Available online at www.sciencedirect.com

SCIENCE DIRECT®

International Journal of Mass Spectrometry 228 (2003) 127–150

www.elsevier.com/locate/ijms

Review

State-of-the-art in inorganic mass spectrometry for analysis of high-purity materials

J. Sabine Becker*, Hans-Joachim Dietze

Central Division for Analytical Chemistry, Research Centre Juelich, D-52425 Juelich, Germany

Received 2 December 2002; accepted 9 May 2003

Dedicated to Prof. Dr. Helmut Schwarz on the occasion of his 60th birthday.

Abstract

Inorganic mass spectrometric methods are widely used for the multielemental determination of elements at the trace and ultratrace level in high-purity materials (e.g., conducting, semiconducting and nonconducting solid samples, high-purity water, organic solutions and solvents). Inductively coupled plasma mass spectrometry (ICP-MS), laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS), glow discharge mass spectrometry (GDMS) and secondary ion mass spectrometry (SIMS) have been applied as powerful mass spectrometric techniques with their multielemental capability for the determination of trace and ultratrace elements in high-purity solid and liquid samples. The detection limits for the analysis of solid samples by inorganic solid mass spectrometry were determined down to sub-ng g^{-1} and for aqueous solution by ICP-MS down to sub-pg L^{-1}.

The aim of this review is to discuss the various inorganic mass spectrometric techniques including new analytical developments and their application for the quantitative determination of trace and ultratrace elements of quite different materials for the semiconductor industry and materials research.

Keywords: High-purity material; Inductively coupled plasma mass spectrometry; Inorganic mass spectrometry; Laser ablation ICP-MS; Trace analysis

---

1. Introduction

With its ability to provide very sensitive, accurate and precise multielemental determinations of trace and ultratrace elements, inorganic mass spectrometry has become established as the most important method in analytical chemistry for the analysis of inorganic materials and is widely used in all fields of modern science and technology, e.g., in materials research or microelectronics, for the characterization of high-purity solid materials, liquid and gaseous samples. The sensitivity and the detection limits of mass spectrometric methods for the analysis of high-purity materials have been essentially improved in the last few decades. Whereas inorganic mass spectrometric techniques for trace element determination in high-purity solid materials such as, e.g., spark source mass spectrometry (SSMS), glow discharge mass spectrometry (GDMS), thermal ionization mass spectrometry (TIMS—together with the isotope dilution technique), secondary ion mass spectrometry (SIMS) were frequently used in past decades, today the trend

---

* Corresponding author. Tel.: +49-2461-61-2698; fax: +49-2461-61-2560.

E-mail address: s.becker@fz-juelich.de (J.S. Becker).

1387-3806/$ – see front matter © 2003 Published by Elsevier Science B.V.
doi:10.1016/S1387-3806(03)00270-7

is to increasingly replace these expensive techniques by powerful and more sensitive inductively coupled plasma mass spectrometry (ICP-MS) or laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) [1–17]. Inorganic mass spectrometric techniques with multielement capability allow the quasi-simultaneous determination of trace and ultratrace contaminants in solid samples with detection limits down to the sub-ng g^{-1} range.

High-purity materials were produced, e.g., by vacuum-induction melting (metals and alloys), inert gas hot pressing (ceramics and semiconductors) or chemical or physical vapor deposition for the synthesis and growth of high-purity materials for micro- and optoelectronics. Investigated high-purity solid materials in respect to trace and ultratrace contaminants are conductors such as high-purity metals, alloys, graphite, or metallic PVD (physical vapor deposition) materials, semiconductors (III–V semiconductors such as GaAs or InP and semiconducting layers) and insulators (e.g., ceramics, oxides, borides, carbides, nitrides of Zr, Ti, Mo, W and so on, and nonconducting layers) with purity better than 99.9% (see Fig. 1). The largest application field for high-purity materials is the microelectronics industry, high-purity carbides of Cr, Zr and B, nitrides of Cr, Ti and Zr or titanium boride are applied, e.g., as wear-resistant materials and coatings. Mass spectrometry is increasingly useful for process control (i.e., trace analysis in high-purity initial materials, intermediate and final products). Besides the analysis of compact bulk (also wires, tapes, or layered structures of devices and others) or powdered materials, the purity of liquid process chemicals (solvents, acids, organics) for microelectronic purposes has to be determined. ICP-MS is applied mainly for the ultrasensitive determination of trace and ultratrace impurities in high-purity water, aqueous, organic solutions and solvents with extremely low detection limits down to the sub-pg L^{-1} concentration range and in addition for the analysis of high-purity solids after decomposition. Similar low detection limits as obtained for the analysis of ultratrace elements in ICP-MS were observed by resonance ionization mass spectrometry (RIMS; 10^6 atoms ^{239}Pu) and accelerator mass spectrometry (AMS). RIMS and AMS were applied especially for the determination of extremely low isotope ratios down to 10^{-6} to 10^{-15} of rare long-lived radionuclides (such as ^{129}I, ^{41}Ca, ^{90}Sr, ^{99}Tc, $^{238-242}$Pu and ^{10}Be, ^{14}C, ^{26}Al, ^{36}Cl), but in the trace and ultratrace analysis of high-purity materials both techniques have practically less significance. The analysis of trace impurities with detection limits at μg g^{-1} and ng g^{-1} levels in electronic materials by AMS especially for depth profile measurements of impurities and dopants in semiconductor materials was described by McDaniel [18].

In order to measure true element concentrations at ultratrace level different problems, such as contamination problems, matrix effects, memory effects and interferences appearing must be considered carefully [19–21]. Trace and ultratrace analysis of high-purity gases will not be discussed in this paper.

Among the spectrometric techniques for trace and ultratrace analysis [such as atomic absorption spectrometry with a graphite furnace (GF-AAS) or electrothermal vaporization (ETV-AAS), optical emission spectrometry with an inductively coupled plasma source (ICP-OES), neutron activation analysis (NAA) and X-ray fluorescence analysis (XRF) and total reflection fluorescence analysis (TXRF)] [22–32] inorganic mass spectrometric techniques possess remarkable properties in respect to sensitivity, multielement capability, detection limits, precision and accuracy of analytical results. TXRF is the leading technique today for the routine analysis of surface contamination of single crystal wafers in the semiconductor field.

Further advantages of plasma mass spectrometric methods are a wide dynamic range of detection of up to 9 orders of magnitude. That means major (matrix), minor and trace elements can be determined without any great experimental effort. Furthermore, the ability to perform precise and accurate isotope ratio measurements can be used for an accurate analysis of trace elements by isotope dilution technique. The state-of-the-art and the progress in precise and accurate isotope ratio measurements achieved by inorganic mass spectrometry has been described in a multitude of publications elsewhere [33–36].

