{88}Sr, ^{85}Rb, ^{75}As, ^{63}Cu and ^{65}Cu were monitored as well, in order to measure their correlation to the selenium isotopes. Six selenium-containing compounds were observed, but only two could be identified (selenocystamine and maybe selenocysteine).

Weathering of minerals, volcanic and biological activities, together with anthropogenic emissions release arsenic into the atmosphere, soil, groundwater systems and the food chain. HPLC coupled to sector field ICP-MS was applied to the speciation of arsenic in water, sediments and plants of the Moira watershed (Ontario, Canada)[35] and in freshwater fish from an arsenic-rich lake (Moira Lake, Ontario, Canada).[36] Two chromatographic separation systems were employed. A PRP-X100 anion-exchange column with a phosphate-buffered mobile phase was employed to separate arsenite (As^{III}), dimethylarsinic acid (DMA), methylarsonic acid (MMA) and arsenate (As^V). The cationic arsenic compounds, such as arsenobetaine (AB), arsenocholine (AC), trimethylarsine oxide (TMAO) and tetramethylarsonium cation (tetra), were resolved with a Zorbax 300 SCX cation-exchange column using 20 mmol L^{-1} pyridine as the mobile phase. The ICP-MS system was an Element 2 (Thermo Finnigan, Bremen, Germany) working at low ($R = 300$) and medium ($R = 4000$) resolution modes. The speciation of water samples revealed the presence of As^{III} (2%) and As^V (98%) in surface water; meanwhile As^{III} represents the major species in bottom water (*ca.* 70%) and sediment pore water (*ca.* 97%). The extraction of As species from soil core samples was carried out by using a mixture of phosphoric and ascorbic acids. The results show that an unknown As-complex (consisting of As, sulfide and organic matter) is responsible for the release of arsenite from the sediment to the adjacent water column. Submerged plants collected from Moira river and Loira lake were found to accumulate arsenic. The presence of inorganic arsenic and organic compounds, such as MMA, DMA, TMAO and tetramethylarsinum ion (tetra), were confirmed in the analysis of emergent and subemergent freshwater plant samples. An unknown As compound (probably an arsenosugar) was detected in submerged plants. The analysis of four fish species from the Moira lake revealed the presence of As^{III}, As^V, MMA, DMA, AB, AC, TMAO and the tetramethylarsonium ion (tetra), apart from two non-identified As-containing species, in all fish samples investigated. For the first time, tetramethylarsonium ion (tetra) was detected in freshwater fish samples.

Table 2 Limits of detection for the speciation of selenium and arsenic compounds by liquid chromatography coupled to sector field ICP-MS (adapted from refs. 32 and 37)

	$R = 300$		$R = 1400$	
	LOD/ μg L^{-1}	Absolute LOD/pg	LOD/ μg L^{-1}	Absolute LOD/pg
Selenocystine	0.008	2	0.002	0.4
Selenocystamine	0.009	2	0.010	2
Selenomethionine	0.016	3	0.004	0.8
Selenoethionine	0.018	4	0.005	0.9
Arsenobetaine	0.049	1.23	—	—
Dimethylarsinic acid	0.054	1.35	—	—
Arsenite (As^{III})	0.090	2.24	—	—
Methylarsonic acid	0.076	1.89	—	—
Arsenate (As^V)	0.072	1.81	—	—

Koellensperger *et al.*[37] undertook arsenic speciation in soil pore water and soil water extracts using ion chromatography ICP-SFMS. The As9-HC ion chromatographic column was able to efficiently separate AB, MMA, DMA, As^{III}, and As^V in about 6 min. The hyphenation to a sector field (Element 1, Thermo Finnigan, Bremen, Germany) working at resolution 300 gave limits of detection with an improvement factor of 1000 compared with Q-ICP-MS (see Table 2). Salt deposition in ICP–MS was avoided with the use of a split interface. The 1 : 10 flow splitting implies a signal decrease by a factor of 10 but, due to the reduction of matrix suppression effects, a signal decrease only by a factor of 5 was observed. All samples revealed only the presence of As^V, and arsenic concentration levels of 0.1–0.3 μg g^{-1} were reported. Due to the lack of reference material, the results obtained were checked by CE-ICP-SFMS and they will be presented in a later section.

