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## Review

# Inorganic mass spectrometric methods for trace, ultratrace, isotope, and surface analysis

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### Abstract

Inorganic mass spectrometric methods are widely used for multielemental determination at the trace and ultratrace level for isotope ratio measurements and surface analysis (depth profiling, imaging) in quite different materials (e.g. conducting, semiconducting, and nonconducting solid samples; technical, environmental, biological, geological, and water samples). The capability of spark source mass spectrometry (SSMS), laser ionization mass spectrometry (LIMS), glow discharge mass spectrometry (GDMS), laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS), secondary ion mass spectrometry (SIMS), sputtered neutral mass spectrometry (SNMS), and inductively coupled plasma mass spectrometry (ICP-MS) have been applied as the most important mass spectrometric techniques with their multielemental capability for the characterization of solid and aqueous samples. The detection limits for the direct analysis of solid samples by inorganic solid mass spectrometry were determined up to sub-ng g<sup>-1</sup> and for aqueous solutions by ICP-MS up to sub-pg L<sup>-1</sup>. This article discusses the most important inorganic mass spectrometric techniques and their application for quantitative determination of trace element, isotope ratio measurements, and in-surface analysis. (Int J Mass Spectrom 197 (2000) 1–35) © 2000 Elsevier Science B.V.

*Keywords:* Inorganic mass spectrometry; Trace analysis; Isotope analysis; Surface studies

### List of abbreviations

AMS	accelerator mass spectrometry	DIHEN	direct injection high-efficiency nebulizer
CE	capillary electrophoresis	ETV	electrothermal vaporization
DF-ICP-MS	double focusing ICP-MS	GDMS	glow discharge mass spectrometry
		GE	guard electrode
		dc GDMS	direct current glow discharge mass spectrometry
		rf GDMS	radio frequency glow discharge mass spectrometry
		GD-OES	glow discharge optical emission spectrometry

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GIMS	gas isotope mass spectrometry
GSSMS	gliding spark source mass spectrometry
HPLC	high performance liquid chromatography
ICP-MS	inductively coupled plasma mass spectrometry
ICP-QMS	quadrupole ICP-MS
INAA	instrumental neutron activation analysis
LA-ICP-MS	laser ablation inductively coupled plasma mass spectrometry
LIMS	laser ionization mass spectrometry
MC	multi-ion counting
MCN	microconcentric nebulizer
$\mu$ -FI	microscale flow injection
RIMS	resonance ionization mass spectrometry
RSC	relative sensitivity coefficient
RSD	relative standard deviation
SEC	size exclusion chromatography
SFC	supercritical fluid extraction
SIMS	secondary ion mass spectrometry
SNMS	secondary neutral mass spectrometry
SPME	solid phase microextraction
SRM	standard reference material
SSMS	spark source mass spectrometry
TIMS	thermal ionization mass spectrometry
TOF	time of flight

## 1. Introduction

Inorganic mass spectrometry [1,2] has proven its ability to provide very sensitive, accurate, and precise multielemental determinations of trace and ultratrace elements, as well as isotope ratios in quite different samples such as high-purity materials (metals [3–5], alloys [6,7], semiconductors [5,8–10], insulators [11,12], nonmetals, e.g. graphite [13]), technical materials (such as ceramic oxides, nitrides, or carbides [12,14–19]), environmental materials (different types of waters [20–22], biological [23–25], medical [26],

or geological [27–30]), and nuclear and radioactive waste samples [31–38].

This article focuses on solid state mass spectrometric techniques such as spark source mass spectrometry (SSMS) [39–42], laser ionization mass spectrometry (LIMS) [27,42–44] including resonance ionization mass spectrometry (RIMS) [45–47], laser ablation inductively coupled mass spectrometry (LA-ICP-MS) [48–53], glow discharge mass spectrometry (GDMS) [54–59], secondary ion mass spectrometry (SIMS) [60–63], and sputtered neutral mass spectrometry (SNMS) [64–66] for the direct analysis of solid samples with respect to trace element concentration, depth, and lateral distribution. Different applications of mass spectrometry in solid state physics will also be presented. Furthermore, thermal ionization mass spectrometry (TIMS) [67,68] is an important mass spectrometric method for precise isotope ratio measurements of inorganic materials and inductively coupled plasma mass spectrometry (ICP-MS) [69–75] has developed into one of the most important and sensitive mass spectrometric techniques. ICP-MS is used not only for the trace, ultratrace, and isotope analysis of aqueous solutions but also for the characterization of solid samples after their dissolution or in combination with a solid sample introduction system. The main features of ICP-MS and selected applications in environmental research, the determination of long-lived radionuclides, and in plasma diagnostics will be discussed in comparison to direct solid mass spectrometric techniques.

An inorganic mass spectrometer consists of the following parts: the ion source for the evaporation, atomization, and ionization of the sample; the mass (and energy) analyzer for the mass (and energy) separation of ion beams that are extracted from the ion source; and the ion detection system. As a function of the initial energy of the ions, the mass spectrometric separation of ion beams is realized in inorganic mass spectrometry using both static or dynamic mass analyzers, such as single magnetic sector field instruments [76,77] or double focusing mass spectrometers (a combination of magnetic and electric sector fields, e.g. Mattauch-Herzog geometry [12,18,72,78], Nier-Johnson geometry or the reverse geometry [22,79–

81], quadrupoles [8,33,34,82–84], time-of-flight (TOF) analyzers [61,85–87], ion traps [88–90], and Fourier transform ion cyclotron resonance mass spectrometers [91]. At present, Faraday cup and ion multiplier as single and multiple ion collector systems are used in commercial mass spectrometers for ion detection.

In inorganic mass spectrometry quite different types of ion sources, based on different evaporation and ionization processes such as spark ion source, glow discharge source, laser ionization source, secondary ion source, sputtered neutral ion source, and inductively coupled plasma ion source, are advantageous for different application fields. Because the mass spectrometric method is determined primarily by the evaporation and atomization method applied (e.g. by thermal or laser-induced evaporation, in a plasma, by electron, or by ion bombardment) and the ionization method (using electron impact ionization, ionization during the sputtering process using ions, resonant or nonresonant laser ionization, and thermal surface ionization) different mass spectrometric techniques can be classified according to the evaporation and ionization method applied. In Fig. 1 the mass spectrometric techniques were divided into methods with simultaneous evaporation (atomization) and ionization processes in the ion source (such as SSMS, ICP-MS, SIMS, LIMS) and methods with “postionization” processes (e.g. SNMS, GDMS, TIMS with two filaments, and LA-ICP-MS). With the “postionization” methods, the processes of evaporation and atomization or sputtering of the sample material are separated in time and space from the processes of ionizing the atomic species. Because of the separation of evaporation and ionization processes in inorganic mass spectrometry both processes can be influenced separately, which may result in easier quantification of analytical results.

## 2. Solid mass spectrometric techniques

A range of solid mass spectrometric techniques are available as excellent tools for trace, isotopic, and surface analysis of solid material. The schematics of

the most important ion sources for solid state mass spectrometry (the spark ion source, the laser ion source, the glow discharge ion source, and laser ablation coupled to the inductively coupled plasma source) are shown in Fig. 2.

### 2.1. Spark source mass spectrometry

SSMS is one of the oldest mass spectrometric techniques [39,40,92]. In the spark ion source a spark plasma is generated between two pin-shaped electrodes of sample material. The sample material is evaporated, atomized, and ionized by electron impact processes in the spark plasma. The relatively high initial energy of ions formed in the spark plasma (some keV) requires the application of a double focusing mass spectrometer (e.g. with Mattauch-Herzog geometry, a combination of electric sector and magnetic sector fields) that is advantageous for the sensitive and simultaneous detection of nearly all elements in one mass spectrum. For ion detection, spark source mass spectrometry uses an ion-sensitive photoplate that integrates the ion beams separated according to their mass to charge ratio. So far the photoplate is the best data storage for ion currents of all elements (isotopes) of the periodic table. Because of the great experimental effort involved in SSMS, no mass spectrometers with a spark ion source are being constructed at the present time.

There are only a few laboratories worldwide that still work with old spark source mass spectrometers constructed in the 1960s and 1970s. At that time SSMS was successfully used for the multielement trace analysis of electrically conducting materials, semiconducting compact materials, and nonconducting samples. Nonconducting samples (their main application in the past was in geological and material research) were analyzed by SSMS after powdering, mixing with a conducting powder (e.g. high-purity graphite or silver), homogenizing, and pressing of two electrodes. For the quantification of the analytical results of solid mass spectrometric techniques, experimentally determined relative sensitivity coefficients [ $RSC$  of a chemical element = ratio of measured (experimental) to certified (true) element concentra-

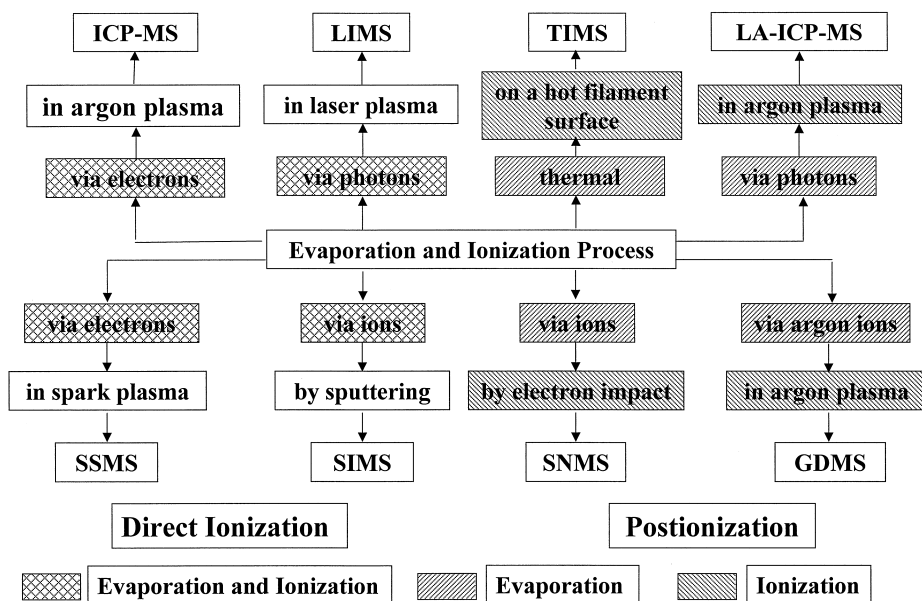


Fig. 1. Mass spectrometric techniques and their classification in respect to evaporation and ionization processes.

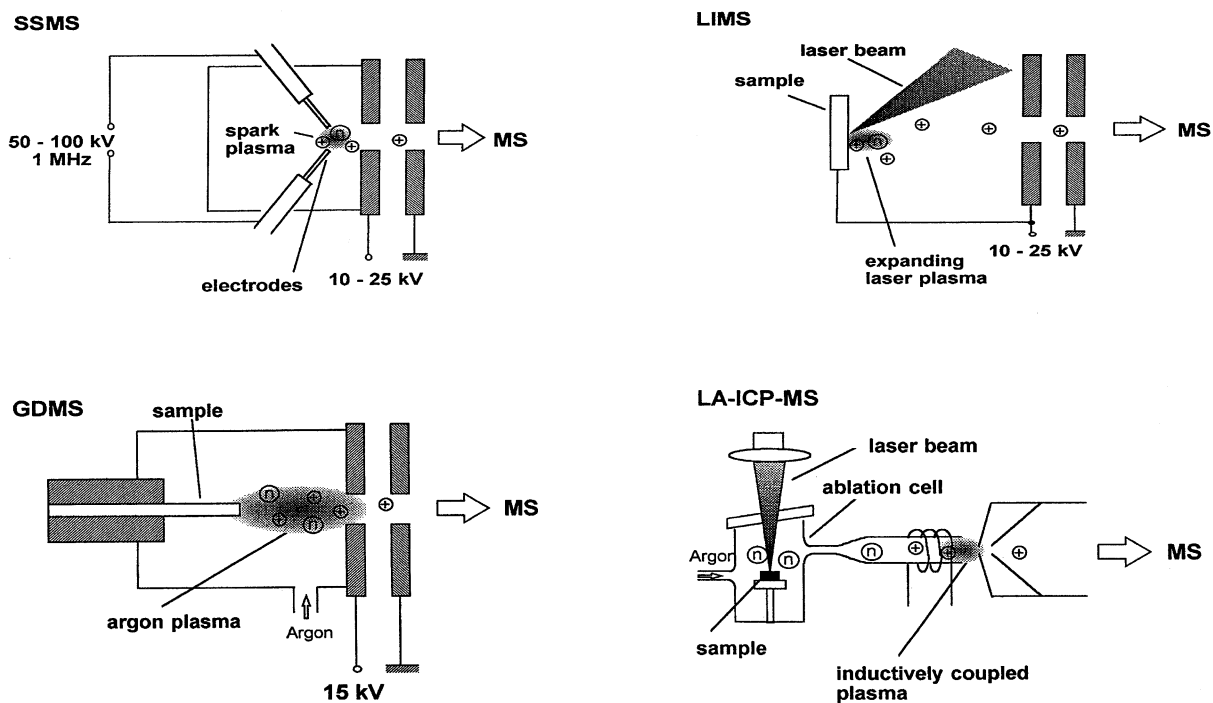


Fig. 2. Schematics of spark ion source, glow discharge ion source, laser ion source, and laser ablation inductively coupled plasma source.

tion in a given matrix] were applied using a standard reference material (SRM) or matrix-matched laboratory standards. Whereas the absolute detection limits of elements in SSMS are in the 0.01–1 ng range, the relative detection limits of elements varied between 1 and 100 ng g<sup>-1</sup>.

A development in SSMS was achieved by Jochum et al. [42,93] using the multi-ion counting (MC) technique with 20 separated Channeltrons 1.8 mm wide for simultaneous electrical ion detection. The sensitivity was increased, compared SSMS, with ion detection using a photoplate by a factor of 20 and the precision of the analytical results was improved. Multi-ion counting SSMS has been applied for trace element determination in homogeneous geological standard reference materials that were prepared by direct fusion of rock samples [94]. The precision of analytical results—which are in good agreement with the reference values—ranges from 2–7%. Using isotope dilution [95] in SSMS with photographic ion detection a precision of 3–10% relative standard deviation (RSD) could be achieved [96] but this technique (preparation of homogeneous conducting electrodes that are spiked with high enriched isotopes) is time consuming and expensive for multielement determination.

Recently, the development of SSMS for the trace analysis of nonconducting single crystals by so-called gliding SSMS (GSSMS) using a special experimental arrangement with a tantalum counterelectrode was proposed by Saprykin et al. [97]. GSSMS allows the direct analysis of glasses and high-purity nonconducting single crystals (e.g. CaF<sub>2</sub>) without any sample preparation. Of course GSSMS is an exotic analytical technique that requires a double focusing sector field spark source mass spectrometer, but possible contamination that occurs in ICP-MS during the dissolution and matrix separation can be avoided.

SSMS was one of the dominant mass spectrometric methods in the trace analysis of high-purity metals, semiconductors, ceramics, and geological samples about 20–30 years ago. However, even at that time SSMS was replaced by GDMS for direct trace analysis on solid samples.

## 2.2. Glow discharge mass spectrometry

At present, GDMS [54–59] is one of the most powerful solid state analytical methods for the direct determination of trace impurities and depth profiling of solids. In comparison to SSMS, glow discharge mass spectrometers—which are commercially produced with a fast and sensitive electrical ion detection at present—allow direct trace element determination in solid materials with more sensitivity and precision in the concentration range lower than ng g<sup>-1</sup> [2].