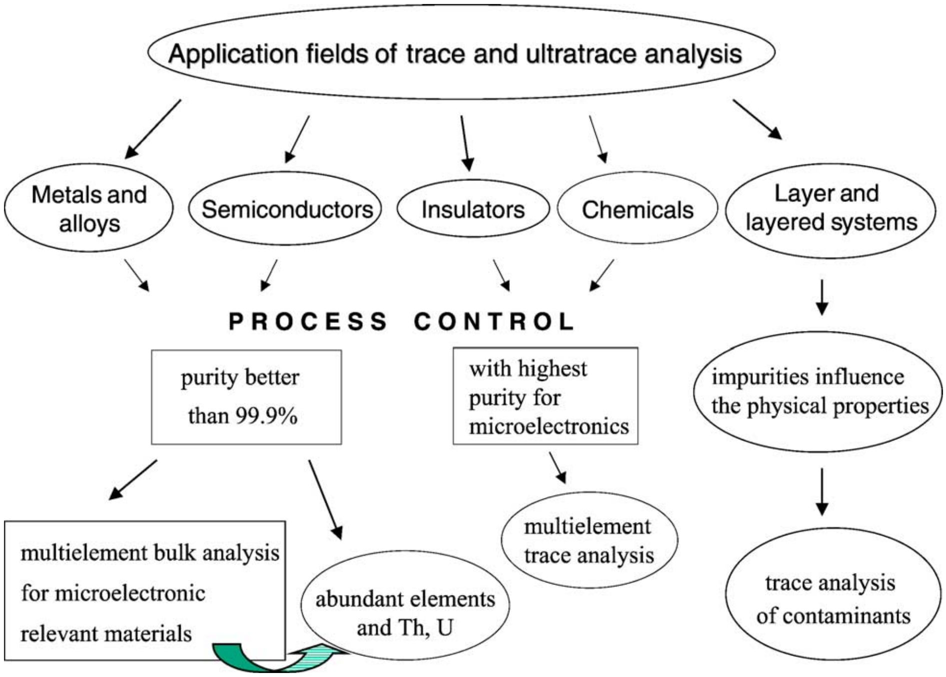

Fig. 1. Application fields of trace and ultratrace analysis.

The aim of this present paper is to describe the progress of inorganic mass spectrometry in the analysis of high-purity materials.

2. Special analytical problems in the analysis of high-purity materials

The analysis of high-purity materials is a challenging task for analytical chemistry. In order to obtain accurate analytical results special analytical problems in extreme trace analysis must be considered [37]. The problems involved in the analysis of high-purity materials increase with decreasing analyte concentration. The detection range and units in the determination of element concentrations are summarized in Table 1. The purity of materials and the common abbreviations are summarized in Table 2.

Sources of systematic errors in ultratrace analysis are connected with sampling, sample handling and

Table 1
Detection range and units in determination of concentration

Weight (g)	Concentration	Unit	^{238}U (atoms mL^{-1})	
10^{-3} (milli)	mg g^{-1}	0.1%	2.53×10^{18}	
10^{-6} (micro)	μg g^{-1}	ppm	2.53×10^{15}	Traces
10^{-9} (nano)	ng g^{-1}	ppb	2.53×10^{12}	Ultratraces
10^{-12} (pico)	pg g^{-1}	ppt	2.53×10^{9}	Ultratraces
10^{-15} (femto)	fg g^{-1}	ppq	2.53×10^{6}	Ultratraces
10^{-18} (atto)	ag g^{-1}		2530	
10^{-21} (zepto)	zg g^{-1}		2.53	
10^{-24} (yocto)	yg g^{-1}		0.00253	

Table 2
Common abbreviation of high-purity of materials

Purity (%)	Abbreviation	Maximum metallic impurities
99.9	39 or 3N	1000 $\mu g\,g^{-1}$
99.99	49 or 4N	100 $\mu g\,g^{-1}$
99.999	59 or 5N	10 $\mu g\,g^{-1}$
99.9996	59.6 or 5N6	4 $\mu g\,g^{-1}$
99.9999	69 or 6N	1 $\mu g\,g^{-1}$
99.99999	79 or 7N	100 $ng\,g^{-1}$

storage of sample. Contamination of samples during sampling, in sample preparation using contaminated tools, vessels and by reagents is often a serious problem. Clean vessels made of an inert high-purity material (quartz, PFA or PFTE) with a small volume and a minimal amount of high-purity reagents should be used. Contamination problems in the analysis of high-purity materials were observed especially for elements with high abundance in the earth's crust (e.g., Si, Al, Fe, Ca, Na, K, Mn, Ti) and of anthropogenic pollution (e.g., Mg, Cu, Cd, Pb, Ni, Zr). In order to exclude dust the use of clean rooms or/and clean benches is advantageous.

Furthermore, instrumental background, memory effect and blank values of the chemicals used must be reduced to a minimum. In respect to blank values of chemicals used it should be noted that no substance is absolutely pure, i.e., the contamination of sample can only be minimized. For the production of high-purity water commercial apparatus (e.g., Milli-Q-Millipore) is useful. For the purification procedure of acids (HNO_3, HCl, H_2SO_4) the sub-boiling distillation technique in commercial quartz apparatus is proposed, whereas the sub-boiling of hydrofluoric acid in PTFE is the method of choice.

Many different decomposition principles have been developed for the huge variety of different high-purity matrices of more and less complex matrix composition. In extreme trace analysis with respect to minimal systematic errors, it should be considered that the decomposition of sample has to be complete, the decomposition procedure should be as simple as possible, residues of a digestion should be quantitatively dissolved in a small volume of ultrapure acids. The accuracy of the analytical procedure including decomposition and measurement of trace elements should be checked with the aid of standard reference materials (SRMs). In addition to possible contamination also losses of trace elements by absorption effects at surfaces on vessels or volatization (e.g., Hg, Se, As, Cd, Zn) and precipitation of analytes should be avoided.

Possible inhomogeneous trace element distribution in solid sample, matrix effects, isobaric interferences and incorrect weighting, dilution, measurement, calibration and evaluation of data are further sources of errors in trace and ultratrace analysis. In order to avoid matrix effects, clogging effects on the cones and disturbing interferences of analyte ions with molecular ions of matrix elements, the chemical separation of matrix and preconcentration of analytes is often used. The procedure for trace–matrix separation (e.g., by liquid–liquid extraction, ion chromatography, volatization, precipitation, electrolysis) should be simple and only small amount of high-purity reagents should be required, whereas the yield of ultratrace must be 100% (except in the application of stable isotopes in the isotope dilution technique and radioactive tracers for process control).