It is recognized that platinum, palladium and rhodium (platinum group elements, PGE) are being widely distributed into the environment, mainly due to surface abrasion of the catalytic converters during car operation. Two experiments were performed to explain the main routes of uptake of platinum group elements (PGE) by plants. Klueppel *et al.*[38] investigated the metabolism of Pt in grass (*Lollium multiflorum*) cultivated on Pt-contaminated and non-contaminated soil. Size-exclusion chromatography was used for the separation of the species, and selected elements, such as C, S, Ca and Pb, which co-elute with Pt, were also investigated. For S and Ca, the higher mass resolution available with a double focusing magnetic field ICP-MS instrument (Element prototype, Finnigan MAT, Bremen, Germany) was applied in order to cope with problems from spectroscopic interferences. With the aim of solving the problems arising from the separation of the grass roots and the soil, a second study[39] was focussed on the bioaccumulation of Pt, and also Pd and Rh, as water-soluble compounds, and Pt, Pd and Rh species formed in grass (*Lollium multiflorum*) cultivated hydroponically. In order to study the bioavailability, metabolism and kinetics of the studied elements, size exclusion chromatography (SEC) coupled on-line with SF-ICPMS (Element 2, Finnigan MAT, Bremen, Germany) was chosen for the analysis of Pt, Pd and Rh, together with nutritional elements in the low molecular mass fraction (< 10 kDa). The highest bioaccumulation factors were obtained for Pd and Rh in roots and for Pt in leaves.

It is generally accepted that Cr^{III} is an essential trace element for humans, but Cr^{VI} is highly toxic. Information about the oxidation state of chromium is very important for many

Table 3 Limits of detection for the speciation of arsenic and mercury compounds by capillary electrophoresis coupled to sector field ICP-MS (adapted from refs. 37 and 41)

	CE-ICP-SFMS LOD/μg L^{-1}	Sample stacking CE-ICP-SFMS LOD/μg L^{-1}
Arsenocholine	12.0	—
Arsenobetaine	12.1	—
Dimethylarsinic acid	5.26	—
Methylarsonic acid	6.02	—
Arsenate (As^{V})	7.67	—
Arsenite (As^{III})	5.74	—
$EtHg^{+}$	84	—
$MeHg^{+}$	54	7
Hg^{2+}	25	4

industrial processes and wastewater purification methods. Vanhaecke *et al.*[40] optimised a method for Cr^{III}/Cr^{VI} speciation in industrial process solution employing a microbore anion exchange column hyphenated to a sector field ICP-MS (Element, Finnigan MAT, Bremen, Germany). Cr^{III} and Cr^{VI} were established to co-elute from the anion exchange column with Cl^{-} and HCO_3^{-}, respectively, such that the signals of both $^{52}Cr^{+}$ and $^{53}Cr^{+}$ suffer from spectral overlap due to the occurrence of $^{40}Ar^{12,13}C^{+}$, $^{35}Cl^{16}OH$ and $^{37}Cl^{16}O^{+}$ ions. At medium resolution ($R = 3000$) both chromium isotopes could be measured interference free.

Capillary electrophoresis coupled to ICP-SFMS

The coupling of capillary electrophoresis to a sector field ICP-MS by Koellensperger *et al.*[37] for arsenic speciation purposes was already mentioned in the last section. The detection limits (see Table 3) obtained by CE-ICP-SFMS ($R = 300$) were found to be 2 orders of magnitude higher than those obtained by ion liquid chromatography ICP-SFMS. Within this study, the electrophoretic separation of six arsenic species (As^{III}, As^{V}, MMA, DMA, AB and AC) was achieved by using borate buffer at pH 9.3. The separation time of CE-ICP-SFMS could be significantly reduced by application of hydrodynamic pressure, and addition of isopropanol improved the sensitivity by a factor 3.

Silva da Rocha *et al.*[41] developed a method for the determination of organic and inorganic mercury species in freshwater systems by capillary electrophoresis with ICP-MS detection. The on-line coupling of CE to Q-ICP-MS and ICP-SFMS for the separation and determination of $EtHg^{+}$, $MeHg^{+}$ and Hg^{2+} was compared. Before injection into the CE system, cysteine was added and thus the mercury compounds were separated as Hg–cysteine complexes in a fused silica capillary column using 20 mM tetraborate decahydrate buffer. Apart from a conventional interface between the CE system and the ICP–SFMS instrument, an increase in sensitivity of the CE system was investigated by using sample stacking techniques for on-line sample preconcentration. Sample stacking (this is, preconcentration) results from the difference in field strength between the aqueous zone and the running buffer. The low detection limits (a few μg L^{-1} of Hg species) (see Table 3) obtained by "sample stacking" CE-ICP-SFMS gives a very sensitive approach that could be applied to solving real life problems of inorganic and organic mercury contamination in freshwater systems.