The glow discharge (see Fig. 2) is a low energy plasma ion source that works at a low pressure of 0.1–10 Torr (mostly using argon as the plasma gas). The Ar<sup>+</sup> ions formed in the glow discharge are accelerated toward the sample cathode and the sample material is sputtered at the cathode surface by ion bombardment. Sputtered atoms and molecules are ionized in the glow discharge plasma (“negative glow”) by Penning and/or electron impact ionization and charge exchange processes. A mathematic modeling of processes in a direct current (dc) glow discharge, which is still the most widely used source in this mass spectrometric technique, is described by Bogaerts and Gijbels [98]. The positively charged ions formed in the argon plasma of the glow discharge source are extracted and accelerated into the double focusing sector field, quadrupole, ion trap, or TOF mass spectrometer, where the ion beams are separated according to their energy-to-charge and mass-to-charge ratio. The separated ions are electrically detected by the photomultiplier or Channeltron.

One of the commercial glow discharge mass spectrometers is the double focusing sector field instrument with Nier-Johnson geometry VG-9000 (VG-Elemental, Thermo Instruments) with a maximum mass resolution ( $m/\Delta m$ ) of 10 000. The capability of this glow discharge mass spectrometer, which allows the determination of trace elements in electrically conducting samples with detection limits up to the ng g<sup>-1</sup> concentration range and with a reproducibility of about  $\pm 10\%$ , has been demonstrated in different groups, e.g. by van Straaten et al. [99]. The most important application of dc GDMS is in routine analysis for multielement determination in high-purity

Table 1  
Comparison of results on high-purity GaAs by GDMS and ICP-MS [8] (concentration in ppb-at)

Element	GDMS <sup>a</sup>	ICP-MS	Element	GDMS <sup>a</sup>	ICP-MS
B	1680	1640 <sup>b</sup>	Cr	3	<5
Mg	<0.5	<1.6	Mn	<0.3	<0.5
Al	(6)	<9	Fe	<0.2	1
Si	(13)	<100	Ni	<0.7	<1
Ca	<5	<3	Zn	<1	<2
V	<0.2	<2	Sn	<1	<0.3

<sup>a</sup> GDMS-VG 9000 (Shiva Technologies Europa).

<sup>b</sup> SIMS-CAMECA 5f.

metallic and semiconducting bulk samples [100]. In Table 1 the results of the determination of trace elements in high-purity GaAs by dc GDMS and ICP-MS are compared. High detection limits for Si in GaAs measured by ICP-MS could be explained by high instrumental background (e.g. quartz torch). Ca and Al could be contaminated during the sample preparation and the determination of Cr is disturbed by isobaric interferences (e.g.  $^{40}\text{Ar}^{12}\text{C}^+$ ). Direct solid state mass spectrometric techniques have important advantages compared to ICP-MS with respect to sample preparation: no or only a few sample preparation steps are required and the contamination danger is significantly lower. Quantification of the analytical results in solid mass spectrometry proves to be difficult, especially if no suitable standard reference material (with the same matrix) is available. Therefore, in our laboratory synthetic matrix matched multielement laboratory standards, e.g. for GaAs [8], were prepared for different analytical tasks. For the determination of trace impurities in perovskite layers ( $\text{La}_{0.65}\text{Sr}_{0.3}\text{MnO}_3$ ) for the solid oxide fuel cell by rf GDMS and LA-ICP-MS, laboratory standards were synthesized from high-purity compounds doped with trace elements in the 20–500  $\mu\text{g g}^{-1}$  range [18]. But the proposed preparation of synthetic laboratory standards and their characterization in connection with the quantification procedure is often the time-consuming step in solid mass spectrometry.

Nonconducting bulk materials are not easy to analyze by dc GDMS due to charging-up effects on the sample cathode surface. In order to increase the application field for dc GDMS, especially for the

characterization of nonconductors with respect to trace impurities, a further development was introduced, e.g. by the application of the secondary cathode technique [101,102] that produces a thin conducting layer on the sample surface during sputtering with  $\text{Ar}^+$  ions of plasma gas. The application of a conducting binder that is mixed with the nonconducting powdered sample before the pressing of the homogeneous mixture to an electrode—similar to the technique applied in SSMS for the analysis of nonconducting powders—is generally used in dc GDMS as well. Both techniques for the analysis of nonconductors by dc GDMS have significant disadvantages. First, the formation of new disturbing molecular ions (e.g. argides or oxides, etc. of secondary cathode or binder material) in mass spectra is observed. Second, the sample surface is contaminated by secondary cathode material of the detection limit increases by the dilution of the powdered sample by the conducting binder. The latter is further connected with possible contamination during the preparation of mixed electrode as well. In order to avoid these difficulties in dc GDMS rf (radio frequency) GDMS was developed as the direct solid state analytical method for compact insulators without any restriction [12,18,54,57,58,80,103–109]. The rf glow discharge ion sources developed in our laboratory were coupled with commercial double focusing mass spectrometers (Nier-Johnson geometry) [80] and with Mattauch-Herzog geometry [12,18]. An experimental arrangement of an rf GD mass spectrometer using the commercial double focusing sector field mass spectrometer with reverse Nier-Johnson geometry (ELEMENT, Finnigan MAT, Bremen), originally with an inductively coupled plasma source, is shown in Fig. 3 [80]. Using this mass spectrometer, analytical measurements at mass resolution  $m/\Delta m = 300, 3000, \text{ and } 10\,000$  are possible. That means a lot of possible interferences of analyte and molecular ions, which were observed in rf GDMS, can be separated at higher mass resolution. The detection limit of rf GDMS in the low resolution mode ( $m/\Delta m = 300$ ) was determined, e.g. for B in high-ohmic GaAs as 10  $\text{ng g}^{-1}$ . Unfortunately, the contamination of the mass spectrometer by GDMS is significantly higher due to significantly higher ion beam current

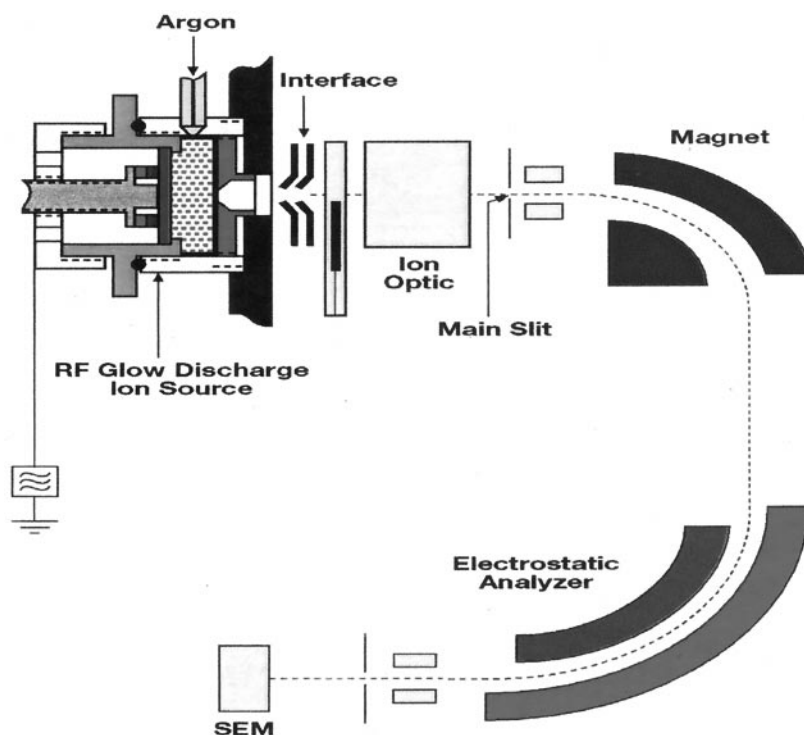


Fig. 3. Rf glow discharge mass spectrometer with reverse Nier-Johnson geometry [80].

compared to ICP-MS and even to LA-ICP-MS; strong memory effects were also observed. So far an ultra-trace analysis in aqueous solution after GDMS is only possible after time-consuming cleaning procedures (including the ion optical lens system). In comparison, the detection limits in rf GDMS using the Mattauch-Herzog instrument with photoplate and electrical ion detection, which was used for systematic investigations of fundamental processes in an rf glow discharge, were determined on different nonconducting ceramics to be in the low  $\mu\text{g g}^{-1}$  range [109]. Studies of ion intensities and energy distributions of atomic ions of analyte, plasma gas ions, residue gas ions, and molecular ions (argides, hydrides, oxides, and others) formed in the glow discharge were performed in order to optimize the trace element analysis in semiconducting and nonconducting materials with the rf GDMS and magnetron rf GDMS [105]. By utilizing an additional magnetic field located behind the flat sample—magnetic enhanced rf GDMS (rf MGDMS)—

the atomization and ionization efficiency was enhanced and the formation of plasma gas ions, residue gas ions, and molecular and cluster ions significantly reduced [105]. Due to the fast development of the more sensitive LA-ICP-MS for analysis of nonconducting materials rf GDMS lost its importance in analytical chemistry.

As a surface analytical technique GDMS can be used for the determination of element concentrations as a function of sputtered depth. But with respect to depth profiling of thin layers using dc GDMS with depth resolution between 50 and 500 nm this technique has a subordinated role compared to the commercially available and cheaper GD-OES (optical emission spectrometry). Furthermore, the capability of alternative mass spectrometric surface analytical techniques (e.g. SIMS and SNMS), which in contrast to GDMS possess the analytical possibility of determination of lateral element distribution, is some orders of magnitude better with respect to depth

resolution. Different applications for the depth profiling of thick nonconducting oxide layers and different multilayer systems using rf GDMS were discussed in [108] and [109].

Unfortunately, due to the more complex and expensive experimental arrangement of an rf GD ion source there is a lack of commercial rf GD mass spectrometers that has limited the spread of this powerful technique. Because lower detection limits (especially in the higher mass range for trace element determination on nonconducting solid samples) are achievable with LA-ICP-MS, rf GDMS as been replaced by this more powerful and universal laser mass spectrometric technique.

### 2.3. Laser-induced mass spectrometric techniques

Lasers are widely used in mass spectrometry as a universal tool for the evaporation and ionization of any solid material (without any restriction with respect to the solid sample material) since the development of the first solid state lasers [39,40]. The most important laser-induced techniques in inorganic mass spectrometry are laser ionization mass spectrometry (LIMS), resonance ionization mass spectrometry (RIMS) and recently the laser ablation ICP-MS (LA-ICP-MS). LIMS is based on the ionization of evaporated and atomized sample material in a laser microplasma under high vacuum conditions (see Fig. 2) and the separation of ion beams requires mass spectrometers with a mass resolution of  $m/\Delta m > 1000$ . In contrast, LA-ICP-MS uses the evaporation of sample material by a laser beam in an argon atmosphere under normal pressure. The ablated sample material is transported with an argon gas stream in an inductively coupled plasma and ionized in an argon plasma. Positively charged ions were analyzed using a double focusing sector field, quadrupole, or TOF instruments. LA-ICP-MS has been gaining increasing importance for the sensitive trace analysis of solid samples in recent years and will replace dc GDMS because a direct analysis of insulators is possible.

In RIMS\* [45–47] one or more lasers are tuned precisely to the wavelength required for the excited states and ionization of evaporated atoms in order to get a highly selective ionization of analyte. RIMS provides ultra-high isotopic selectivity and sensitivity with detection limits up to  $10^6$  atoms per sample. The different excitation processes and recent developments of RIMS, especially for the ultratrace determination of long-lived radioisotopes in environmental, biomedical and technical samples, are reported in [47].

Obviously, the application of a high vacuum ion source in LIMS and RIMS is a great advantage, e.g. for reducing the formation of disturbing molecular ions, but these mass spectrometric trace analytical techniques are rarely used worldwide because of the very expensive experimental arrangement. LIMS has been replaced by LA-ICP-MS. RIMS will be important in ultrasensitive trace analysis and isotope ratio measurements of long-lived radionuclides in the future if cheaper tuneable diode lasers are applied.

Again, LA-ICP-MS is in comparison to other discussed methods (in spite of the disadvantage of a higher molecular ion formation rate in the ICP) the promising solid state mass spectrometric technique of the future. Many studies are underway at present to solve the interference problems of molecular and atomic ions, e.g. by the application of higher mass resolution in double-focusing sector field mass spectrometry for the separation of isobaric interferences that result in significantly higher detection limits of elements or by the application of a collision cell in ICP-MS in order to dissociate the molecular ionic species. The experimental arrangement of LA-ICP-MS using a noncommercial laser ablation chamber coupled to the commercial double-focusing ICP-MS “ELEMENT” (Finnigan MAT, Bremen) or a quadrupole-based ICP-MS is shown in Fig. 4.

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\* RIMS and accelerator mass spectrometry (AMS), as highly selective and ultrasensitive mass spectrometric techniques for ultratrace analysis and the determination of isotopic ratios and as extremely expensive mass spectrometric methods, only play a subordinate role in ultratrace analysis. These inorganic mass spectrometric techniques and their applications are discussed elsewhere [47,126,127].



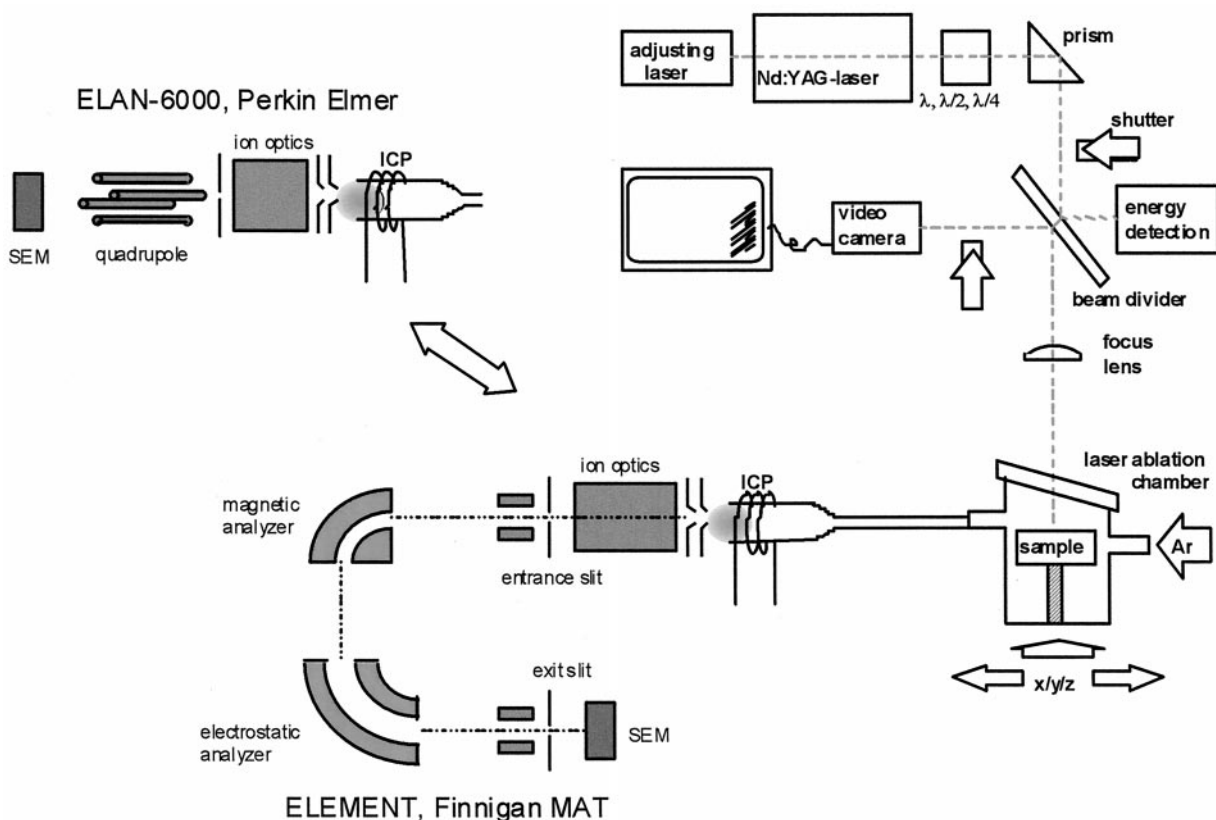


Fig. 4. Experimental arrangement of LA-ICP-MS using a double-focusing sector field mass spectrometer or quadrupole ICP-MS, respectively.