3. Inorganic mass spectrometric techniques

The evolution of mass spectrometric methods in the past few decades for trace and ultratrace analysis of high-purity materials has been determined by the development of ion sources and mass spectrometric separation techniques. Inorganic mass spectrometry uses several types of ions source, i.e., spark ion source, glow discharge, laser ion source, secondary ion source, sputtered neutral ion source and inductively coupled plasma ion source. The schematics of the most frequently applied ions sources in inorganic mass spectrometry are given in Fig. 2. More details on different ion sources together with the mass spectrometric separation system used are described elsewhere [1–4,6]. The mass spectrometric method is mainly determined by the method used to evaporate the sample material (e.g., in a plasma, by thermal or laser-induced

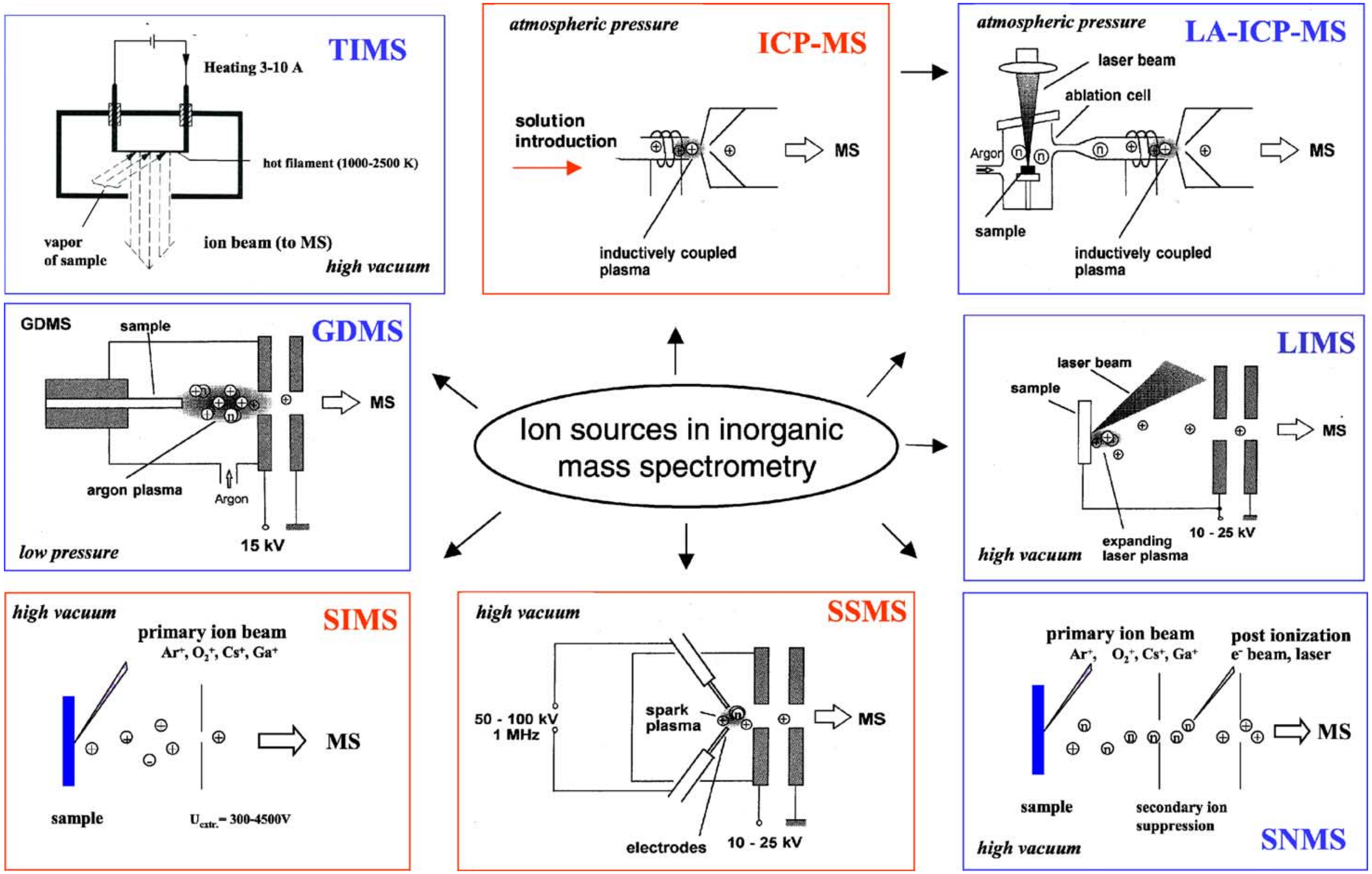

Fig. 2. Overview on principle of ion sources in inorganic mass spectrometric techniques.

evaporation, by electron or by ion bombardment) and the method for ionizing the atomized sample, e.g., by electron impact ionization, ionization during the sputtering process using primary ions, resonant or nonresonant laser ionization or thermal surface ionization [4]. SSMS, ICP-MS, SIMS and LIMS (laser ionization mass spectrometry) allow a simultaneous evaporation (atomization) and ionization process via electrons, photons or ions in different types of plasma in the ion source. In contrast, a separation of evaporation (atomization) of the sample material and the ionization process of the atomic or molecular species in time and space is realized in GDMS, SNMS, LA-ICP-MS [4]. Ion sources under ultrahigh vacuum are, e.g., spark ion source, laser ion source or secondary ion source. Whereas the glow discharge ion source works at low Ar pressure, the only ion source where ions were produced at atmospheric pressure is the inductively coupled ion source.

As a function of the initial energy of the ions (from low eV to keV range) static instruments (single magnetic sector field or double-focusing mass spectrometers combination of magnetic and electric sector field) or else dynamic mass analyzers (quadrupole analyzer or time-of-flight (TOF) analyzers) were applied for the mass spectrometric separation of ion beams in inorganic mass spectrometry. In commercial mass spectrometers Faraday cup and ion multipliers as single and multiple ion collector systems are used for ion detection.

3.1. Spark source mass spectrometry (SSMS)

SSMS (Fig. 2 shows the schematic of a spark ion source) is one of the oldest inorganic mass spectrometric techniques [38–40] which in the past was long the leading technique for the analysis of high-purity materials. SSMS was mainly applied for simultaneous and sensitive multielement determination in trace analysis especially for electrically compact conducting (high-purity metals or alloys) and low-resistance semiconductors of nearly all elements of the periodic table with detection limits down to the low $\mathrm{ng\,g^{-1}}$ concentration range. Nonconducting materials (e.g., high-purity ceramics, such as Al_2O_3, SiC, SiN, ZrO_2 and others) were analyzed after powdering and mixing with high-purity graphite or silver and pressing to compact electrodes. Due to the great experimental effort required by SSMS and the time-consuming evaluation of measured data via ion-sensitive photoplate, SSMS is in practical use in only a few laboratories worldwide. The last development using an old SSMS was carried out by Jochum et al. [41], who constructed an expensive multiple ion collector system with 20 separated channeltrons. SSMS was replaced firstly by LIMS and GDMS and recently by LA-ICP-MS for application in direct trace analysis of high-purity solid samples.