Gas chromatography coupled to ICP-SFMS

De Smaele *et al.*[42] were the first to couple capillary gas chromatography (CGC) to ICP-SFMS for the simultaneous speciation of organometallic compounds present in a synthetic sample. Transient signals of Sn, Hg and Pb were monitored together with Xe as an internal standard. In order to obtain accurate results, on the one hand the magnetic field moved between the isotopes ^{120}Sn and ^{126}Xe, and on the other ^{202}Hg and ^{208}Pb. In this way the mass difference between the analytes was shorter in order to avoid drift of the magnetic field. This first approach to multielement determination of transient signals showed that the number of isotopes that can monitored simultaneously depends on the analyte concentration, the duration of the transient signal, the mass difference between the analytes and the precision required.

Yang *et al.*[43] describes the use of a sensitive method for the accurate and precise determination of dibutyltin (DBT) and tributyltin (TBT) in sediments by species specific isotope dilution plasma source mass spectrometry. Using GC for sample introduction and analyte separation, a performance comparison was made between quadrupole ICP-MS and sector field ICP-MS detection. The method was validated by analysing the PACS-2 certified reference material marine sediment (NRCC, Ottawa, Canada). An improvement higher than 2-fold in the precision of calculated $^{120}Sn/^{117}Sn$ ratios was obtained for both TBT and DBT in standards using GC-ICP-SFMS as compared with GC-Q-ICP-MS. The precision obtained for GC-ICP-SFMS in the analysis of the certified reference material (1.59–1.62% RSD) was slightly better than the one obtained by GC-Q-ICP-MS (1.64–3.31% RSD). Method detection limits of 0.4 and 0.3 ng g^{-1} for TBT and DBT, respectively, were obtained using GC-ICP-SFMS, based on processing a 0.5 g sample. These superior limits of detection arise from the three-fold enhancement in signal-to-background ratio obtained with the sector field machine.

Multicollector inductively coupled plasma mass spectrometry

Multicollector ICP-MS is based on a relatively recent technique for measuring isotope compositions at high precision and accuracy, usually only achieved with thermal ionisation mass spectrometry (TIMS). The real simultaneous detection of isotopes eliminates classical sources of uncertainty in quadrupole based ICP-MS isotope ratio measurements which are due to the sequential scanning mode and plasma flicker noise. The high ionisation efficiency of the plasma source allows the measurement of a wide range of elements, including those that are not accessible to thermal ionisation sources. A good example is the case of mercury, with a first ionisation potential of 10.4 eV. Here, MC-ICP-MS opens a new field of environmental applications.[18,44]

The majority of MC-ICP-MS instruments available on the market are either single- or double-focusing with up to nine Faraday cages in the detector assembly. A scheme of multicollector inductively coupled plasma mass spectrometer is shown in Fig. 3.

The achievable precision on isotope ratios varies for different elements and the isotope pair of interest. The precision reported on isotope ratios when using MC-ICP-MS instruments is mostly in the range of 100–200 ppm.[45] For example, isotope ratios of $^{207}Pb/^{206}Pb$ and $^{208}Pb/^{206}Pb$ have been measured with precisions better than 40 ppm.[46]

In order to improve abundance sensitivity, which is limited due to the use of Faraday detectors, ion counting systems have been added to the multicollector device in the latest generation MC-ICP-MS instruments.

In multicollection mode the MC-ICP-MS is used with a fixed magnetic field, thus limiting the mass range that can be measured simultaneously to some percent (between 10 and 30) of the mass of interest. Therefore, the use of internal standards is limited to elements in the same mass range, *e.g.*, Tl for mass bias correction of Pb or Hg.