LA-ICP-MS is able to characterize unknown samples rapidly (much faster than by SSMS, GDMS, and LIMS) with respect to their major, minor, and trace element composition. Without any quantification procedure LA-ICP-MS yielded semiquantitative results with an error factor of concentration 2 to 3. One of the important problems in trace analysis by LA-ICP-MS—by analogy with the other mentioned solid mass spectrometric techniques—is the quantification of analytical results that requires standard reference materials with a similar matrix composition. For the most important application field of LA-ICP-MS (geological research) many different suitable geological and glass standard reference materials are available. Using standard reference materials in LA-ICP-MS analytical results for trace analysis were obtained with an accuracy of better than 10% and a precision of 2–5% is also possible. This is demonstrated by LA-ICP-MS

measurements [a commercial laser ablation system (CETAC LSX 200) was coupled to the quadrupole-based Elan 6000 (Perkin Elmer, Sciex)] on geological glass reference standards in our laboratory. Table 2 compares the results of trace element determination by LA-ICP-MS [110] that are in good agreement with the reference values [111]. The quantification of analytical results was performed via the determination of RSCs using the SRM BCR2-G. If no SRM is available—appropriate for all solid state mass spectrometric techniques—the preparation of synthetic (matrix-matched) solid standard samples is performed from the compounds of the matrix elements doped with trace impurities in given concentrations [8,50,112].

Furthermore, due to a lack of suitable SRM, different calibration techniques using aqueous standard solutions are proposed. Houk and associates

Table 2

Results of LA-ICP-MS on glass geological standard (basalt KL2 from the Kilauea d volcano, Hawaii) in comparison to reference value [111] (concentration in  $\mu\text{g/g}$ )

Element	Measured value	Reference value
Cr	286 $\pm$ 4	300 <sup>b</sup>
Co	43.0 $\pm$ 1.1	42 <sup>a</sup>
Zn	120 $\pm$ 27	111 <sup>b</sup>
Cu	104 $\pm$ 5	104 <sup>b</sup>
Ga	19.4 $\pm$ 0.4	19 <sup>b</sup>
Rb	8.6 $\pm$ 0.3	9.4 <sup>b</sup>
Y	26.4 $\pm$ 1.0	26.9 <sup>b</sup>
Zr	158 $\pm$ 6	159 <sup>b</sup>
Nb	15.1 $\pm$ 0.6	16.2 <sup>b</sup>
Sn	1.98 $\pm$ 0.24	1.6 <sup>c</sup>
Cs	0.10 $\pm$ 0.02	0.12 <sup>b</sup>
Ba	117 $\pm$ 6	126 <sup>a</sup>
La	12.5 $\pm$ 0.6	13.2 <sup>a</sup>
Pr	4.50 $\pm$ 0.21	4.62 <sup>a</sup>
Nd	21.1 $\pm$ 0.9	22.1 <sup>b</sup>
Sm	5.54 $\pm$ 0.30	5.63 <sup>a</sup>
Eu	1.92 $\pm$ 0.11	1.96 <sup>b</sup>
Gd	5.91 $\pm$ 0.32	5.97 <sup>a</sup>
Tb	0.96 $\pm$ 0.05	0.96 <sup>b</sup>
Dy	5.22 $\pm$ 0.34	5.33 <sup>b</sup>
Ho	1.00 $\pm$ 0.08	0.988 <sup>a</sup>
Er	2.44 $\pm$ 0.15	2.65 <sup>a</sup>
Tm	0.33 $\pm$ 0.01	0.33 <sup>a</sup>
Yb	2.05 $\pm$ 0.21	2.11 <sup>a</sup>
Lu	0.26 $\pm$ 0.04	0.294 <sup>b</sup>
Hf	4.03 $\pm$ 0.37	4.12 <sup>a</sup>
Ta	0.95 $\pm$ 0.05	0.955 <sup>a</sup>
Th	0.93 $\pm$ 0.07	1.08 <sup>b</sup>
U	0.54 $\pm$ 0.04	0.557 <sup>b</sup>

<sup>a</sup> RSD <5%.

<sup>b</sup> RSD 5–15%.

<sup>c</sup> RSD >15%.

[113] described a general procedure for uniting the ease of calibration of solution methods with laser ablation for the direct analysis of solids by combining dry aerosol particles from both sources in an inductively coupled plasma. This technique, using solution standards to calibrate the response of LA-ICP-MS, does not require the knowledge of an internal standard element. One problem for quantification using standard solution could be in the different evaporation rate of analytes in solid sample and in solution. Calibration using the tandem introduction of dried solution aerosols with laser-ablated particles in ICP-MS, proposed by Günther [114] and Krause [115], requires

the knowledge of an internal standard at known concentrations.

An important application field for LA-ICP-MS is the micro-local analysis of solid samples with lateral resolution of a few  $\mu\text{m}$ , especially in geological research. The lateral resolution depends strongly on the focused laser beam, laser power density, and properties of the solid sample. Campbell and Humayun [116] studied the trace element distribution in iron meteorites with a lateral resolution of 10–20  $\mu\text{m}$  by LA-ICP-MS using the CETAC LSX 200 coupled to the double focusing ICP-MS ELEMENT, Finnigan MAT. Concentration profiles of Ru, Rh, and Pd across and iron meteorite surface (linescan of 1.3 mm length) and concentration profiles for Cu, Rh, Pd, W, Re, Os, Ir, and Pt at a depth of  $\sim 30 \mu\text{m}$  are measured using this powerful surface analytical technique.

In order to study the applicability of LA-ICP-MS for depth profiling on thick nonconducting layers, a multilayer system consisting of  $\text{La}_{0.65}\text{Sr}_{0.3}\text{MnO}_3$  and Ni-cermet deposited on yttria-stabilized zirconia by plasma deposition (as demonstrated in Fig. 5) with a total layer thickness of 127  $\mu\text{m}$  [112], was investigated. Such ceramic layered material is relevant for the solid oxide fuel cell. The depth profiles for selected matrix elements via measurement of the ion intensities  $^{139}\text{La}^+$ ,  $^{89}\text{Y}^+$ ,  $^{60}\text{Ni}^+$ ,  $^{142}\text{Ce}^+$ , and  $^{55}\text{Mn}^+$ , layer by layer as a function of depth, demonstrate the limitation of this surface analytical technique—namely an insufficient depth resolution in this experiment. The depth resolution can be improved by an optical gating (application of an aperture in order to avoid the transport of material to deeper layers, the so-called “snowplough effect” and crater wall effects). A depth resolution in the low  $\mu\text{m}$  range is achievable with LA-ICP-MS; this is sufficient especially for the characterization of thick ceramic or technical oxide layers. An advantage of LA-ICP-MS is the possibility of fast depth profiling by the scanning mode (rastering) of different layers of  $\mu\text{m}$  thickness in a few minutes.

Furthermore, LA-ICP-MS has been used for the in situ trace element analysis (Rb and Sr in the 40–150  $\mu\text{g g}^{-1}$  concentration range) of individual fluid inclusions

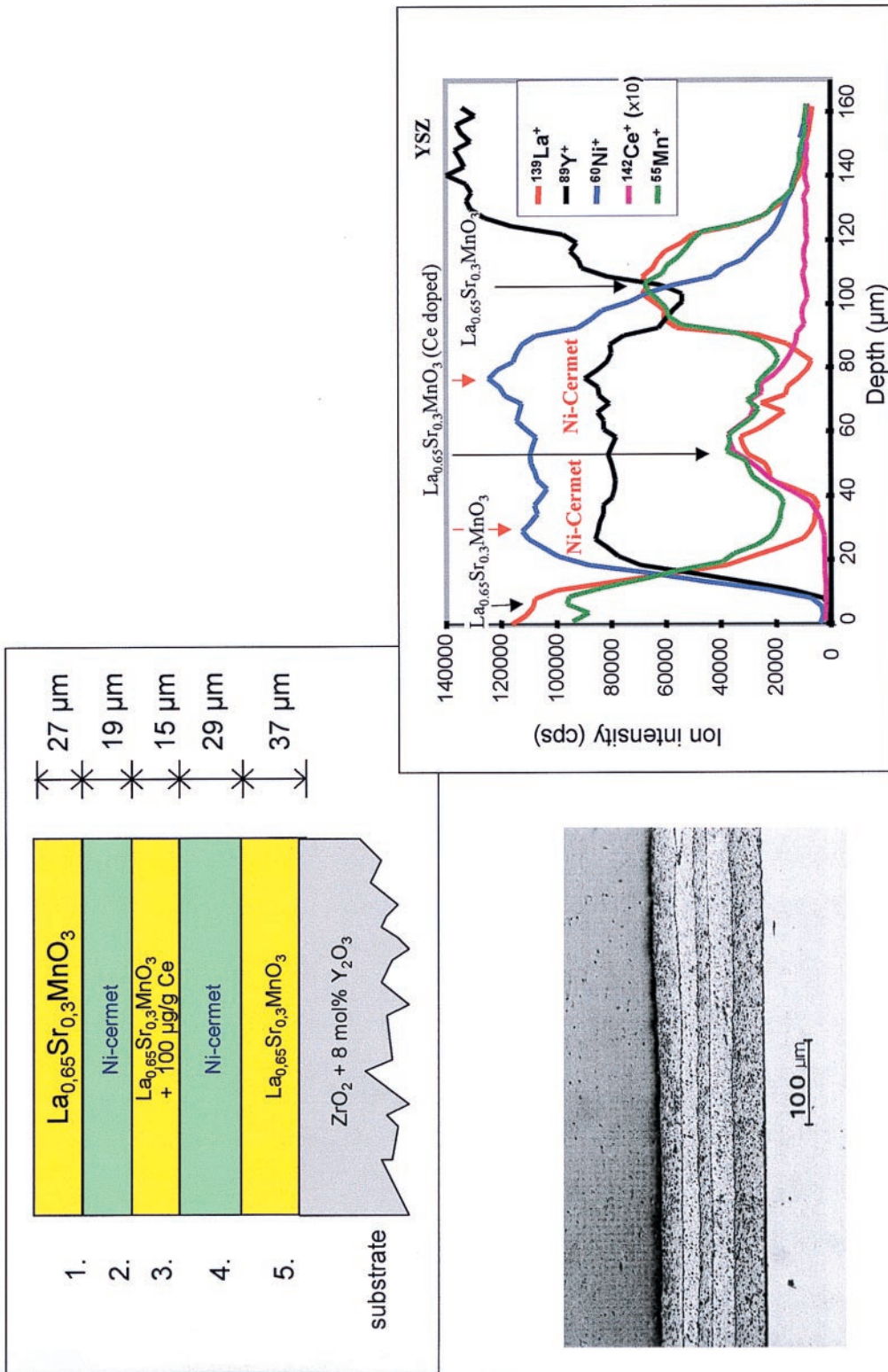


Fig. 5. Depth profiles on a ceramic multilayer system by LA-ICP-MS.

Table 3

Main features of SSMS, GDMS, LIMS, LA-ICP-MS, and SSMS

*Advantages*

Simultaneous determination of almost all trace, minor, and major elements (except noble gases)

in conducting, semiconducting, and nonconducting solid materials

Low relative detection limits: 0.001–0.1  $\mu\text{g g}^{-1}$  (absolute detection limits: 0.01–1 ng)

Small sample amount is consumed: 1–3 mg of solid material for one analysis

Precision of trace element determination: using RSC:  $\pm 5$ –20% (RSD)by isotope dilution:  $\pm 2$ –10% (RSD)*Limits*

Inhomogeneities in solid samples

Standard reference materials with similar matrix composition for quantification required!

→ Determination of relative sensitivity coefficients (RSC) or quantification via measured calibration curves.

(laser spot: 25–30  $\mu\text{m}$ ) with artificially prepared fluid inclusions as external standards by Ghazi et al. [117].

The main features of SSMS, GDMS, LIMS, and LA-ICP-MS are summarized in Table 3. Solid state mass spectrometric techniques are replaced increasingly by ICP-MS for trace, ultratrace, and isotope analysis. Table 4 compares the advantages and limits of solid state mass spectrometric techniques for the determination of trace and ultratrace impurities in high-purity materials with those of ICP-MS, which often requires matrix separation.

#### 2.4. Secondary ion mass spectrometry and sputtered neutral mass spectrometry

SIMS and SNMS are the most important mass spectrometric techniques for surface analysis, bulk and layer analysis, depth profiling, the determination

of contamination, and element distribution on a solid sample surface. The principles of both ion sources are shown in Fig. 6. In SIMS and SNMS the sample materials are sputtered by bombardment of the sample surface with a focused primary ion beam ( $\text{Ar}^+$ ,  $\text{Cs}^+$ ,  $\text{Ga}^+$ ,  $\text{O}^-$ ,  $\text{O}_2^+$ ) of sufficiently high ion energy (some keV). The implanted primary ions penetrate into the solid surface to different depths (1–10 nm) and transfer their kinetic energy as a function of their sample material, primary ion energy, and mass. Part of the transferred energy that is returned to the solid surface via impact cascades induces the sputtering of positively and negatively charged atomic and molecular ions and neutrals [118]. The latter are sputtered with the highest intensities. In SIMS the secondary positive or negative ions were analyzed, but in SNMS the secondary sputtered ions were suppressed by a

Table 4

Comparison of solid state mass spectrometric methods and ICP-MS for ultratrace analysis on high-purity solid materials

	Solid state mass spectrometric methods, e.g. SSMS, GDMS, LA-ICP-MS, SIMS	ICP-MS
Sample preparation	None or minimal	Disolution and dilution necessary (expensive if matrix separation required)
Quantification possibility	Matrix matched reference materials, required (difficult if no SRM available)	Excellent using aqueous standard solutions
Precision	For homogeneous samples: mostly <10%	Isotope dilution: 1–5%
Accuracy	Good, only if SRM available	Good
Contamination danger	Low	Enormous
Inhomogeneous sample	Difficult for bulk analysis	No problems if enough homogenized sample materials is dissolved
Time-consuming step	Quantification of analytical results if synthetic laboratory standards must be prepared	Sample preparation steps (mass separation)

SRM—Standard reference material.

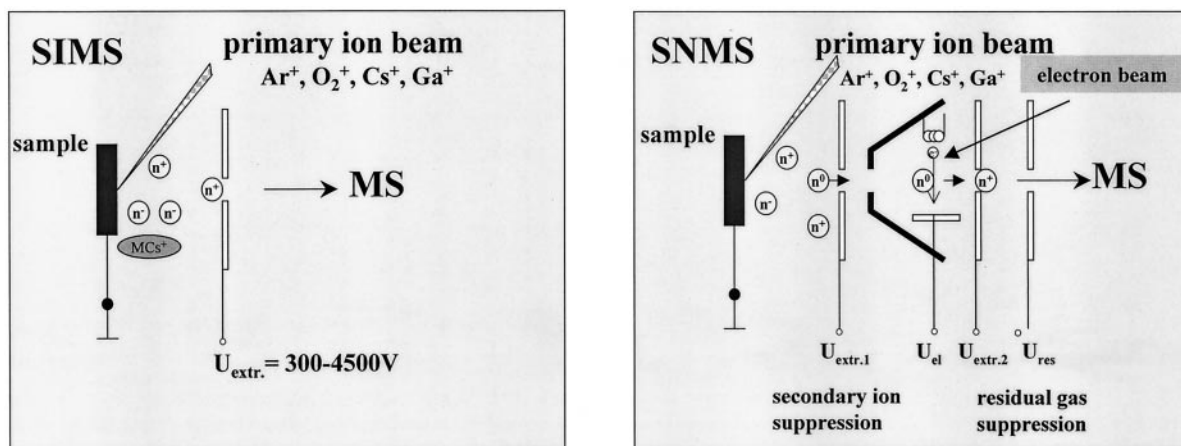


Fig. 6. Principle of secondary ion source and sputtered neutral ion source.

repeller voltage and the sputtered neutrals that were postionized either in an argon plasma (“plasma SNMS” [66,118,119]) by electron impact ionization (“e-beam SNMS” [67,68,120,121]) or laser postionization [63] are used for the surface analysis.