3.2. Laser ionization mass spectrometry (LIMS)

Due to the limits of SSMS in respect to analysis of nonconducting samples, laser ionization was introduced in mass spectrometry (LIMS) by Honig and Woolsten [42] 40 years ago. In some cases, commercial spark source mass spectrometers have been expanded into laser ionization mass spectrometers by applying a replaceable spark and laser ion source [39,43,44]. With the LIMS technique the solid material is evaporated and ionized simultaneously by means of a focused pulsed laser in a laser microplasma formed in the spot area of the irradiated sample under high vacuum conditions [39]. A schematic of the laser ion source is shown in Fig. 2. Similar to SSMS, LIMS [43,44] is a multielement method which allows major, minor and trace elements to be determined simultaneously with a wide dynamic range of up to 10^9 in any kind of solid (metals, alloys, semiconductors or insulators) without any restriction. A great effort has been made over a considerable period of time in developing commercial laser ionization mass spectrographs with TOF analyzer (e.g., LAMMA—laser microprobe mass analyzer, Leybold Hereaus AG and LIMA—laser ionization mass analyzer, British Cambridge Mass Spectrometry Company). In recent years, both instruments have been a valuable tool for the qualitative characterization of microsamples for application in microelectronics, including the impurities in dielectrics, microlocal analysis, depth profiling and analysis of thick ceramic layers [44]. The limited low mass resolution of conventional TOF instruments was improved by insertion of an ion reflector. In spite of excellent absolute detection limits down to 10^{-18} to 10^{-20} g [45] a drawback was the problems involved in the quantification of analytical results and the poor reproducibility. LIMS with a double-focusing sector field Mattauch–Herzog mass spectrograph (EMAL 2) with ion sensitive photoplate detection was developed in Russia [44]. No commercial mass spectrometers have been available for nearly 10 years and LIMS has been increasingly replaced by LA-ICP-MS.

3.3. Glow discharge mass spectrometry (GDMS)

GDMS is accepted today as one of the most powerful and sensitive solid-state analysis methods for the trace and ultratrace analysis of solid samples and is routinely applied by companies producing different high-purity metals or alloys [46]. The schematic of a glow discharge ion source is drawn in Fig. 2 and details on several processes in a glow discharge plasma are discussed in refs. [47–49]. The most frequently used glow discharge ion source in GDMS—direct current (dc) glow discharge—is realized as a hollow cathode or Grimm-type glow discharge. The advantageous features of dc glow discharge sources is a simple experimental arrangement, the production of stable ion beams in such sources, high sensitivity and very low detection limits down to $0.1\,\mathrm{ng\,g^{-1}}$ for high-purity metals, relatively low costs and the possibility of sensitive detection of nearly all chemical elements. The commercial dc glow discharge mass spectrometer VG 9000 from VG Instruments is especially well suited and is applied for trace and ultratrace analysis on high-purity metals and depth profiling of conducting and semiconducting samples in routine analysis mode. For the trace analysis of nonconducting samples different techniques (e.g., mixing of sample with high-purity metal powder or use of secondary cathode) have been developed [50–52].

Whereas dc GDMS is applied mostly for high-purity metals, radio frequency (rf) GDMS was developed especially for the characterization of nonconducting ceramic materials or glasses and thick ceramic layers [47,53]. Double-focusing mass spectrometers, one with Mattauch–Herzog geometry and another with reverse Nier–Johnson geometry (Element, Finnigan MAT), were used for many years in our laboratory together with an rf glow discharge ion source [54,55] for the analysis of different compact materials. Detection limits of trace elements, for example, in a GaAs matrix of rf GDMS were measured in the $\mathrm{ng\,g^{-1}}$ range. Due to significantly higher ion beam current compared to ICP-MS and to LA-ICP-MS, strong memory effects were observed in rf GDMS. Rf GDMS is of no longer of any significance in the trace analysis of high-purity materials and has been replaced, for example, at our laboratory by LA-ICP-MS, which is more powerful, simpler, faster and cheaper.

Instrumental developments in GDMS using a double-focusing sector field ICP-MS with Mattauch–Herzog geometry [56], with dynamic ion separation systems (quadrupole and TOF analyzers [57,58]) or together with very expensive Fourier transform mass spectrometers [2] which possess the highest possible mass resolution are not sensitive enough so that these instruments were used mainly for basic research and not for the analysis of high-purity materials.

3.4. Thermal ionization mass spectrometry (TIMS)

For a long time TIMS was the dominating analytical technique for precise and accurate isotope analysis [36,59]. Its application in the trace and ultratrace element analysis of high-purity materials was realized by the use of isotope dilution analysis (IDA) based on the measurement of isotope ratios [3,60,61]. TIMS has today only slight practical significance in the trace analysis of high-purity materials due to the great experimental effort required for time-consuming sample preparation (decomposition of solid sample and trace–matrix separation), the lack of multielement capability and restriction mainly to elements with ionization potential $<6\,\mathrm{eV}$.

3.5. Secondary ion mass spectrometry (SIMS) and secondary neutral mass spectrometry (SNMS)

Both solid analytical techniques, which are important in the investigation of sample surfaces, use a primary ion beam for sputtering the sample material. Details of the principles of a secondary ion source and a sputtered neutral source (see Fig. 2) are described elsewhere [62–65].

Whereas in SIMS large matrix effects (up to 6 orders of magnitude) and high molecular ion formation occurs, which do not allow a semi-quantitative analysis, in SNMS the composition of sputtered neutrals roughly corresponds to the matrix composition. That means a semi-quantitative analysis can be performed in SNMS with an error factor of 2–3 (also if no SRM for quantification is available). SIMS is due to lower detection limits in comparison to SNMS well suited for trace element analysis if SRMs with analogue matrix (e.g., from Charles Evans and Associates, USA) are available.

At present, a few SIMS and SNMS instruments are commercially available on the analytical market with double-focusing sector field mass spectrometers (e.g., CAMECA IMS-6f), quadrupole-based instruments (SIMS 4500, FEI Company) and TOF-SIMS 300 (ION-TOF) with main application fields in the semiconductor industry (surface contamination and depth profiling) or a multi-ion collector SIMS (NanoSIMS 50 from Cameca). A multiple ion collector, NanoSIMS, is used for precise isotope ratio measurements in the sub-micron range, especially for geological applications.

3.6. Inductively coupled plasma mass spectrometry (ICP-MS)

ICP-MS, at the present time, is the most frequently used inorganic mass spectrometric technique for the characterization of high-purity materials—especially for any liquid solutions [66–70].

In principle, different experimental arrangements and applications of ICP-MS have been described in the literature [2,4,6,70]. For solution introduction in the ICP-MS different types of nebulizers (Meinhard nebulizers, microconcentric and ultrasonic nebulizers without and with desolvators, high-pressure or direct-injection high-efficiency nebulizers) have been used [2,4,6,13,71–74]. The mass spectrometric separation of ion beams is realized in ICP-MS using both static and dynamic mass analyzers, such as single magnetic sector field instruments (e.g., Isoprobe: multi-ion collector instrument with collision cell MC-ICP-CC-MS, Micromass UK Ltd., Manchester, UK) or double-focusing sector field mass spectrometers (ICP-SFMS, combination of magnetic and electric sector field with reverse Nier–Johnson geometry), quadrupoles (ICP-QMS) without and with collision cells (from Agilent Technologies, Japan; Perkin-Elmer/Sciex, Concorde, Ont., Canada; ThermoElemental, Cambridge, UK; Micromass UK Ltd., Cambridge, UK; Varian, Melbourne, Australia and others), time-of-flight analyzers (ICP-TOFMS, e.g., from LECO Corporation, USA), ion traps and Fourier transform ion cyclotron resonance mass spectrometers (ICP-FT-ICR-MS) [2,4,6,70]. At present Faraday cup and ion multipliers—as single and multiple ion collector systems—are used in commercial ICP mass spectrometers for ion detection. An overview of ICP-MS instrumentation is given in Fig. 3 [34].