A main obstacle to accurate isotope ratio determination

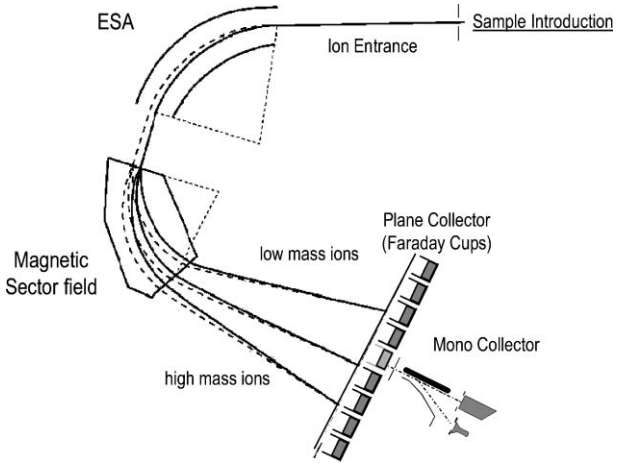

Fig. 3 Scheme of a multicollector inductively coupled plasma mass spectrometer.

using MC-ICP-MS is the correction for instrumental mass bias. In comparison to TIMS, the mass bias can easily be in the percent range, *i.e.*, up to 4 orders of magnitude higher, and additionally drifting over time. Artifacts can be generated either due to spectroscopic interference, or due to a different behaviour of the mass bias produced during the measurement of a sample and the measurement of the isotopic standard used for correction.[47] The same problem, of course, also applies to the measurement of transient signals, and is even more pronounced because the analyte signal itself is drifting over time. Nevertheless, MC-ICP-MS is opening the doors towards new applications in environmental and biological sciences.

Metal speciation and MC-ICP-MS

As the ICP is perfectly suited for hyphenation to chromatographic separation techniques like GC or HPLC, multicollector ICP-MS opens the possibility of precisely determining element isotope ratios within speciation applications. This approach will be invaluable in the attempt to further elucidate environmental, biological and geochemical pathways and the fate of elements and element species. Of special concern in terms of isotope ratios will be the question of isotope fractionation processes occurring during the cycling of certain elements in the environment and in biological systems. Precise isotope ratio determination in connection with the species information may well help to establish and understand biogeochemical and environmental cycles and distinguish between sources and sinks of potentially hazardous compounds.

So far, only a few papers have been published using MC-ICP-MS as a detector for coupling techniques in speciation analysis, most likely due to the fact that these instruments are quite expensive and are in general used for geochemical applications. Furthermore, in an on-line speciation approach, isotope ratios have to be determined on relatively short, transient signals, complicating the data evaluation.

Several factors have to be taken into account in order to achieve precise and accurate isotope ratio results: the isotope ratio calculation method used, the mass bias correction method applied, the effect of possibly co-eluting matrix compounds, the fact that chromatography can induce fractionation due to different retention for the same species incorporating different isotopes, and finally the fact that the instrumental mass bias itself may be prone to drift during the elution of a peak, as a result of the sample arriving in the plasma and ion extraction region. Another factor that might count is the suggestion that chromatography itself may induce fractionation. Anbar *et al.*[48] described that during the elution of iron from an ion exchange column the heavier iron isotope was enriched in the first amount of iron eluting from the column, and Wehmeier *et al.*[49] suggested chromatographic separation between $^{123}SbMe_3$ and $^{121}SbMe_3$ eluting from a packed column GC.

Another issue of concern is the sample preparation. As soon as matrix separation, digestion, extraction, derivatization or even simple dilution are necessary, the original isotope ratio in the sample might be affected. Contamination is one well known problem, as well as non-quantitative reactions, *e.g.*, reactions during matrix separation may provoke changes in the isotope ratio of interest.

The few papers on speciation using MC-ICP-MS published so far in an attempt to obtain precise and accurate isotope ratios on element species describe GC coupled to MC-ICP-MS for the elements sulfur, lead, mercury and antimony (see Table 4). HPLC coupled to MC-ICP-MS has been applied to the speciation of mercury and the separation of neodymium and uranium.

For the determination of sulfur isotope ratios in an isotopic gas standard (PIGS 2010, IRMM), SF_6, GC was coupled to the Isoprobe MC-ICP-MS (Micromass, UK) with a hexapole collision cell.[50] Sample preparation was limited to dilution of the pure gas in argon. Chromatographic peaks of 1.5 s base width were obtained. The peaks revealed considerable tailing: this resulted in uncertainty for the definition of peak integration limits, leading to uncertainty in the isotope ratio calculations. A non-uniform behaviour of the isotope ratio development during peak elution due to the peak tailing was visible when plotting single point isotope ratios (Fig. 4). For data evaluation, peak integration limits were defined by the determination of a "uniform isotope ratio zone" inside the chromatographic peak. This integration method resulted in a precision of 0.03–0.05% RSD on $^{32}S/^{34}S$, depending on the concentration injected.