A few SIMS and SNMS instruments are commercially available with double focusing sector field mass spectrometers (e.g. CAMECA IMS-5f), quadrupole-based instruments (SIMSLAB, VG Elemental, and INA 3, Specs), and TOF-SIMS (CAMECA) [62].

In SIMSLAB from VG Scientific, both surface analytical techniques (SIMS and SNMS) are realized (see Fig. 7). In this instrument different types of primary ion sources are available. Ar<sup>+</sup>, Cs<sup>+</sup>, Ga<sup>+</sup>, or O<sub>2</sub><sup>+</sup> primary ions were accelerated in the ion source on the sample surface. The sputtered secondary ions (for SIMS) or the postionized sputtered neutrals (for SNMS)—the postionization is carried out by an electron beam in an ionizer box (right hand scheme in Fig. 7)—were separated after extraction in a quadrupole analyzer and detected with a single-ion Channeltron.

The main features of SIMS and SNMS with single ion collection are summarized briefly in Table 5. In order to quantify the analytical results, the measured ion intensities were corrected, in general, by the RSCs of chemical elements that were experimentally determined using standard reference materials. The RSCs varied in SIMS as a function of the primary ions used (their mass, kinetic energy, ion current, angle of

incidence, etc.) and the matrix composition by up to six orders of magnitude; that means large matrix effects do not allow a semiquantitative analysis. Due to high molecular ion formation by sputtering, even a qualitative trace analysis is difficult by a complex matrix composition of the investigated material. Important SIMS applications are the determination of implanted elements and contamination in bulk and layered metals, semiconductors, and insulators using suitable standard reference materials (e.g., from Charles Evans and Associates, Redwood City, CA). In spite of large matrix effects and a high molecular ion formation rate, SIMS is able to determine the distribution of trace or implanted elements as a function of sputter rate (which correlates with the depth) using SRM for quantification with good accuracy and precision, as demonstrated for the GaAs matrix in [8].

In contrast to SIMS, in SNMS—where the evaporation and ionization processes are decoupled—the matrix effects are significantly lower because the composition of sputtered and postionized neutrals corresponds more closely to the composition in the solid sample (compared to the sputtered secondary ions in SIMS). That means the RSCs of elements varied by about one order of magnitude and a semiquantitative analysis could be carried out because of the lack of a suitable SRM. A semiquantitative measurement in SIMS is possible by the well-established “Cs molecular ion SIMS,” that is, the application of

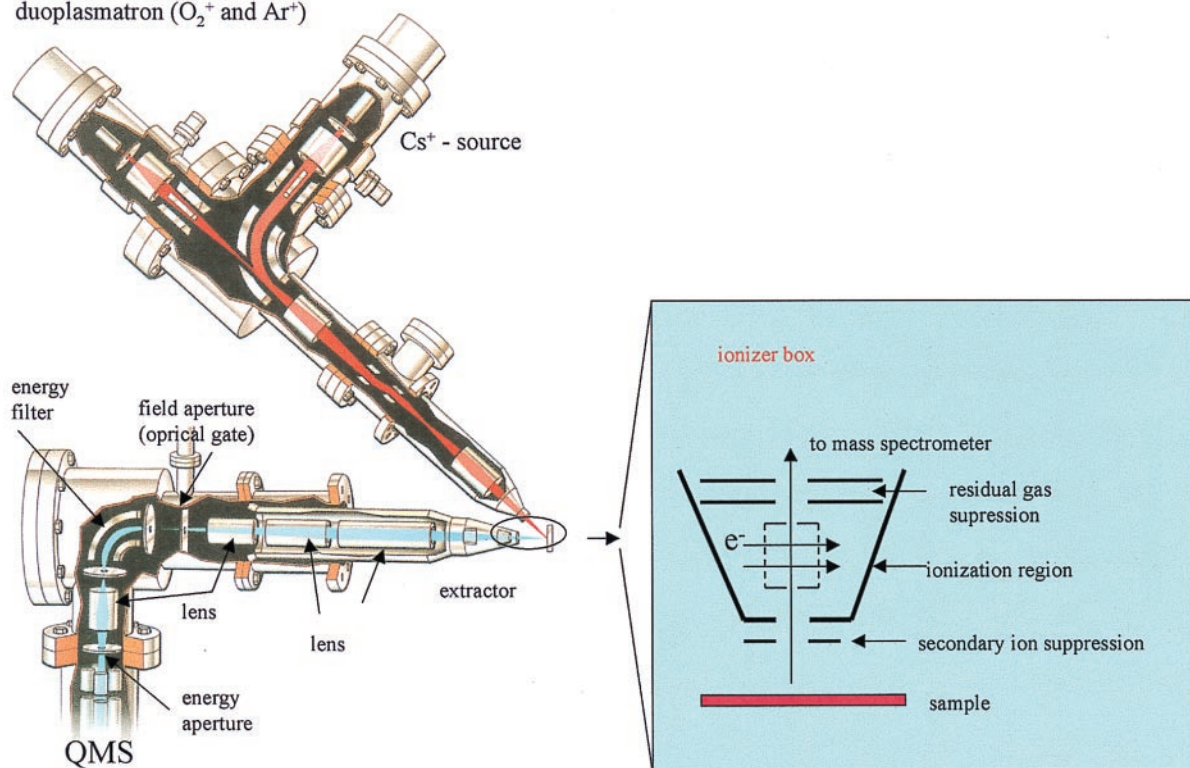
duoplasmatron ( $O_2^+$  and  $Ar^+$ )

Fig. 7. Schematic of a combined SIMS/SNMS instrument (SIMSLAB, VG Scientific).

diatomic  $MCs^+$  molecular ions ( $M$ , metal or nonmetal atom) that are formed by bombardment of a solid surface with  $Cs^+$  primary ions in SIMS. Caesium molecular ions are very suitable species because caesium is a monoisotopic and reactive element and

formed stable molecular ions. By the application of  $MCs^+$  molecular ions, measured at a mass that is 133 u higher than the mass of  $M^+$ , it was possible to avoid interferences that are observed at the mass of analyte ion  $M^+$ . It is advantageous for analytical

Table 5  
Main features of SIMS and SNMS

	SIMS	SNMS
Evaporation Ionization	Using primary ions: $Ar^+$ , $Cs^+$ , $O_2^+$ , $O^-$ , $Ga^+$	Using primary ions: $Ar^+$ , $Cs^+$ , $O_2^+$ , $Ga^+$ Post ionization of neutrals: plasma, e-beam, laser (resonant, nonresonant)
Detection limit	$0.001-1 \mu g g^{-1}$	$10-100 \mu g g^{-1}$
RSC	$10^2-10^6$	0.3-3
Calibration	10-20% RSD <sup>a</sup>	10-20%, RSD <sup>a</sup>
Depth resolution	<5 nm	<5 nm
Lateral resolution	1-5 $\mu m$	1-5 $\mu m$
Applications	Depth profiling, imaging, trace analysis	Depth profiling, imaging
Instruments	CAMECA IMS 6f, TOF-SIMS	SIMSLAB (VG Scientific), INA 3 (Specs)

<sup>a</sup> Using implantation standards.

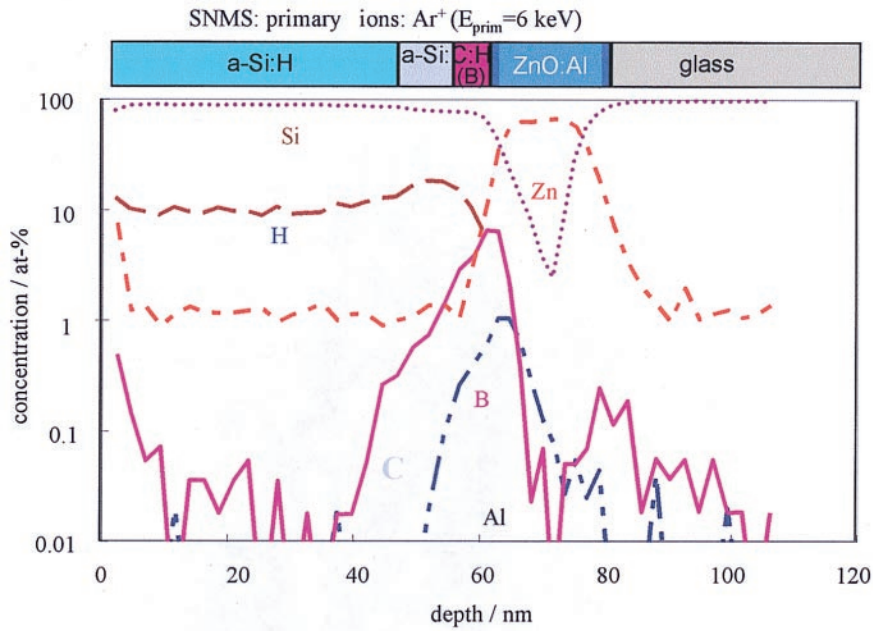
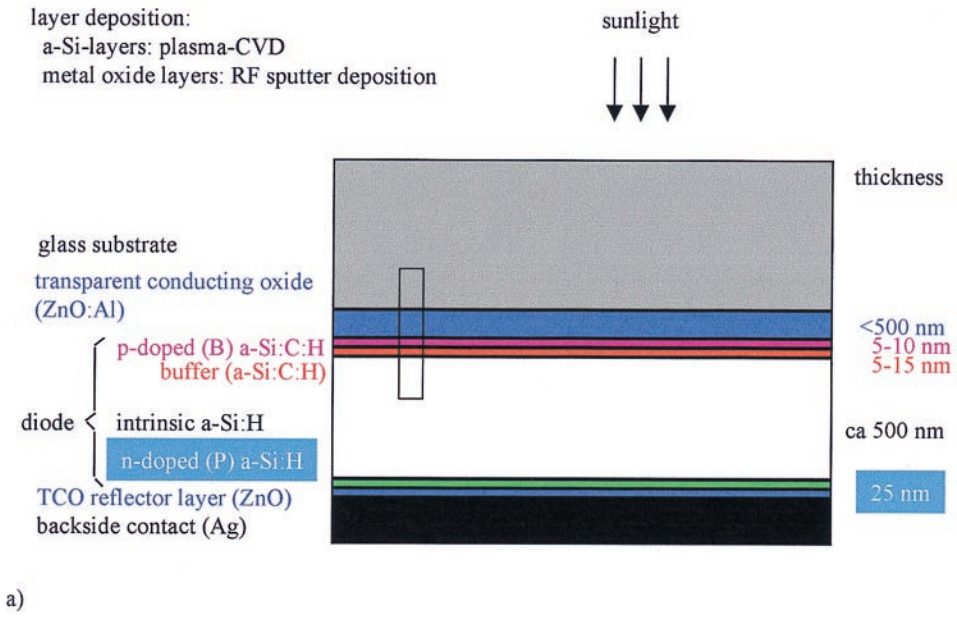


Fig. 8. Schematic of solar cell structure (a) and depth profile of a part of solar cell marked above using SNMS (b).

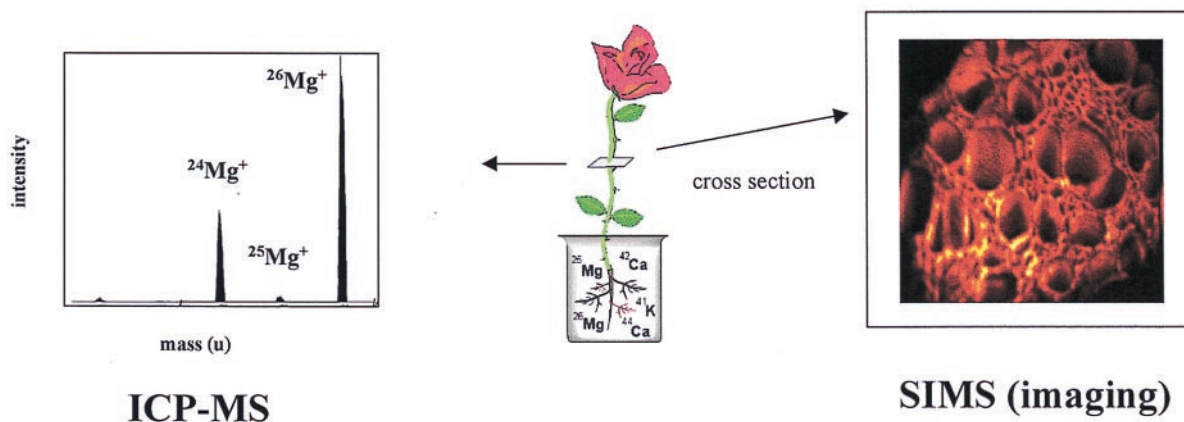


Fig. 9. Tracer experiments for investigation of transport phenomena in plants.

purposes that the formation of these  $\text{MCs}^+$  molecular ions in SIMS is less dependent on a matrix [122]. This technique is widely applied for bulk analysis and depth profiling in the routine mode.

The capability of both these surface analytical techniques is demonstrated in the following two examples. The most important application field of SIMS and SNMS is depth profile analysis. Fig. 8 demonstrates the depth profile by SNMS on part of a thin film layered structure on a glass substrate of a solar cell based on amorphous silicon (see schematic of a solar cell structure, Fig. 8, top) [65]. In spite of

the complicated thin layered structure of amorphous silicon layers doped with H, C and H, C, H, and B, respectively, with thickness in the 5–500 nm range, SNMS allows a quantitative depth profiling (using model layers for the determination of relative sensitivity factors) with a depth resolution of a few nm.

A finely focused primary ion beam can be used for sputtering of the solid surface to determine the lateral element distribution. In order to investigate the distribution and transport of mineral elements in plants in tracer experiments the aqueous nutrient solution was doped

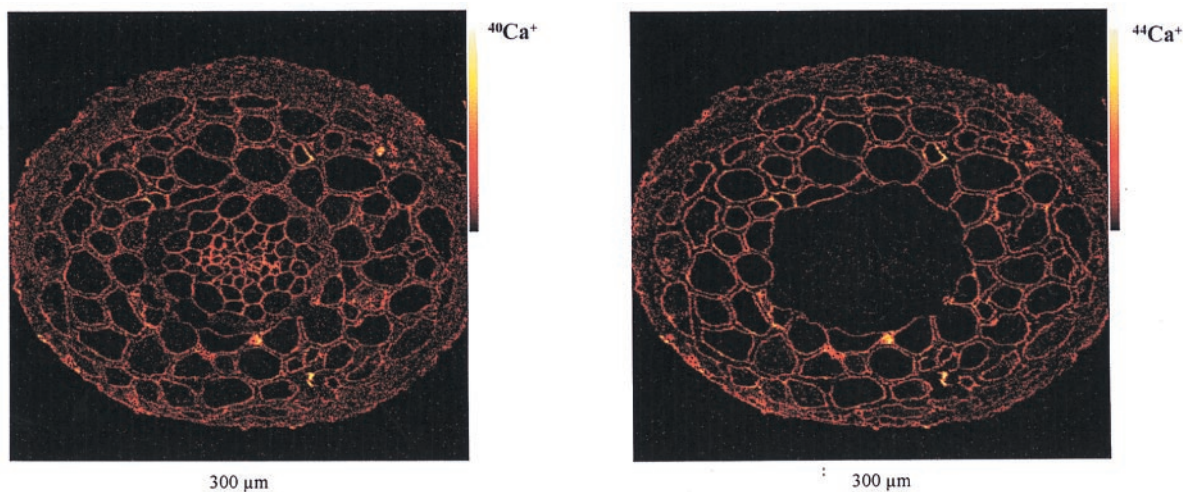


Fig. 10. SIMS imaging of  $^{40}\text{Ca}^+$  and doped  $^{44}\text{Ca}^+$  of a cross section of a root from a Norway spruce.