The lowest detection limits for trace element determination were observed in the sub-fg mL^{-1} range for elements in the high mass range (where no disturbing interferences exist) by double-focusing sector field ICP-MS (ICP-SFMS) such as the “Element” from ThermoFinnigan or PlasmaTrace from Micromass with a single ion collector [13,69]. Multiple ion collectors in ICP-MS (MC-ICP-MS, e.g., from ThermoFinnigan, Bremen, Germany; Nu Instruments, UK, and Micromass UK Ltd., Cambridge, UK) can be used for accurate trace element determination using IDA. Furthermore, by ICP-SFMS a lot of isobaric interferences of molecular ions with atomic ions of analyte can be separated at high mass resolution. Difficult to determine elements due to isobaric interferences with molecular ions were measured at higher mass resolution ($m/\Delta m = 4000$ or 12,000). The detection limits of these elements in aqueous solutions measured by

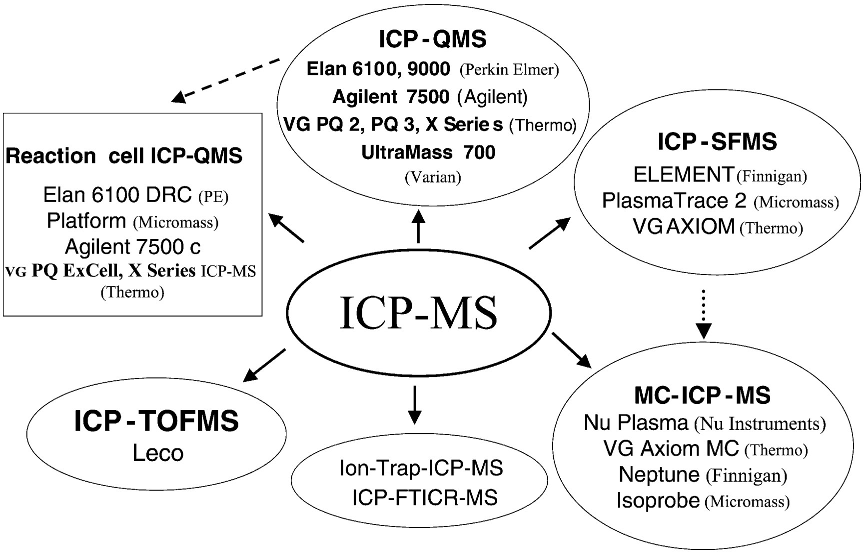

Fig. 3. Overview on ICP-MS instrumentation [34].

sector field ICP-MS in the low mass range are mostly in the ng L^{-1} range [71,72]. The detection limits in quadrupole ICP-MS are higher due to lower sensitivity, higher background and interference problems arising [73].

The application of the collision cell represents important progress in ICP-MS instrumentation which is relevant for improving the detection limits in ICP-MS for the analysis of high-purity materials. Recently, an excellent review on the application of the collision cell in ICP-MS was given by Tanner et al. [74], which describes the design, operation and application of the collision cell in ICP-MS.

The advantage of ICP-MS is the fast calibration procedure and trace for ultratrace analysis of a multitude of aqueous solutions of elements in short time because the ion source of an ICP-MS works at atmospheric pressure. Furthermore, an easy coupling of each ICP mass spectrometer type with alternative sample introduction systems for solids (e.g., laser ablation (LA) or electrothermal evaporation (ETV)), liquids (high-performance liquid chromatography (HPLC), capillary electrophoresis (CE)) or gases (gas chromatography (GC)) can be realized.

3.7. Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS)

LA-ICP-MS is a very sensitive solid analytical technique which allows the fast analysis of high-purity solid samples without sample preparation. In comparison to ICP-MS for the analysis of solution by LA-ICP-MS, time-consuming sample preparation for solid materials can be avoided and the danger of contaminations during the determination of trace analysis can be reduced to a minimum. In LA-ICP-MS the evaporation of sample material by a focused laser beam (see Fig. 2) is carried out mostly in an argon atmosphere under normal pressure. The coupling of a laser ablation system to ICP-MS is very easy—a schematic LA-ICP-QMS using a commercial laser ablation system together with the quadrupole ICP-MS (Elan 6000) is shown in Fig. 4. Basic investigations on the laser ablation process (e.g., of transport of particles, fractionation effects, influence of experimental parameters such as laser power density, wave length, pulse frequency on laser ablation process or molecular ion formation) and application of LA-ICP-MS are described in different papers [4,6,15,16,75–94]. Furthermore, with LA-ICP-MS a rapid "fingerprinting"