Krupp *et al.*[51–53] also performed lead isotope ratio measurements, and they compared the precision achieved on isotope ratios for a transient signal of a lead species by coupling GC to quadrupole ICP-MS and two different MC-ICP-MS systems. They reported an improvement in the $^{207}Pb/^{206}Pb$ ratio obtained for a 3.5 s base width transient peak from 0.2% RSD with quadrupole ICP-MS to 0.015% RSD using MC-ICP-MS as the detector. Detection limits were 60 fg absolute for the Q-ICP-MS coupling, and as low as 3 fg for a multicollector system. In both approaches they obtained isotope ratio precision of 0.02–0.07% RSD for highly abundant isotopes on a signal of 3.5 s peak base width obtained by the repeated injection of $PbEt_4$ into the GC-MC-ICP-MS system. Mass bias

Table 4 Specific applications of separation techniques coupled to MC-ICP-MS

Element	Species	Matrix (type of sample)	Separation	Instrument	Reference
S	SF_6	PIGS 2010, IRMM CRM (gas)	GC	Isoprobe	50
Pb	$PbEt_4$	SRM981 CRM (derivatized Pb; injected as $PbEt_4$ in organic solvent)	GC	Axiom, Isoprobe	52,53
Hg	Inorganic Hg (as $HgEt_2$), MeHg	Fish tissue (digested; derivatized and injected in organic solvent)	GC	Axiom	54
Sb	Me_3Sb	Anaerobic digested sewage sludge (gas)	GC	Isoprobe	49
U	—	Liquid standards	HPLC	Neptune	55
Hg	MeHg	DORM-2 fish muscle CRM (extraction and spike)	HPLC	Axiom	56

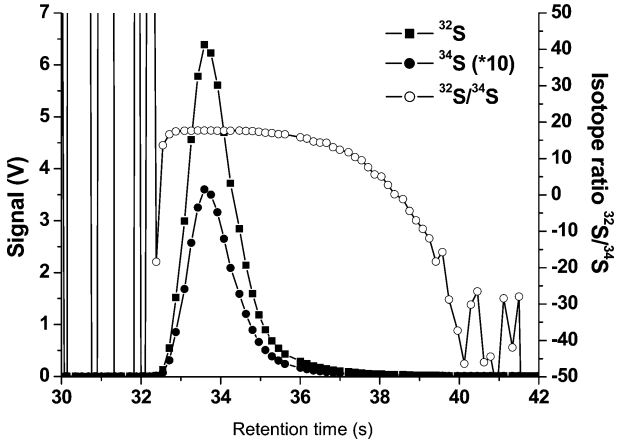

Fig. 4 Peak obtained for the injection of SF_6 into a GC-MC-ICP-MS system. The data for ^{34}S are enhanced by factor 10 for better visualization. The development of the isotope ratio $^{32}S/^{34}S$, displayed by open circles, shows significant drift towards the peak end.

was corrected using a linear approach with a mass bias factor calculated from the $^{203}Tl/^{205}Tl$ isotope ratio, simultaneously monitored during the GC run. The $PbEt_4$ had been derivatized from isotopic lead standard SRM 981, and satisfying accuracy was obtained for all lead isotope ratios, showing that the sample preparation step did not significantly alter the lead isotope distribution.

Methylmercury (MeHg) and inorganic mercury (as $HgEt_2$) in fish tissue were measured by GC coupled to an Axiom MC-ICP-MS.[54] Samples were digested, derivatized with $NaBEt_4$ and extracted in hexane. Replicate injections were made into the GC-MC-ICP-MS instrumentation. Peaks were subject to significant tailing, and the same peak integration method of uniform isotope ratio zone integration was employed as described for the sulfur measurements. For injection of 50 and 500 pg (absolute amounts, as Hg) MeHg standards, isotope ratio precision $<0.01\%$ RSD was obtained for $^{202}Hg/^{198}Hg$. Mass bias correction was performed using the $^{203}Tl/^{205}Tl$ ratio obtained simultaneously by aspirating thallium solution during the GC run. The obtained isotope ratio values were compared to the IUPAC isotope ratio abundance, as no suitable isotopic mercury standard is available.