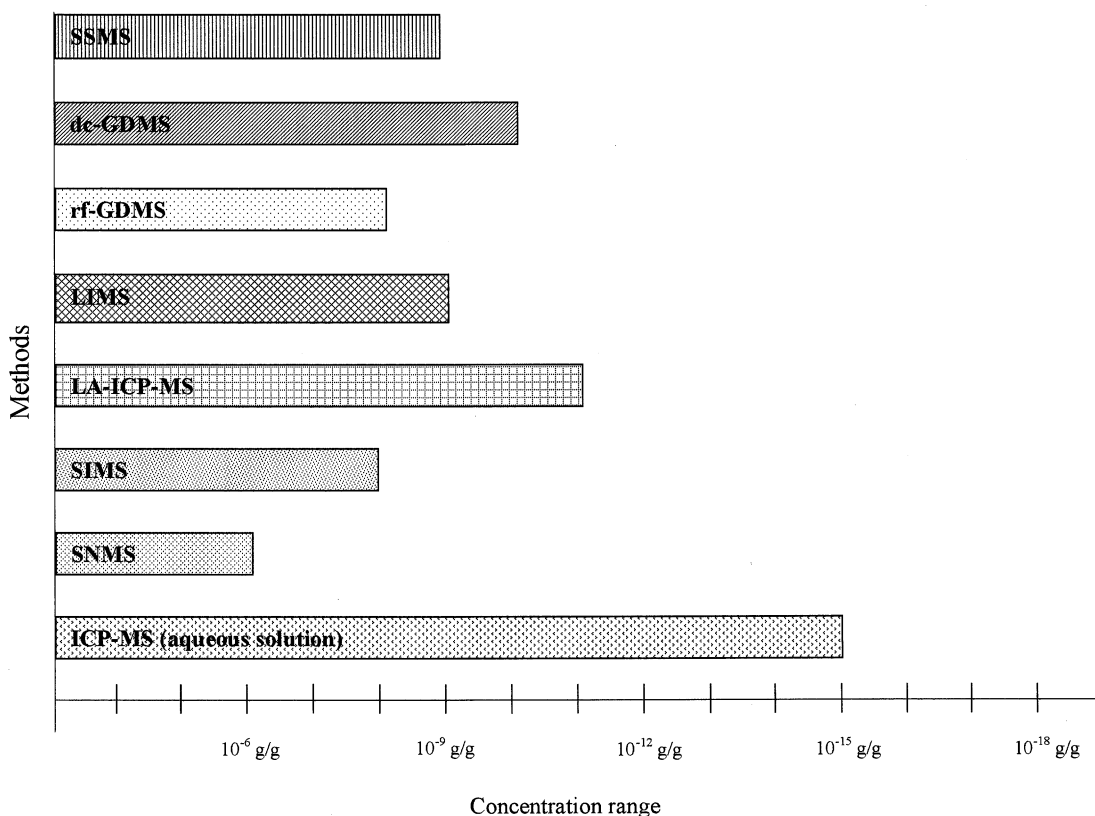


Fig. 11. Detection limits in inorganic mass spectrometry.

with highly enriched stable isotopes  $^{25}\text{Mg}$ ,  $^{26}\text{Mg}$ ,  $^{42}\text{Ca}$ ,  $^{44}\text{Ca}$ , and  $^{41}\text{K}$  (see Fig. 9). Whereas the lateral distribution of the highly enriched doped isotopes in a cross section of part of the plant was measured using the SIMS ion microscope mode (isotope ratio measurements are performed as well), the precise isotope ratios and the element concentrations (using the reverse isotope dilution technique) in nutrient solution taken from parts of the plant were determined by ICP-MS [71].

Figure 10 compares the isotope distribution of natural  $^{40}\text{Ca}$  and doped  $^{44}\text{Ca}$  in a cross section of a root of a Norway spruce. These measurements, carried out by SIMS using  $^{69}\text{Ga}^+$  primary ions (10 keV, 0.1 nA, Ionoptika) with a lateral resolution  $<0.1 \mu\text{m}$ , can be used to study the mechanism of mineral element uptake and kinetics of transport processes in plants as a function of time. About 20 min after the start of the tracer experiment a barrier was observed

for the transport of highly enriched isotopes in the middle of the root [123].

With respect to isotope analysis, SIMS and SNMS with single-ion collectors are well suited for precise isotope ratio determination, as demonstrated by the characterization of the highly enriched  $^{187}\text{Os}$  sample in comparison to ICP-MS in our laboratory [124].

Double focusing sector field mass spectrometers with multi-ion collector SIMS IMS 1270 and NANO-SIMS 50 for precise isotope ratio measurements and simultaneous multicollection imaging for very small samples are now available from CAMECA.

In Fig. 11 the detection limits of inorganic state mass spectrometric techniques are compared. The lowest detection limits were observed in ICP-MS on high-purity aqueous solutions. The detection limits in ICP-MS on solid samples are some order of magnitude higher considering the dilution factor of digested sample, the

## Fields of Application in Inorganic Mass Spectrometry

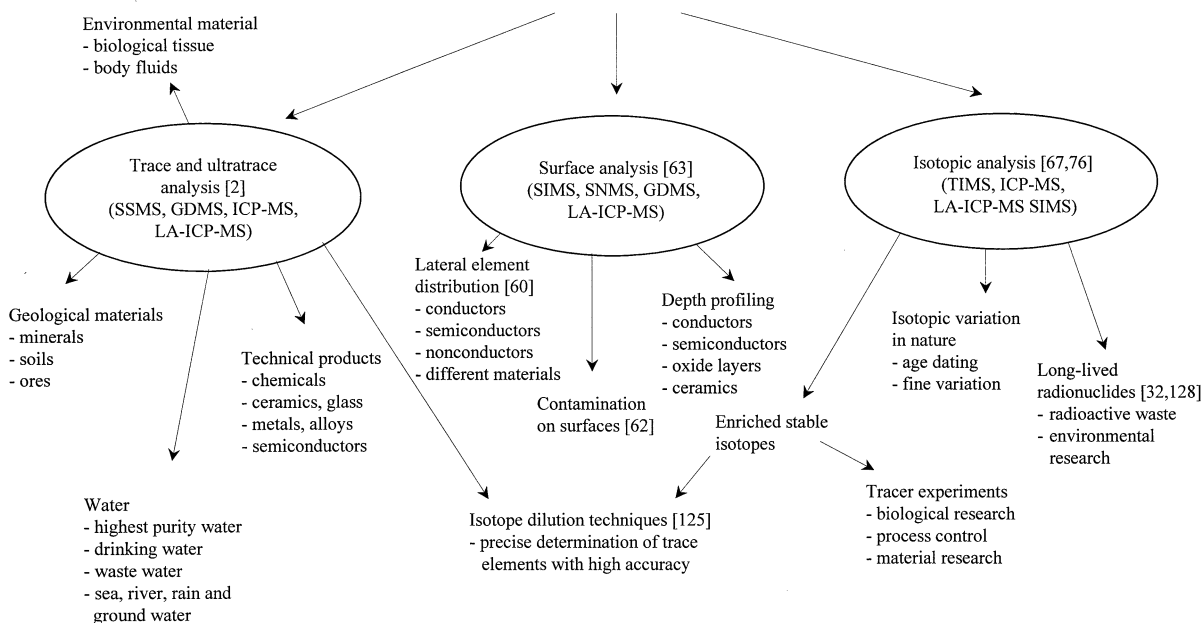


Fig. 12. Fields of application in inorganic mass spectrometry.

blank values of chemical used, and possible interferences with molecular ions. The fields of application in inorganic mass spectrometry are summarized in Fig. 12.

### 2.5. Thermal ionization mass spectrometry

Thermal ionization mass spectrometry is a well recognized analytical technique for the precise and accurate measurement of isotopic ratios for different elements with a precision of better than 0.01% [67]. In TIMS a small volume (1–10  $\mu\text{L}$ ) of aqueous sample solution, which contains some ng to  $\mu\text{g}$  of the analyte to be analyzed, is deposited on a cleaned filament surface (e.g. high-purity Re) and evaporated to dryness. The most frequently applied technique in TIMS works with two filaments arranged opposite each other. One of the filaments is used for the evaporation of the sample by thermal heating and the other for ionization of evaporated atoms and molecules on the hot filament surface. Ions formed by thermal ionization possess low initial energies (0.1–0.2 eV), therefore mostly single magnetic sector field mass spec-

trometers were used for ion separation. At present, two magnetic sector field instruments (e.g. MAT 262, Finnigan MAT, Germany or Sector 54 from Micromass, UK) are commercially available on the analytical market. Instruments with a multiple collector are important for precise isotope analysis.

Mass discrimination in the instrument (e.g. ion optical system or ion detector) and mass fractionation effects (caused during the evaporation of the sample, where the measured isotope ratio changes with time) are limiting factors for the accuracy of measured isotopic ratios in TIMS [68]. Different effects could be considered by different internal calibration or by using isotopic standards (e.g. from the National Institute of Standards and Technology, Gaithersburg, MD or the Institute of Reference Materials and Measurements, Geel, Belgium) with well-known isotopic ratios of an element of interest.

The capability of TIMS in precise isotopic ratio measurements (as the major application field of this analytical technique) is used in accurate trace element determination by the isotope dilution method using

highly enriched isotopic spikes. An excellent review of the isotope dilution technique using TIMS including selected applications is given by Heumann [125]. TIMS requires an often time-consuming sample preparation (digestion of solid samples and trace-matrix separation) and therefore has been replaced by the more sensitive ICP-MS in the past few years.

### 3. Inductively coupled plasma mass spectrometry

Inductively coupled plasma mass spectrometry was developed by the coupling of an inductively coupled plasma source at normal pressure with a quadrupole based mass spectrometer by Date and Gray in 1975 [128]. At present ICP-MS is the most frequently used and popular inorganic mass spectrometric technique [69] for a fast and sensitive multielement determination of elements at the trace and ultratrace concentration level and for the isotopic analysis of a wide variety of materials. This is demonstrated by the rapid growth of ICP mass spectrometer installations worldwide, such as different types of quadrupole-based or double focusing sector field instruments (e.g. from Hewlett Packard, Wilmington, DE; Perkin Elmer, Sciex, Norwalk, CT; VG Elemental, Winsford, UK; Micromass, Manchester, UK; Varian GmbH, Mulgrave, Victoria, Australia; Spectro, A. I. GmbH, Kleve, Germany; Seiko Instruments, Japan; and Finnigan MAT, Bremen, Germany) with single and multiple ion collection. Simultaneously, a rapid increase in the number of analytical publications in all fields of ICP-MS has been observed [69]. Nowadays an axial TOF-ICP-MS is available from LECO (Renaissance, LECO, St. Joseph, MI) for a faster analysis (30 000 spectra per second) than quadrupole ICP-MS. This property is advantageous for the application of coupling techniques (e.g. HPLC-, CE-, or LA-ICP-MS) and speciation analysis, and could be applied for the characterization of microsolution (droplet analysis) or geological inclusions (using single laser pulse).

In comparison to the discussed solid state mass spectrometric techniques in ICP-MS, a high elemental sensitivity and excellent low detection limits up to pg

$L^{-1}$  concentration range in aqueous solution are achieved (see Fig. 11) [2,69,129]. A schematic of a quadrupole ICP-MS (Platform ICP-MS with hexapole lens, Micromass) is shown in Fig. 13. The sample solution is transported by a peristaltic pump and nebulized in a spray chamber. The aerosol formed is transported with argon in the ICP torch, evaporated in the inductively coupled plasma (plasma temperature: 5000–8000 K), the chemical compounds were dissociated into their atomic constituents, and the neutrals were ionized at a high degree of ionization (>90% for chemical elements with an ionization potential <8 eV).

The positively charged ions that were used for the analysis are flying from argon plasma (at 760 Torr) via an interface (at  $\sim 1$  Torr) between the sampler and skimmer cones into the high vacuum of the mass analyzers, where the ions are separated according to their mass-to-charge ratio (and energy-to-charge ratio in double focusing sector field instruments) and detected by a photomultiplier. The main features of ICP-MS are given in Table 6.

An interesting advantage of ICP-MS is the very simple sample introduction at atmospheric pressure that allows different, easy-to-apply sample introduction systems for liquid, solid, and gaseous samples (gas chromatography, ICP-MS) and coupling techniques (HPLC, CE, USN, laser ablation, ETV, hydride generation, etc.). The most important sample introduction systems in ICP-MS [33,34,83,130–156] are summarized in Fig. 14. An excellent overview of sample introduction devices including the multitude of nebulizer types applied in ICP-MS is given by Montaser [69].

Considering the variety of sample introduction systems, beginning from the most frequently used pneumatic nebulizer to on-line coupling techniques, including separation of chemical elements, a multitude of different applications of ICP-MS (see Fig. 12) have been described in the literature for routine analysis as well as methodological developments. The largest application field is in environmental research (followed by geological research). In particular, ICP-MS is important for the determination of essential and toxic elements in environmental materials, where ICP-MS is used mostly as a sensitive multielement

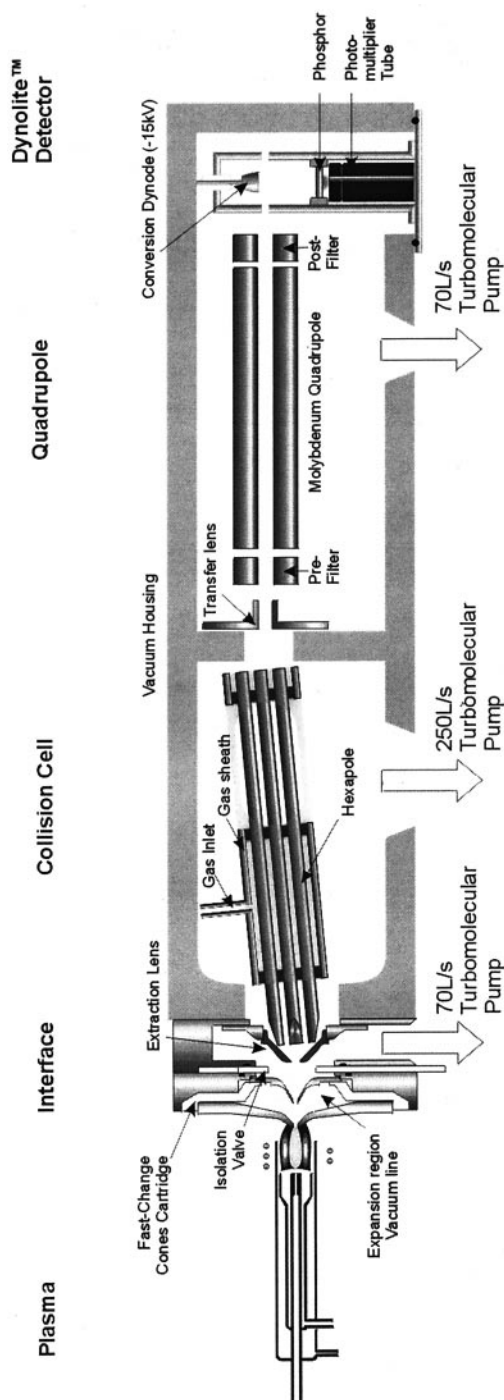


Fig. 13. Schematic of quadrupole ICP-MS platform with a hexapole lens (courtesy of Micromass).

mental trace and ultratrace analytical technique. Obviously, the main feature of ICP-MS is its multielemental capability. But, to an increasing extent, single element determination (often of difficult to analyze elements especially in the lower mass range, such as Al, Cr, Fe, As, and Se) has become the topic of research papers. Furthermore, interest is increasing in the determination of some group elements [such as the rare earth elements, actinides, or platinum group elements (PGE)], e.g. growing interest in the determination of noble metals as environmental contaminants is the result of automobile emission since the introduction of PGE-containing catalysers.