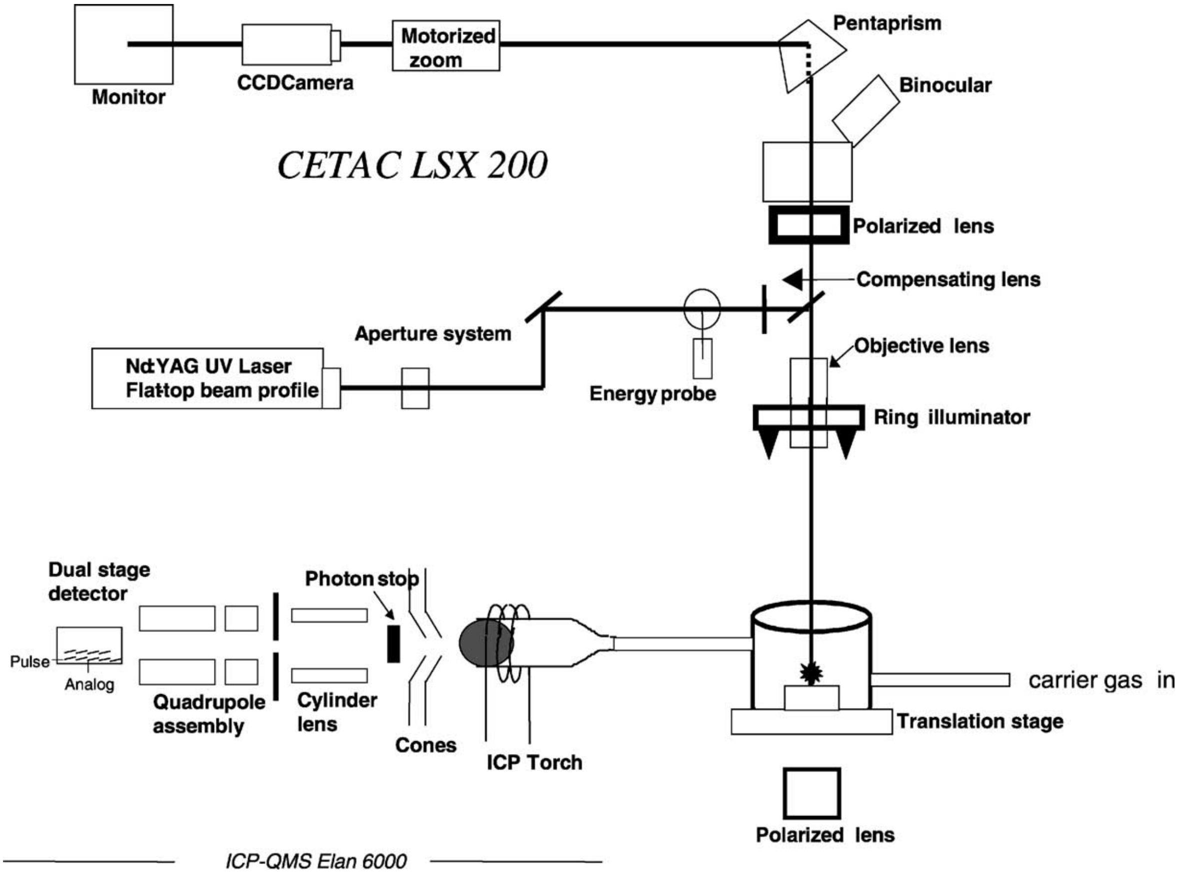

Fig. 4. Experimental arrangement of LA-ICP-QMS.

of unknown solid samples can be performed. For example, Leach and Hieftje [95] identified 33 alloys of different matrix compositions (for elemental concentration >0.1%) using single-shot LA-ICP-TOFMS. A major advantage of LA-ICP-MS is the possibility of performing spatially resolved analysis, which can be used for the micro-local analysis of inhomogeneities in any materials.

Table 3 summarizes some features of inorganic mass spectrometric methods, such as the detection limit, the variation of the relative sensitivity coefficients (RSC) of elements, the accuracy and the precision, the advantages and the limits for determination of trace elements in high-purity solid materials. The precision of quantitative trace element determination is mostly between 2 and 5% R.S.D. (relative standard deviation) for homogeneous sample materials.

4. Quantification of analytical results

The task of inorganic mass spectrometry is obtain accurate and precise element concentrations, therefore a careful quantification of analytical results is required. Often quantification is hampered if no SRM with similar matrix composition and certified trace element concentrations exists. Such SRMs (e.g., from NIST) are available for only a few metals (e.g., Cu, Fe, Al, Zn, Zr and alloys) and semiconductors (e.g., Si). Unfortunately, usually only a few selected trace

Table 3
Comparison of inorganic mass spectrometric methods for determination of trace elements in high-purity solid materials

Method	Detection limit ($\mu g\,g^{-1}$)	RSC	Calibration	Accuracy/precision (with SRM)	Advantage	Limits
GDMS	0.0005–0.1	0.2–5	SRM	++/++	High sensitive	Insulators
SIMS	0.001–0.1	10^3–10^6	Ion implanted standards	+/+	Surface analysis	Matrix effect, molecular ions
SNMS	10–100	0.3–3	Ion implanted standards	+/+	Surface analysis	High detection limit
SSMS	0.001–0.1	0.3–3	SRM	+/+	High sensitive at high $m/\Delta m$	Expensive
LIMS	0.001–0.1	0.8–2	SRM	+/+	For insulators high sensitive	Expensive
ICP-MS	0.000001–0.001	–	Solution calibration	++/++; IDA: +++/++	Fast, cheap, high sensitive	Decomposition, interferences
LA-ICP-MS	0.0001–0.001	0.3–3	SRM, solution calibration	+/+	Fast, high sensitive, insulators	Interferences

element concentrations in the given matrix are certified. Whereas solid mass spectrometry in general requires SRMs for quantification (e.g., for the determination of RSCs) ICP-MS more frequently uses SRMs for verifying the accuracy of analytical data. In contrast to solid mass spectrometry, the quantification possibilities in ICP-MS are very easy (also without SRMs) using calibrated standard solutions with a well-defined analyte concentration. Due to this advantage and the good accuracy and precision of trace element determination ICP-MS is increasingly used for the certification of trace element concentrations in SRMs.

4.1. Calibration of inorganic mass spectrometry using solid standard reference materials or synthetic laboratory standards

The quantification of measured ion intensities, e.g., in SSMS, LIMS or LA-ICP-MS, can be carried out using experimentally determined RSCs as the correction factor. The RSCs of elements are a function of the matrix composition, chemical and physical properties of the elements and sample, the evaporation and ionization process and experimental parameters. For the determination of relative sensitivity coefficients (RSC = measured value/certified value) one standard reference material (similar matrix) is required, but only those elements can be quantified, for which element concentrations in the standard reference material have been certified with reliable values. Correction using RCSs, for a long time, was the dominant calibration procedure in solid mass spectrometric techniques. The range of RSCs varied in SSMS and SNMS from 0.3 to 3 for most elements, in GDMS and LIMS between 0.2 and 5 and in LA-ICP-MS between 0.2 and 3 (see Table 3). In contrast, a large variation of RSCs as a function of matrix and experimental parameters of up to 6 orders of magnitude is observed in SIMS.

If more SRMs (at least 3) with differentiated concentrations of trace elements but similar matrices are available, quantification of the analytical results obtained by solid state mass spectrometry can be performed using calibration curves—similar to quantification in ICP-MS on aqueous solutions. This procedure is more time-consuming and the element concentrations should be in the calibration range. Calibration via calibration curves was demonstrated for the determination of U and Th in zeolites by LA-ICP-MS [80] and for trace analysis in platinum by GDMS [96].

Because often no matrix-matched reference material is available synthetic laboratory standards with the same matrix composition prepared in different laboratories can help for quantification purposes. For example, van Straaten et al. [96] doped high-purity platinum powder with selected trace elements (from 1 to 1000 $\mu g\,g^{-1}$) and proposed a quantification procedure by external calibration for the trace analysis of high-purity platinum by GDMS. Synthetic laboratory standards were also produced in our laboratory for trace element determination, e.g., in ceramic components of the solid oxide fuel cell [81], graphite [77] and for GaAs [66]. Synthetic (matrix-matched) solid standard samples were prepared from the high-purity matrix doped with trace elements in given concentrations. For example, Pickhardt and Becker [77] prepared a homogeneous graphite standard with 14 trace elements (0.5 $\mu g\,g^{-1}$) and determined an accuracy of 1–7% with an R.S.D. of 2–13%.