Wehmeier *et al.*[49] report the measurement of isotope ratios on trimethylantimony (Me_3Sb) produced by anaerobic digestion of sewage sludge in a laboratory fermenter. Standard gas samples and real samples were analysed by cryotrapping–cryofocusing capillary GC coupled to the Isoprobe MC-ICP-MS. For data evaluation, they used two different approaches, full peak integration and integration of the peak centre only, the second method resulting in better isotope ratio precision of 0.02% RSD. Bracketing with gaseous Me_3Sb was chosen as the mass bias correction method. The chromatograms obtained revealed significant chromatographic isotope fractionation, surprisingly showing that the isotopically heavier $^{123}SbMe_3$ eluted first from the column. $SbMe_3$ in the gas produced during anaerobic fermentation in laboratory sewage sludge digesters was then measured using the cryotrapping–cryofocusing GC-MC-ICP-MS. The antimony isotope calculation showed a significant enrichment of ^{123}Sb with a $\delta^{123}Sb$ of 19.6 and 10.4‰, respectively, for two different fermentation experiments, contradictory to the hypothesis that lighter isotopes should be preferred and enriched during biologically mediated methylation reactions.

In a recent publication, Günther-Leopold *et al.*[55] coupled HPLC to the Neptune MC-ICP-MS and also found a significant drift of the point-to-point isotope ratios during peak elution for the measurement of the uranium isotope ratio $^{235}U/^{238}U$. A careful evaluation of the reason for this drift was performed by directly comparing injections of the same sample *via* HPLC and *via* a flow injection system. An isotope ratio shift of the same order of magnitude was observed for both kinds of sample introduction, thus excluding chromatographic fractionation on the HPLC column as the major source of this drift. The overall effect of isotope ratio drift during the transient signal was found to be less important for lower absolute measured intensities as well as for smaller isotope ratios. Thus, it was stated that the observed isotope ratio drift is supposedly due to instrumental shift in mass bias over the peak width.

Clough *et al.*[56] coupled HPLC to MC-ICP-MS in order to reduce the uncertainty derived from isotope ratio measurements for the precise determination of methylmercury in a CRM using species specific isotope dilution. Their procedure of isotope ratio determination during the elution was based on a steady-state-approach, averaging data points for isotope pairs during the peak maximum. The instrumental mass bias was corrected using the $^{203}Tl/^{205}Tl$ signal obtained from thallium mixed with the mobile phase of the HPLC. By using the MC-ICP-MS, they could minimise the uncertainty budget for methylmercury determination in DORM-2 reference material to 0.7%, compared to 4.1% when using Q-ICP-MS.

Conclusions

There is no question that ICP-SFMS systems are no longer a novel analytical technique. They have proved themselves to be a valuable addition to trace element determination. Their good detection capability and exceptional resolving power results in important features for challenging applications, such as speciation analysis. Their main limitation lies in their slower speed when scanning large *m*/*z* ranges on fast transient signals. However, it is expected that future instrumental developments will establish the use of sector field instruments for trace metal speciation as a routine analysis method.

Although the coupling of GC and HPLC to MC-ICP-MS as a detector has been described in very few publications, valuable information can be drawn from these experiments, which so far mainly stress the problems that are associated with the analysis. The points discussed and evaluated concern chromatographic fractionation effects, drift in mass bias during peak elution, mass bias correction procedures and peak integration, *i.e.*, data evaluation strategies. Contradictory results have been reported for chromatographic fractionation on the GC or HPLC columns, and the drift of mass bias during peak elution. These findings give rise to many questions which are unsolved for the moment. Especially, the correction for mass bias still poses a major problem, and it remains the main obstacle to accurate isotope ratio determination using MC-ICP-MS coupling. However, although the results reported clearly reveal that lots of work still has to be done before GC or HPLC coupling to MC-ICP-MS will be routine, the enormous potential for environmental applications is evident. With respect to this, the preliminary study carried out by Krupp *et al.*[54] using GC-MC-ICP-MS for the speciation of mercury in fish is an interesting example. The isotopic composition of methylmercury was compared with the isotopic composition of inorganic mercury in a whale liver sample. In the same GC run, the mercury isotope ratios were determined for the two species, indicating an enrichment of heavier mercury isotopes in methylmercury compared with inorganic mercury. This finding is in contrast to the usually observed enrichment of lighter isotopes during biological element cycling. Although inconclusive at present, these results clearly reveal the need for further investigation.

The use of these methods may help to discover or better understand biological and geochemical element cycles, be it for essential elements like selenium, or for toxic elements like mercury.

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