In general, methodological developments yield an improvement in the performance of ICP-MS (sensitivity, detection limits, accuracy and precision, reduction of sample sizes, etc.). Such methodological improvements of ICP-MS are also required in the semiconducting industry for routine analysis and process control (e.g. for the characterization of high-purity water, acids, organic solvents, and semiconducting materials). One of the serious problems in ICP mass spectrometry (and in the other inorganic mass spectrometric techniques also) is that a multitude of different isobaric interferences with analyte ions appear. Where the separation of isobaric interferences of atomic ions (e.g.  $^{92}\text{Zr}^+$  and  $^{92}\text{Mo}^+$  with  $m/\Delta m \approx 52\,000$ ) necessitates high resolution, Fourier transform ion cyclotron resonance mass spectrometers, are required. In practical analytical work the determination of element concentration or isotope ratio is performed via interference-free isotopes. In order to allow routine analysis if no interference-free isotopes exist, mathematical correction formulae are included in the software. Furthermore, doubly-charged atomic ions and a multitude of molecular ions can disturb the quantitative determination or isotope ratio determination of the analytes. Such interferences can often be separated using commercial double focusing sector field ICP-MS with a maximum mass resolution of 12 000. All these interferences, especially the molecular ions (e.g.  $\text{MO}_n^+$ ,  $\text{MH}_n^+$ ,  $\text{MAr}^+$ ,  $\text{MCl}^+$ ,  $\text{MN}^+$  with an M-matrix element,  $\text{Ar}_n\text{X}_m^+$  with X=H, O, N, Cl, and others) formed in an argon plasma and behind the sampler cone in ICP-MS, complicate the analysis of

Table 6  
Main features of ICP-MS

#### Advantages

Easy, rapid, and sensitive analytical technique for simultaneous determination of almost all matrix, minor trace, and ultratrace elements (except noble gases) in aqueous solution with high dynamic range  $10^8$   
 Excellent sensitivity and very low detection limits:  $0.001\text{--}0.1\text{ ng L}^{-1}$   
 Small sample amount of analyte: in ng to fg range  
 Nearly complete evaporation of aqueous solution and dissociation of sample molecules at  $5000\text{--}8000\text{ K}$ , high ionization degree (90% for elements with ionization potential  $<8\text{ eV}$ )  
 Easy to quantify using standard solution:  
 Precision of trace element determination: external calibration or standard addition  $\pm 2\text{--}5\%$  (RSD); isotope dilution:  $\pm 1\text{--}3\%$  (RSD)  
 Precise isotope ratio measurements with single ion collector:  $0.02\%$  (RSD)  
 Simple sample introduction in the ICP at atmospheric pressure  $\rightarrow$  easy for coupling techniques (HPLC, ETV, LA, CE, and others)  
 Mostly simple sample preparation for solid samples (no problems for inhomogeneous samples)

#### Limits

Molecular ion formation that leads to interferences with atomic ions of analyte.

trace elements through isobaric interferences with the atomic ions of the analyte. Such molecular ions are a significant limiting factor in ICP-MS. In routine analysis empirical formulae are often used for their correction. In spite of the empirical correction of such

interferences in many applications, great efforts were made in order to suppress apparent interferences (e.g. by application of high resolution ICP-MS using special sample introduction by desolvation [157], hydride generation [158], electrothermal vaporization [159],

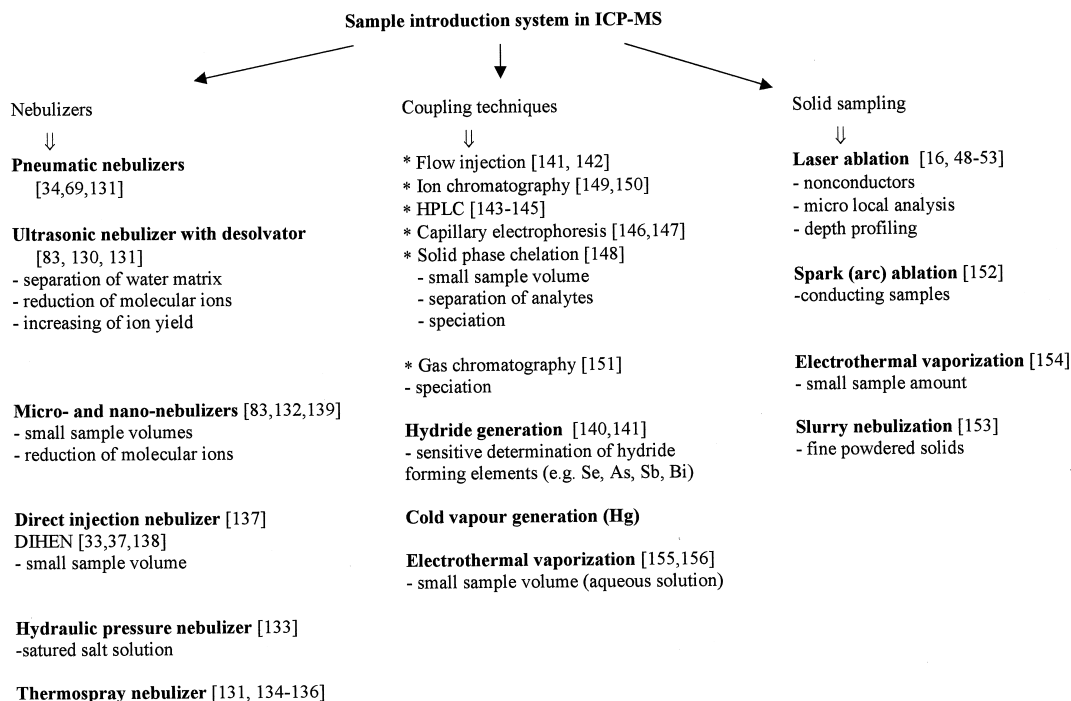


Fig. 14. Classification of a different sample introduction system in ICP-MS.

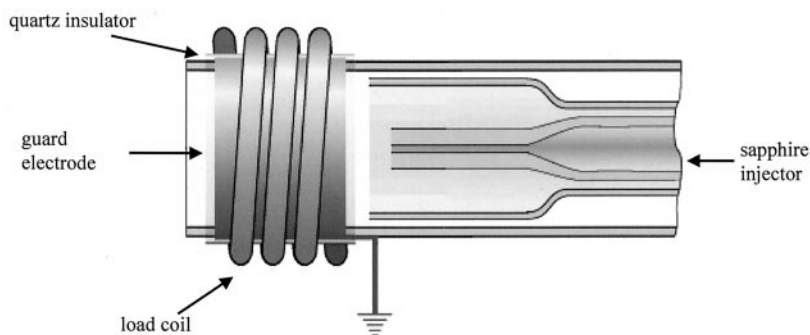


Fig. 15. Plasma shielded torch (GE—guard electrode, courtesy of Finnigan MAT).

thermospray and membrane separator [160], laser ablation [161], the application of so-called cool plasma techniques (at low rf power and increased nebulizer gas flow rate) [162], and others. In order to reduce the interferences of molecular ions and atomic ions of analyte the dissociation of disturbing molecular ions in a dynamic reaction cell is proposed in two commercial instruments from Micromass [163] with a gas-filled hexapole lens that works as an ion optical lens (see Fig. 13), and Perkin Elmer [164–167] using a quadrupole dynamic reaction cell between the ion lens system and the quadrupole analyzer.  $\text{NH}_3$ ,  $\text{CH}_4$ ,  $\text{H}_2$ , He, and others were successfully used as a reaction gas for different applications. The reaction gas first causes the dissociation of some argon molecular ions (e.g.  $\text{ArO}^+$ ,  $\text{ArH}^+$ ,  $\text{Ar}_2^+$ , etc.) by a collision-induced reaction (charge transfer and proton transfer reactions). Second, it causes the neutralization of  $\text{Ar}^+$  with  $\text{NH}_3$  as the reaction gas was observed, thus reducing the  $\text{Ar}^+$  intensity by eight orders of magnitude and allowing the determination of  $^{40}\text{Ca}$  in the sub  $\mu\text{g L}^{-1}$  range [165]. Third, the thermalization of ions in inductively coupled plasma (from eV ion energy to lower than 0.1 eV) results in a better transmission of ions, a higher ion intensity, and a decrease of detection limits of elements.

Gray proposed plasma shielding with quadrupole-based ICP-MS for measurements under “cool” plasma conditions to reduce the molecular ion formation in ICP-MS [168]. This effect of removing the molecular ions formed behind the sampling cone using a shielded torch was studied by different Japanese

groups [169–171] and a reduction of some disturbing molecular ions (e.g.  $\text{ArH}^+$ ,  $\text{Ar}_2^+$ ,  $\text{CO}_2^+$ , and  $\text{ArO}^+$ ) was observed under “cool” plasma conditions. But in ICP mass spectra new molecular and cluster ions, such as the water cluster ions, were observed with high ion intensities [172,173]. In Fig. 15 the schematic of the plasma-shielded torch [GuardElectrode (GE), Finnigan MAT] is demonstrated. The grounded platinum electrode for plasma shielding is located between the quartz ICP torch and the rf load coil [174]. Plasma shielding results in a decrease of secondary discharge, reduction of kinetic energy of ions, and leads to an improvement of sensitivity. In Fig. 16 the sensitivity with and without a shielded torch are compared in a double-focusing sector field ICP-MS using a microconcentric nebulizer and mini-cyclonic spray chamber for selected long-lived radionuclides [129]. Through the application of plasma shielding the detection limit, e.g. for  $^{239}\text{Pu}$ , was determined to be  $0.3 \text{ pg L}^{-1}$  (compared to  $1.7 \text{ pg L}^{-1}$  without a shielded torch). For selected radionuclides of actinides in high-purity water measured by DF-ICP-MS using an ultrasonic nebulizer for solution introduction [129], the detection limit, the radioactivity (in  $\text{kBq L}^{-1}$ ), the half-life of these long-lived radionuclides, and the reference value using the double focusing ICP-MS PlasmaTrace [175] are summarized in Table 7. On the other hand, the application of the shielded torch under hot plasma conditions yielded an increase of oxide ion intensities compared to the unshielded torch [129].

Extremely sensitive analytical techniques with

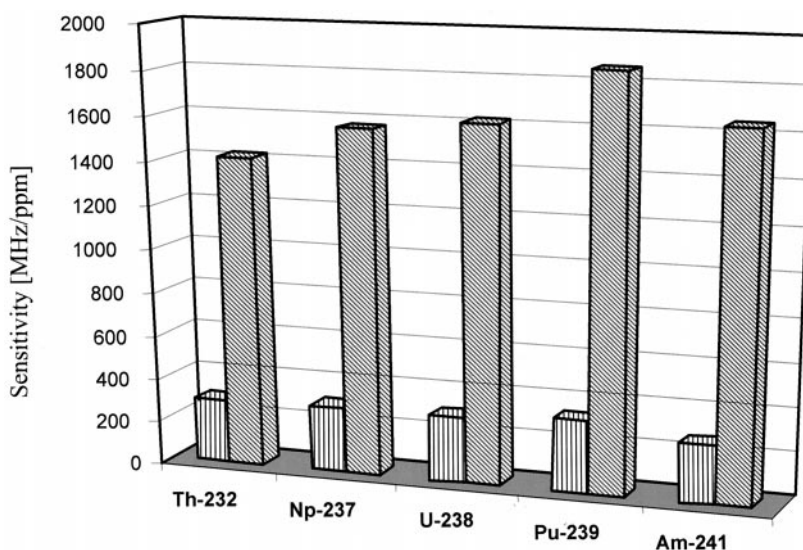


Fig. 16. Comparison of sensitivity of long-lived radionuclides in DF-ICP-MS with and without shielded torch. (diagonal lines, with shielded torch, vertical lines, without shielded torch).

very low detection limits are important for the determination of radionuclides in order to avoid contamination of the instrument and to reduce the dose to the operator and the volume of radioactive waste solution. Therefore, analytical techniques have been developed using enrichment procedures, coupling techniques, and micronebulization for a small sample amount [20,21,32–37,128]. For example, by the application of the direct injection high efficiency nebulizer (DIHEN, J.E. Meinhard Associates) in quadrupole-based ICP-MS the ultrasensitive and precise determination of radionuclide concentration ( $^{226}\text{Ra}$ ,  $^{230}\text{Th}$ ,  $^{237}\text{Np}$ ,  $^{238}\text{U}$ ,  $^{239}\text{Pu}$ , and  $^{241}\text{Am}$  with detection limits of up to

$0.012 \text{ ng L}^{-1}$ ) and isotope ratios of Th, U, and Pu was performed with solution uptake rates from  $0.085$  to  $0.001 \text{ mL min}^{-1}$  [33].

A further reduction of sample amount is possible by application of microscale flow injection in ICP-MS ( $\mu\text{-FI-ICP-MS}$ ). In order to handle  $\mu\text{L}$  of an aqueous solution of long-lived radionuclides, a commercial high-performance liquid chromatography (HPLC) injection valve was coupled to a microconcentric nebulizer for small droplet formation. The basic principle is demonstrated above in Fig. 17. Small sample volumes (up to  $1 \mu\text{L}$ ) were injected using the HPLC injection valve via a sample loop in a continuous flow of 2% nitrid acid. The solution is nebulized by micronebulization (MicroMist) in a mini-cyclonic spray chamber and transported with Ar into the inductively coupled plasma of an ICP-MS. At the bottom of Fig. 17, the transient signals of a  $10 \text{ ng L}^{-1}$  and  $100 \text{ ng L}^{-1}$   $^{237}\text{Np}$  solution (sample loop:  $20 \mu\text{L}$ ) are shown. The precision of five repeated measurements was found to be 2.0% RSD and 1.6% RSD, respectively, in this experiment [128]. The sample size for one transient signal of  $^{237}\text{Np}^+$  was  $0.2 \text{ pg}$  and  $2 \text{ pg}$ .