4.2. Calibration using aqueous standard solutions and highly enriched isotope spikes in ICP-MS and LA-ICP-MS

The most common quantification procedures using aqueous standard solutions in ICP-MS are external calibration (a calibration curve using aqueous standard solutions with increasing analyte concentration is produced before measuring the sample solution) and standard (analyte) addition (where the standard solutions with different analyte concentrations for calibration were added to the sample solution). The standard addition technique is applied especially in routine mode in ICP-MS to consider matrix effects. A third quantification procedure is the application of IDA [60,61], which is increasingly used for accurate trace element determination. In IDA a highly enriched isotope tracer or “spike” of the element to be determined with a well-known concentrations is added to the sample so that the determination of impurities in high-purity materials is performed by measuring changed isotope ratios in the sample-spike mixture compared to those in the sample and high-enriched isotope tracer.

These three different calibration strategies in ICP-MS were introduced for solution-based calibration in LA-ICP-MS. The external calibration technique was developed in our laboratory for geological and ceramic samples using lithium borate fused targets [75] and applied if a high-purity matrix-matched blank target is available (e.g., for graphite) [77]. The standard addition technique was developed for high-purity materials (e.g., platinum) if no blank sample with higher purity than the investigated material is available [15]. As a one-point calibration the isotope dilution technique is advantageous for small sample amounts and was applied for Ag and Pb determination in platinum and palladium nanoclusters [83,97]. As the experimental arrangement for solution calibration in LA-ICP-MS for all the calibration techniques discussed we proposed the single gas flow injection. In this case, the high-enriched isotope solution is nebulized using an ultrasonic nebulizer (USN) or microconcentric nebulizer with desolvator (Aridus) coupled to a laser ablation chamber where the aerosol is mixed with laser-ablated material in the laser ablation chamber [97]. The nebulizer gas flow rate for USN or Aridus, which is used as the carrier gas flow for the transport of dry aerosol from USN via a laser ablation chamber into the ICP, was optimized in respect to maximum analyte ion intensity. The dry mixed aerosol is atomized and ionized in the inductively coupled plasma at an rf power of 1150 W. In all solution-based calibration strategies the different element sensitivities in LA-ICP-MS and ICP-MS must be considered. These differences in sensitivities were corrected using a defined correction factor via an internal standard element. For example, Cu with known concentration was chosen for the application of the isotope dilution technique for Pb determination in high-purity platinum certified reference material NIST 681 [83,97]. In solution calibration all elements can be easily determined and no standard reference material is required. The matrix effects were considered by matrix matching, but the possible fraction effect must be minimized by optimization of experimental parameters.

5. Application of inorganic mass spectrometry for trace and ultratrace analysis

Inorganic mass spectrometric techniques are universal and sensitive analytical methods for the characterization of quite different types of materials. Some selected application fields for inorganic mass spectrometry in trace and ultratrace analysis are summarized in Fig. 1. SSMS, GDMS, ICP-MS and LA-ICP-MS are used for the multielement determination of trace and ultratraces in metals, semiconductors, insulators and technical products. By surface analytical methods such as SIMS, SNMS, GDMS and LA-ICP-MS an additional determination of contamination on surfaces, lateral elemental distribution and depth profiling can be performed.

5.1. Application of inorganic mass spectrometric methods in trace analysis of metals, alloys and semiconductors

All solid state mass spectrometric methods (e.g., SSMS, GDMS or LA-ICP-MS) allow the multielement analysis of trace elements in any solid material with a minimum of sample preparation. An example of a recent SSMS application on high-purity indium by a Japanese semiconductor company (DOWA MINING CO., LTD. [98]) is given in Table 4. The excellent detection limits for light elements—abundant in nature and therefore difficult to determine—(such as Al, Si, P, S, K and Ca) in the low ng g^{-1} range are quite remarkable. For these elements the detection limits were determined mainly by blank values. It should be noted that SSMS with the given detection limits in the low ng g^{-1} range is one of the rare trace analytical techniques which is able to determine the purity of 69–79 material. The sum of impurity of indium given in Table 4 is $<0.65\,\mu g\,g^{-1}$, that means the purity in respect to analyzed elements is 99.999935%.

Table 4
Results of trace analysis of high-purity indium and zinc by SSMS and GDMS [98]

High-purity indium concentration ($\mu g\, g^{-1}$)[a]			High-purity zinc concentration ($\mu g\, g^{-1}$)[a]		
Al < 0.005	Mn < 0.01	Cd < 0.07	Na < 0.01	Ca < 0.05	Cd < 0.05
Si < 0.005	Fe < 0.01	In < 0.02	Al < 0.01	Cr < 0.03	Sb < 0.01
P < 0.005	Ni < 0.01	Sn < 0.06	Si < 0.01	Fe < 0.01	Sn < 0.01
S < 0.005	Cu < 0.01	Sb < 0.04	S < 0.03	Ni < 0.01	Tl < 0.01
Cl < 0.01	Zn < 0.02	Te < 0.07	Cl < 0.03	Cu < 0.05	Pb < 0.01
K < 0.01	Ge < 0.04	Au < 0.04	K < 0.01	Ag < 0.01	Bi < 0.01
Ca < 0.01	As < 0.02	Ti < 0.08			
Cr < 0.01	Se < 0.03	Bi < 0.06			

DOWA MINING CO., LTD., Semiconductor Materials Group, Tokyo.

[a] Shape of sample: shot, ingot, disk, rod for MBE.

Fifteen years ago Grasserbauer [9] demonstrated the difficulties of mass spectrometric techniques (GDMS, SSMS and SIMS) in the ultratrace analysis of high-purity refractory metals (e.g., high-purity molybdenum and tungsten). Whereas for Fe and Ni in molybdenum the data measured by three different solid mass spectrometric techniques are in sufficient agreement, for some elements such as Ca, K, Mg, Si, As and Cr, the measured concentrations varied by 1 order of magnitude and more. Nowadays, using ICP-MS it is possible to determine accurate trace element concentrations in any matrix after a complete digestion due to significantly better calibration possibilities. In order to determine the true element concentration in a high-purity refractory material with a high melting point an independent absolute analytical non-mass spectrometric technique was applied which does not require a standard reference material—therefore neutron activation analysis was used for comparison. In contrast significantly better agreement of trace element concentrations in the low ng g^{-1} range measured by SSMS and GDMS was found by Mykytiuk et al. [99]. The authors demonstrated the excellent detection limits for a lot of elements in the sub-ng g^{-1} range for the plasma mass spectrometric techniques applied; e.g., detection limits down to 0.4 ng g^{-1} (Mn in GDMS) and 0.8 ng g^{-1} (Mg in SSMS) were determined.

Carbon and gases, such as hydrogen, oxygen, nitrogen and noble gases are very difficult to determine by mass spectrometry. Wiedemann et al. [100,101] used SSMS with photographic ion detection for the characterization of high-purity GaAs single crystals in respect to the determination of C, B, N, O, F (due to high blank values) in the low ng g^{-1} range.