The most important problem in the determination of long-lived radionuclides in radioactive waste or

Table 7  
Detection limits for actinides in high-purity water by double focusing sector fields ICP-MS

Nuclide	Half life [years]	"ELEMENT" [129]		"Plasma Trace" [175] [ $\text{pg L}^{-1}$ ]
		[ $\text{pg L}^{-1}$ ]	[ $\text{kBq L}^{-1}$ ]	
$^{230}\text{Th}$	$7.5 \times 10^4$	0.08	$6.2 \times 10^{-8}$	20
$^{232}\text{Th}$	$1.4 \times 10^{10}$	0.1	$4.1 \times 10^{-13}$	
$^{233}\text{U}$	$1.6 \times 10^5$	0.07	$2.5 \times 10^{-8}$	
$^{238}\text{U}$	$4.5 \times 10^9$	0.2	$2.4 \times 10^{-12}$	20
$^{237}\text{Np}$	$2.1 \times 10^{16}$	0.05	$1.3 \times 10^{-9}$	2
$^{239}\text{Pu}$	$2.4 \times 10^4$	0.04	$9.4 \times 10^{-8}$	5
$^{243}\text{Am}$	$7.9 \times 10^3$	0.05	$3.6 \times 10^{-7}$	

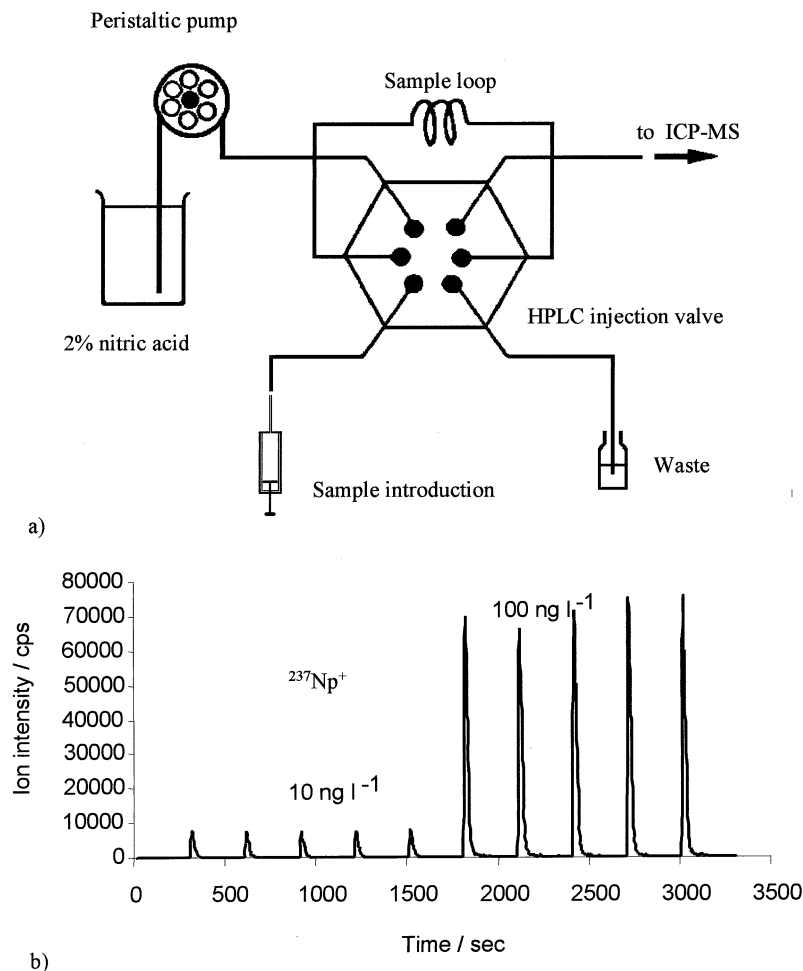


Fig. 17. Principle of microscale flow injection ICP-MS (a) and the application for the determination of  $^{237}\text{Np}$  (b) [129].

environmental samples is the existence of isobaric interferences of radioactive nuclides and stable isotopes at the same nominal mass. In past years on-line ion chromatography has been increasingly used for the determination of long-lived radionuclides in quite different materials [176–178]. In order to determine spallation nuclides in an irradiated (with 800 MeV protons) tantalum target of a spallation neutron source [179] analytical methods using HPLC-ICP-MS [143,144,180] and CE-ICP-MS [147] were developed in our laboratory. Due to expected isobaric interferences from long-lived spallation radionuclides and stable spallation isotopes, HPLC and CE are useful for the chemical separation of analytes before mass

spectrometric measurement. Both separation techniques are coupled on-line to a double-focusing sector field ICP-MS. In Fig. 18 the ICP mass spectrum of spallation nuclides of dysprosium after HPLC separation is shown. The abundance distribution of spallation nuclides, which is in agreement with the theoretically calculated distribution, is quite different from the isotopic pattern in natural samples. The sample volume that was analyzed by HPLC-ICP-MS  $10\ \mu\text{L}$  can be reduced significantly in the nL range by CE-ICP-MS (see the experimental arrangement in Fig. 19) [147]. Fig. 20 shows the ICP mass spectrum of lanthanides with the natural isotopic pattern measured by on-line CE-ICP-MS with the sensitive dou-



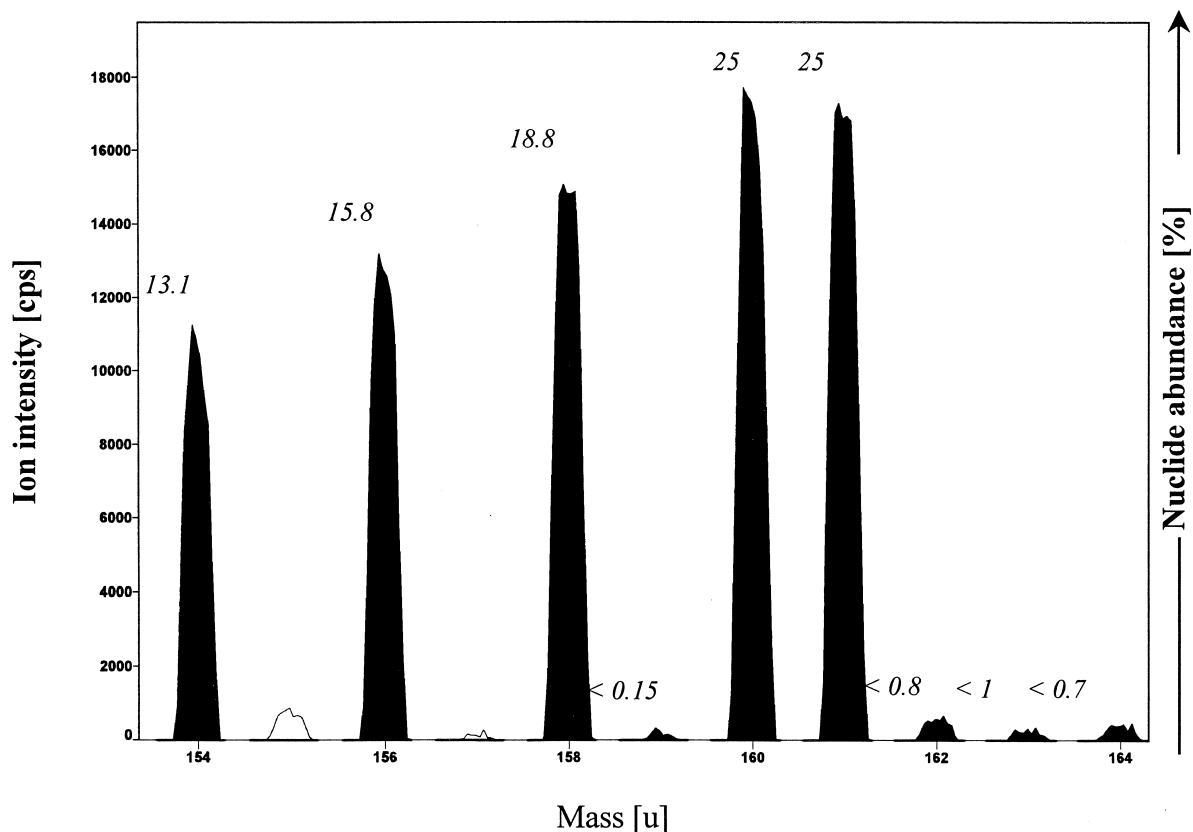


Fig. 18. Mass spectrum of spallation dysprosium in irradiated tantalum target measured by HPLC-ICP-MS.

ble focusing sector field ICP-MS in the low resolution mode. The sample volume of 30 nL volume, which was well separated with respect to the analytes by capillary electrophoresis, was transported from CE via a special interface and introduced by a microconcentric nebulizer into the inductively coupled plasma

of the mass spectrometer. The concentration of each lanthanide element could be reduced in this experiment to the low  $\mu\text{g L}^{-1}$  range. The sample size of each lanthanide element was 30 pg.

The application of microanalytical techniques such as  $\mu\text{-FI-ICP-MS}$  (see Fig. 17) is of special interest

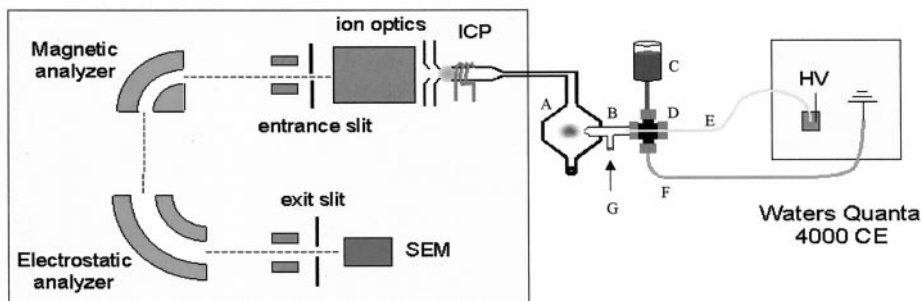


Fig. 19. Experimental arrangement of CE-ICP-MS using a double-focusing sector field ICP-MS.

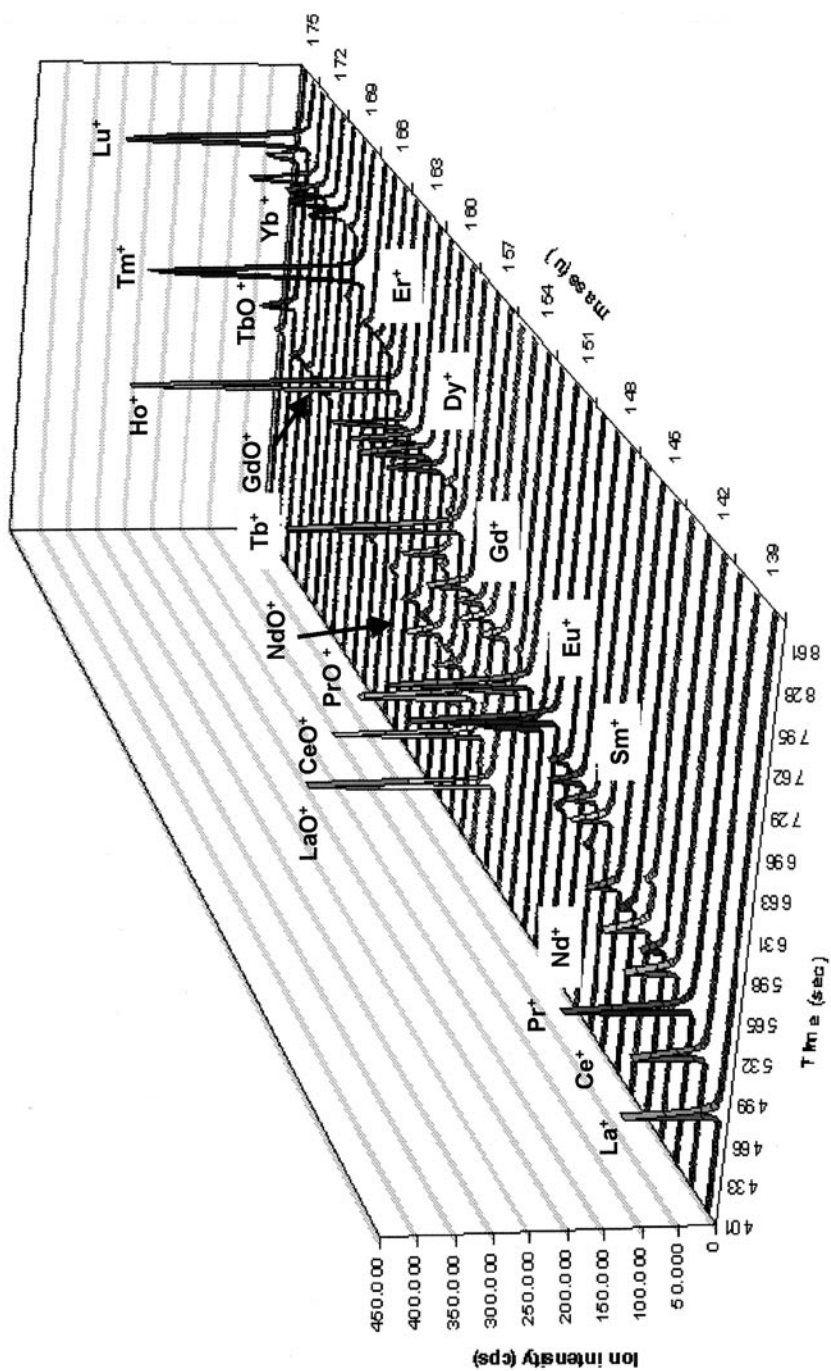


Fig. 20. ICP mass spectrum of lanthanides separated by capillary electrophoresis.

even in environmental research where very small sample volumes have to be characterized, e.g. for Cr determination in DNA [181]. In Fig. 21 (at the top) the measurements of transient signals of  $^{52}\text{Cr}^+$  for  $10\ \mu\text{g L}^{-1}$  Cr concentration in small sample volumes of aqueous solution (sample loop  $20\ \mu\text{L}$ ) using  $\mu$ -flow injection in combination with a double focusing sector field ICP-MS are shown. For the separation of isobaric interference of  $^{52}\text{Cr}^+$  and  $^{40}\text{Ar}^{12}\text{C}^+$  the measurements were performed at a mass resolution of  $m/\Delta m = 3000$ . This is connected with a loss in sensitivity of about one order of magnitude compared to the measurement at low mass resolution ( $m/\Delta m = 300$ ). Ten repetitions of solution injection ( $20\ \mu\text{L}$  sample loop, Cr concentration  $10\ \mu\text{g L}^{-1}$ ) yielded a precision of 1.3% RSD. This good precision is the precondition for the application of flow injection in isotope dilution analysis. The use of isotope dilution combined with flow injection is demonstrated by the determination of Cr in DNA. Because of the small DNA volume available the diluted sample (1:10) is injected using the described  $\mu$ -flow injection principle in a continuous flow of 2%  $\text{HNO}_3$  that is spiked with highly enriched  $^{53}\text{Cr}$  solution. The isotopic abundance of  $^{53}\text{Cr}$  was 84.3%; the Cr concentration was  $1\ \mu\text{g L}^{-1}$  in this experiment. At the bottom of Fig. 21, each  $20\ \mu\text{L}$  of two sample solutions with a natural isotope composition of chromium concentrations of 10 and  $5\ \mu\text{g L}^{-1}$ , respectively, were injected into the continuous flow of  $^{53}\text{Cr}$  spiked solution. The dispersion of flow injection was considered by using a  $10\ \mu\text{g L}^{-1}$  Co solution as described in [182].

The investigation of fundamental processes in living organisms and the effects of environmental conditions on life is a major field of analytical chemistry. An important topic is the determination of trace element composition in biomedical materials such as body fluids [183,184], human or animal tissues, organs, bone, hair, etc. In order to clarify the mechanisms of the tumor processes which are one of the most serious long-term consequences of the Chernobyl nuclear power plant accident, we studied the element distribution in the thyroid tissues of people living in the Chernobyl region. Small sample amounts (up to 1 mg of the thyroid tissues) were obtained from

persons who had undergone an operation for thyroid cancer. Therefore, an analytical procedure for the multielement determination of trace elements in a small sample amount using SRM 1566a Oyster Tissue and SRM 1577 Bovine Liver was developed [185]. One problem for the analysis of such small sample amounts could be the possible inhomogeneity of materials that results in inadequate precision and accuracy. The homogeneities of powdered standard reference materials are being studied by SIMS investigations. Thyroid tissues were dissolved before ICP-MS analysis by microwave digestion with a mixture of high-purity nitric acid and hydrogen peroxide. The accuracy of ICP-MS measurements on thyroid samples was verified by instrumental neutron activation analysis (INAA). A comparison of the results of ICP-MS and INAA on a thyroid sample is demonstrated in Table 8. The advantage of the non-destructive INAA lies in the possibility of analyzing the sample without any preliminary chemical treatment, thus overcoming almost all problems of contamination. However, only a few elements with long-lived radionuclides could be measured with INAA, which requires powerful irradiation facilities, a specially equipped laboratory, more time, a higher amount of sample, is very expensive, and produces radioactive waste. Therefore, INAA can be used mainly as an absolute reference method (without standards).

Anomalies in elemental distribution (significantly higher concentrations of Ca, Sr, Zn, Fe, Mn, V, As, Cr, Ni, Pb, U, Ba, and Sb) of thyroid tissues from exposed compared to unexposed persons were detected by the analysis of 84 samples. Such changes of chemical composition could promote the development of pathology due to mutagenic and carcinogenic properties of some elements (As, Cr, Pb, or U) [185].

Beside the determination of total elemental concentration, which is relevant for numerous analytical questionnaires, there is a growing awareness that the chemical form in which trace elements occur in environmental samples or in living organisms should be known. Speciation, which includes the determination of different oxidation states of elements or the type of chemical bonding with inorganic or organic partners, is therefore a rapidly growing research field

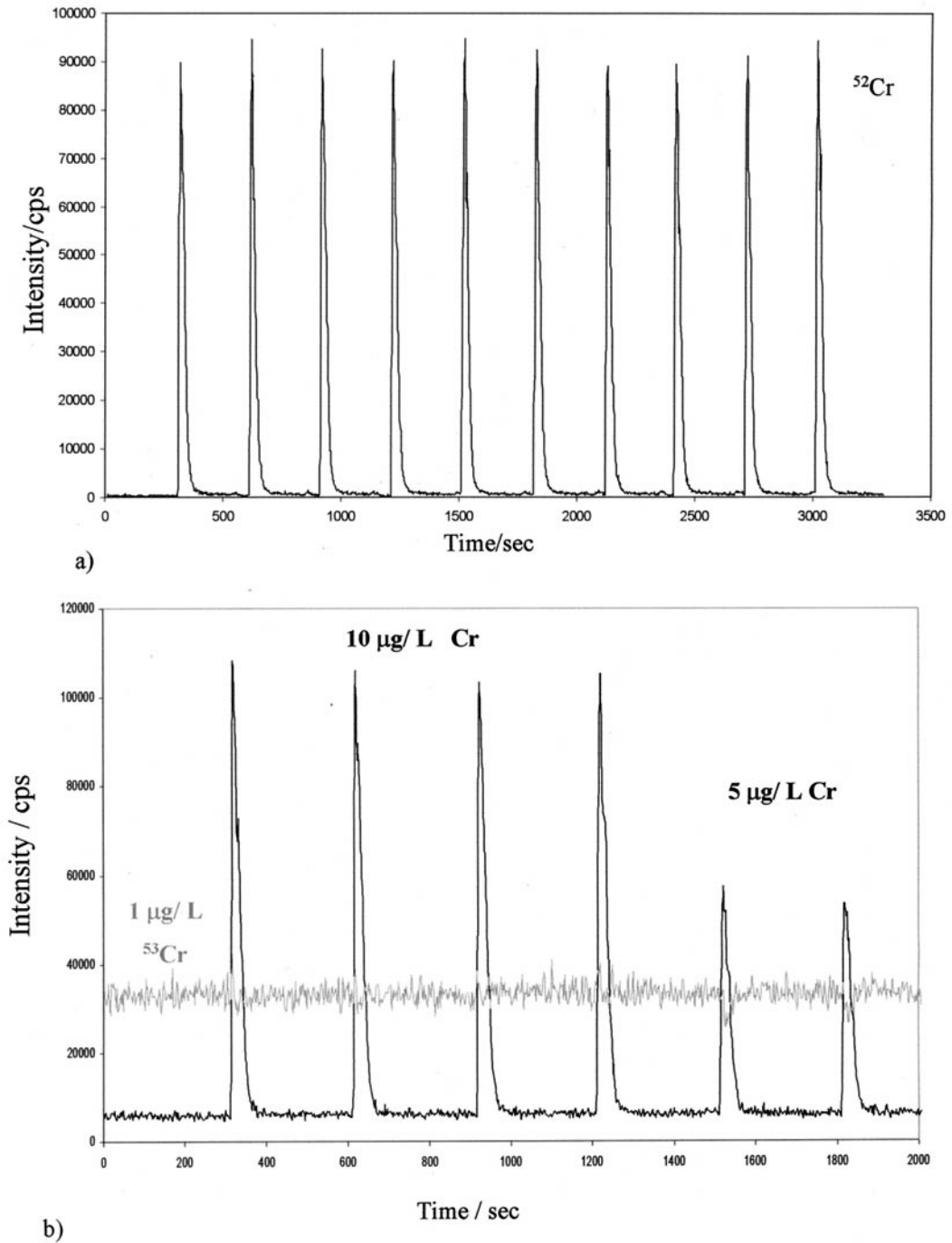


Fig. 21. Cr determination in a small sample volume of aqueous solution using  $\mu$ -FI-ICP-MS, (a) transient signal of  $^{52}\text{Cr}^+$  for  $10\ \mu\text{g L}^{-1}$  (sample loop  $20\ \mu\text{L}$ ); (b) application of isotope dilution for the determination of Cr in  $20\ \mu\text{L}$  sample solution injected in a continuous flow of  $1\ \mu\text{g L}^{-1}$  high enriched  $^{53}\text{Cr}$  solution.

Table 8  
Comparison of ICP-MS and INAA (concentration in  $\mu\text{g/g}$ )

Element	ICP-MS	INAA
Ca	3630 $\pm$ 400	3780 $\pm$ 390
Cr	2.2 $\pm$ 0.2	2.0 $\pm$ 0.3
Fe	182 $\pm$ 20	191 $\pm$ 22
K	250 $\pm$ 29	249 $\pm$ 29
Na	435 $\pm$ 55	438 $\pm$ 35
Sb	42 $\pm$ 4	40 $\pm$ 6
Se	1.8 $\pm$ 0.3	1.4 $\pm$ 0.2
U	0.065 $\pm$ 0.004	0.068 $\pm$ 0.010
Zn	323 $\pm$ 35	394 $\pm$ 39

in ICP-MS using different on-line coupling techniques for the separation of different species. The most frequently applied coupling technique is ion chromatography (especially HPLC), e.g. for the separation of Cr (III) (essential for living organisms) and the toxic and carcinogenic Cr (VI) or for the separation of a multitude of arsenic compounds with a large difference in toxicity [187].

A simultaneous determination of arsenic, selenium, and antimony species using HPLC-ICP-MS is described by Lindemann et al. [188]. Recent trends in speciation using ICP-MS with different on-line separation techniques [HPLC, CE, GC, SPME (solid phase microextraction), SFC (supercritical fluid extraction), SEC (size exclusion chromatography), and others] are reviewed in [189–191].

#### 4. Precise measurements of isotope ratios by inorganic mass spectrometry

An important and common feature of all the discussed mass spectrometric techniques is their capability to determine isotope abundances. This article did not consider the mass spectrometric techniques for very precise isotope analysis over the gaseous phases [GIMS (gas isotope mass spectrometry)] that are used for the exact determination of isotope ratios, atomic weights of elements, and a redetermination of the Avogadro constant [192]. Nevertheless, because of the instrumental development of mass spectrometers with multi-ion collectors in the past few years, new techniques increasingly allow precise isotope ratio

determination. TIMS has occupied a favoured position in the last few decades for routine measurements (e.g. for isotope ratio measurements of stable isotopes in nature and radiogenic elements in the nuclear industry; for tracer experiments using stable isotopes or long-lived radionuclides; quality assurance of fuel material; reprocessing plant, nuclear material accounting, and radioactive waste control; and especially for age dating and others). For example, Callis and Abernathy [193] developed a rapid high-precision analytical technique for the determination of isotope ratios of uranium and plutonium by total sample volatilization using multiple-filament thermal ionization mass spectrometry with a commercial multicollector instrument (VG-354, VG Isotopes). Run-to-run reproducibility of  $<0.02\%$  RSD has been obtained for isotope ratios of U and Pu.

At present TIMS is being increasingly replaced for precise isotope ratio measurements by ICP-MS due to its excellent sensitivity, good accuracy, and standard deviation including an easier sample preparation in terms of analyte separation and purification steps. Furthermore, ICP-MS, which is applicable for nearly all elements (TIMS is difficult for elements with high ionization potential), offers a significantly higher sample throughput, is less time consuming, requires smaller sample sizes (up to the sub-pg range), and does not suffer from time-dependent mass discrimination effects.

The good precision of isotope ratio measurements of long-lived radionuclides by ICP-QMS and double focusing sector field ICP-MS with a single ion collector has been demonstrated in different articles [32–34,37,73,83,129]. In Table 9 the results of isotope ratio measurements using quadrupole-based ICP-MS and double focusing sector field ICP-MS on  $^{230}\text{Th}/^{232}\text{Th}$  and  $^{239}\text{Pu}/^{240}\text{Pu}$  are compared. DF-ICP-MS with a shielded torch allows an isotope analysis of Pu at the  $10\text{ pg L}^{-1}$  level with sufficient accuracy and precision.

Table 10 compares the different inorganic mass spectrometric techniques with respect to their precision and sample size [129,193–197]. The influence of different effects (mass discrimination, space charge, interferences, stability of ion current) on the accuracy and precision of isotope ratio measurements in plasma

Table 9

Determination of isotope ratios of long-lived radionuclides by ICP-MS (ICP-QMS ELAN 6000, PE Sciex; DF-ICP-MS ELEMENT, Finnigan MAT) [129]

Isotope ratio	Precision		Amount of analyte (concentration)	
	ICP-QMS	DF-ICP-MS	ICP-QMS	DF-ICP-MS
$^{230}\text{Th}/^{232}\text{Th} = 0.001$	0.6%	0.34%	255 pg (1 $\mu\text{g/L}$ )	0.5 pg (5 ng/L)
$^{239}\text{Pu}/^{240}\text{Pu} = 0.17$	4%	0.3%	3 pg (12 ng/L)	0.5 pg (5 ng/L)
		13.8%		5 fg (10 pg/L)

source mass spectrometry was discussed by Heumann et al. [76].

Significant progress for the instrumental improvement of ICP-MS aimed at obtaining a better precision of isotope ratio measurements was achieved by introduction of the multicollector device (MC-ICP-MS) [194,195]. For example, Lee and Halliday [194], measured the  $^{182}\text{W}/^{183}\text{W}$  isotope ratio by MC-ICP-MS with a precision of 0.006% RSD. Using laser ablation for sample introduction in an MC-ICP-MS a precision of 0.009% RSD for the  $^{182}\text{W}/^{183}\text{W}$  isotope ratio was determined by Halliday et al. [196]. Christensens et al. [198] determined Pb isotopes with high precision in Fe-Mn crusts by ICP-MS using laser ablation for solid introduction.

Multi-ion collection is an ideal tool for overcoming the transient nature of laser ablation signals but, at present, high resolution MC-ICP-MS with Faraday cups [196,198] requires higher ion currents and therefore higher analyte concentration in solution and more ablated solid material for ICP-MS and LA-ICP-MS.

In contrast, the use of secondary ion multipliers in ICP-MS allows the measurements of low ion currents and therefore a reduction in sample size of the analyte up to the fg range is possible [129]. Nowadays, multi-ion collector sector field ICP mass spectrometers from Micromass and VG Elemental are available on the analytical market.

## 5. Investigation of molecular and cluster ion formation in inorganic mass spectrometry

In all the discussed mass spectrometric techniques, molecular and cluster ions formed with (sometimes) high intensities in plasmas or by sputtering, appear in the mass spectra. These ionic species disturb the mass spectrometric determination of trace elements due to isobaric interferences with atomic ions of analyte. As discussed previously, the quantification of analytical results and the determination of isotope ratios are often difficult in all inorganic mass spectrometric

Table 10

Comparison of precision and sample size for isotope ratio measurements using different mass spectrometric methods

Isotope ratio	Method	Precision	Sample size	Reference
$^{235}\text{U}/^{238}\text{U} \sim 1$	MC-TIMS	0.007%	100–200 ng	Callis and Abernatey [193]
$^{35}\text{U}/^{238}\text{U} \sim 1$	ICP-QMS	0.05%	255 pg	Becker and Dietze [37]
$^{234}\text{U}/^{238}\text{U} \sim 0.01$		0.56%		
$^{235}\text{U}/^{238}\text{U} \sim 1$	DF-ICP-MS	0.026%	255 pg	Becker and Dietze [129]
		0.2%	0.5 pg	
$^{34}\text{S}/^{32}\text{S} \sim 0.05$	ICP-QMS (hexapole lens)	<0.3%	50–250 $\mu\text{g}$	Mason et al. [163]
$^{235}\text{U}/^{238}\text{U} \sim 0.007$	LA-ICP-QMS	1.7%	some mg	Becker and Dietze [129]
$^{230}\text{Th}/^{232}\text{Th} \sim 0.0015$		4%		
$^{182}\text{W}/^{183}\text{W} \sim 2$	MC-ICP-MS	0.006%	500–1000 ng	Lee and Halliday [194]
$^{182}\text{W}/^{183}\text{W} \sim 2$	MC-LA-ICP-MS	0.009%	some mg	Halliday et al. [196]
$^{63}\text{Cu}/^{65}\text{Cu}$	GDMS	<0.3%	some mg	Adrians [197]
$^{107}\text{Ag}/^{109}\text{Ag}$ (in pure metals)				

techniques due to incomplete knowledge of ion formation processes.

On the other hand, mass spectrometry is an excellent and important analytical tool for basic research of molecular and cluster ion formation in a plasma or by sputter processes. By comparison of the relative ion intensities in mass spectrometric measurements and experimental bond dissociation energies, we found a correlation, e.g. for oxide ions  $\text{MO}^+$  of lanthanide elements in SSMS, LIMS, and ICP-MS [199–201]. This correlation of the measured relative molecular ion intensities with bond dissociation energies could be attributed to the electronic structure of lanthanides. Energetically stable molecular ions with empty, half-filled, and filled  $4f$  orbitals (this is true of La, Gd, and Lu, respectively) appear in the investigated mass spectra with the highest ion intensities. A correlation of measured  $\text{MO}^+$  ion intensities and experimentally determined or theoretically calculated bond energies of oxides was first described in laser mass spectrometry using a LAMMA 500 (laser microprobe mass analyzer, Leybold Hereaus AG, Cologne) by Michiels and Gijbels [202].

The correlation for the diatomic argon molecular ion intensities in DF-ICP-MS and bond dissociation energies has been discussed in recent articles [199,200]. The theoretical investigation of the argon molecular ions for elements of the second and third period in the periodic table of elements by means of quantum chemical calculation (LCAO-DFT-LDA) indicated that small binding energies were obtained for metal argide ions at the beginning of the period and that the bond energies rose with increasing atomic number. The higher intensities of nonmetal argon molecular ions in comparison to the metal argide ions in DF-ICP-MS can be interpreted as a result of higher stability. Furthermore, the correlation of  $\text{MAr}^+$  ions found in ICP-MS with bond dissociation energies was used for the determination of unknown bond dissociation energies. A similar distribution of cluster ions  $\text{Ca}_n\text{F}_m^+$  observed in SSMS and LA-ICP-MS by ultratrace analysis in a high-purity  $\text{CaF}_2$  single crystal. This distribution is interpreted via theoretical investigation of bond dissociation energies by Kaschner et al. [203].

The influence of the laser and plasma parameters (such as wavelength, laser power density, pulse length, plasma temperature, electron and ion density, and others) on the physical and chemical processes in a laser-induced plasma with respect to the formation of molecular and cluster ions was investigated for different materials (e.g. graphite [204], boron nitride [205], boron nitride/graphite mixture [201], boron carbide [206], tungsten oxide/graphite mixture [207], lanthanide oxide/graphite mixture [199], and superconductors [208]). The clusters formed in laser plasmas are of interest for the formation of thin layer composition by laser-induced plasma deposition [209]. Recently, Giapintzakis et al. [210] compared the positively charged molecular ions formed in a laser plasma by the infrared and ultraviolet laser ablation of a  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  target using a TOF-MS and found (similar to LIMS measurements in [207]) the formation of nonstoichiometric cluster ions. The authors proposed the introduction of oxygen by a pulsed nozzle near the plume, which should enhance the formation of oxides in order to prepare stoichiometric thin superconducting films.

## 6. Conclusions

Numerous, quite different applications demonstrate the excellent capability of inorganic mass spectrometry in determining very low element concentrations due to its low detection limits for the characterization of a variety of materials. Beside the solid state mass spectrometric techniques that allow the direct multielement determination of analytes in the  $\text{pg g}^{-1}$  range with a minimum of sample preparation, ICP-MS, especially with on-line coupling techniques [electrothermal vaporization (ETV), HPLC, capillary electrophoresis, ion chromatography, flow injection] with detection limits in the  $\text{sub fg mL}^{-1}$  range is an excellent tool for the analysis of aqueous solutions. The significance of ICP-MS in precise isotope ratio measurements at ultratrace levels is increasing, especially when multicollector and/or double focusing sector field instruments are used.

Knowledge of the formation, abundance distribu-

tion, and electronic stability of molecular and cluster ions is of great analytical significance if mass spectrometers with low mass resolution (e.g. quadrupole ICP-MS) are applied in trace and isotopic analysis.

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