However, for such ultratrace analysis a careful (often time-consuming) cleaning procedure for the ion source is required and quantification is difficult if no standard reference material exists. Van Straaten et al. [96] analyzed the prepared synthetic laboratory platinum standards and measured 14 trace elements in the ng g^{-1} and μg g^{-1} concentration range with detection limits from 3 to 30 ng g^{-1}. The detection limits of trace analysis on a high-purity platinum sample (NIST SRM 681) measured by GDMS vs. LA-ICP-MS (using solution-based calibration) [15] are summarized in Table 5. The detection limits and the accuracy of analytical results in LA-ICP-MS are mostly better than in GDMS. LA-ICP-MS with solution calibration allows all metallic (and some nonmetallic) trace elements to be analyzed. Recently, IDA in LA-ICP-MS using a solution-based calibration method was developed for the determination of Ag and Pb on small amounts of platinum and palladium nanoclusters for future nanoelectronic application [97].

In spite of large matrix effects and a high molecular ion formation rate, SIMS is able to determine the trace element concentration in metals or semiconductors using suitable SRMs. For quantification purposes in SIMS (and SNMS) implanted calibration standards can be used where the distribution of the implanted

Table 5
Detection limits of trace element determination on a high-purity platinum sample (NIST SRM 681) in LA-ICP-QMS using solution-based calibration [15] and GDMS [96]

Element	Detection limit ($\mu g\,g^{-1}$)	
	LA-ICP-MS	GDMS
Co	0.05	n.d.
Cu	0.04	0.009
Zr	0.01	n.d.
Rh	0.003	0.006
Ag	0.002	0.01
Pd	0.003	0.005
Hf	0.006	n.d.
Ir	0.001	0.03
Pb	0.003	1
U	0.003	n.d.
R.S.D. (%)	5	5–10
Accuracy (%)	<8	<15
Analysis time (h)	≈1	≈2

n.d.: Not determined.

element is a function of the sputter rate (which correlates with the depth). For example, Zn, B, Si, Sn, S, Se and Te were determined in a synthetic GaAs laboratory standard (doped with 10 elements in the $\mu g\,g^{-1}$ range—prepared by the liquid encapsulation vertical Bridgeman technique) using single-element ion-implanted GaAs certified reference standards (Charles Evans & Associates) for quantification with good accuracy and precision as demonstrated in ref. [66]. In order to determine the concentrations of doped elements ICP-MS and ICP-AES (inductively coupled plasma atomic emission spectrometry) were applied after the digestion of a synthetic GaAs laboratory standard in high-purity HNO_3/H_2O_2 mixture. By using the results of SIMS, ICP-MS and ICP-AES for a selected piece of synthetic laboratory GaAs standard, relative sensitivities (RSCs) of elements were determined in SSMS, rf GDMS and LA-ICP-MS. These RSCs were used as correction factors of the measured concentration in unknown GaAs samples [66]. In order to reduce matrix effects in ICP-MS, a procedure for complete GaAs matrix separation in a chlorine–argon stream at 280 °C was evaluated. The recoveries of 24 elements after the chlorination of GaAs matrix was nearly 100% for most elements. The detection limits of ultratrace analysis after trace–matrix separation (in the low $ng\,g^{-1}$ range and below) were better by about 1 order of magnitude compared with measurements without matrix separation [66].

The coupling of an rf glow discharge ion source to the double focusing sector field ICP-MS “Element” (Finnigan MAT) and its application for the trace analysis of high-purity GaAs is described in ref. [102]. The detection limits for the determination of trace impurities in GaAs matrix measured by rf GDMS are down to $1\,ng\,g^{-1}$ (at low mass resolution: $m/\Delta m = 300$) and $10\,ng\,g^{-1}$ (at medium mass resolution: $m/\Delta m = 3000$). Whereas Si determination by ICP-MS (after chemical dissolution) is very difficult due to the volatility of some silicon compounds solid state mass spectrometry is more suited. A comparison of the results of silicon determination by rf GDMS [$(1.1 \pm 0.2) \times 10^{19}$ atoms cm^{-3}] and SIMS [$(1.2 \pm 0.2) \times 10^{19}$ atoms cm^{-3}] in a Si doped GaAs single crystal demonstrated the capability of the analytical techniques [102].

In respect to the characterization of trace and ultratrace elements in high-purity materials, pioneering work in TIMS in combination with IDA was done in Heumann’s working group, e.g., by the determination of U, Th, Ca, Fe, Cr, Ni, Cu and Cd in high-purity refractory metals or high-purity titanium and cobalt after trace–matrix separation [103–105]. For example, Beer and Heumann [105] determined uranium ultratraces in a cobalt matrix with a detection limit of $0.007\,ng\,g^{-1}$. The analysis of long-lived radionuclides at ultratrace level in microelectronic-relevant high-purity materials is of special importance because the radioactive elements disturb the electronic properties of devices. In spite of excellent low detection limits in the low ppt range in solid samples and the possibility to obtain accurate analytical data using the isotope dilution technique after matrix separation TIMS is practically no longer used due to the great experimental efforts required.

In general, the analytical procedures of GDMS, SIMS, LIMS, SIMS, TIMS and SSMS applied for trace and ultratrace element determination in high-purity materials and the experimental equipment required are expensive so that worldwide easier and cheaper techniques—the more sensitive solid-state mass spectrometric technique LA-ICP-MS [4,16,75,76] and ICP-MS after decomposition of solid samples—were developed and applied resulting in similar low or lower detection limits for most trace elements, shorter analysis time, better accuracy and precision.

Recently, Vogl [61] demonstrated the capability of ID-ICP-MS for the determination of Cd and Tl in high-purity Zn (CRM 325/2R) which yielded the most accurate data in comparison to ICP-MS and was used for certification of SRMs. Selected applications of inorganic mass spectrometry in trace and ultratrace analysis of high-purity conducting and semiconducting materials are summarized in Table 6.

Matrix separation (liquid–liquid extraction) was applied for the trace analysis of trace impurities in Ta, Sc, zircaloy and GaAs matrix by ICP-MS in our laboratory [66,106,111,118]. For example, bis(2-ethyl-hexyl)orthophosphoric acid in toluene was used to separate zirconium in zircaloy matrix from an aqueous phase at pH 2 containing most impurities in the given matrix [111]. Thirty-four trace elements were determined in zircaloy-4 (NIST SRM 360 b) by an external calibration and isotope dilution technique using ICP-QMS (Elan 5000), whereas trace impurities in high-purity GaAs (99.9995%) were determined by ICP-SFMS after the separation of matrix elements by chlorination of GaAs in a chlorine–argon stream at 280 °C. The detection limits of trace elements in the low $\mathrm{ng\,g^{-1}}$ range were about 1 order of magnitude better than without matrix separation [66]. We found that ultratrace analysis by ICP-SFMS on ultrapure GaAs after matrix separation yielded comparable results (also the detection limits are similar) at the low ppb range as were obtained by direct solid mass spectrometric techniques (GDMS). Considering the time-consuming sample preparation steps for ICP-MS measurements solid-state mass spectrometric measurements are advantageous.

In spite of the necessary sample preparation steps, nowadays most applications of trace and ultratrace analysis on metals and semiconductors are performed by ICP-MS.

5.2. Application of inorganic mass spectrometric methods in trace analysis of nonconductors

Table 7 summarizes the application of inorganic mass spectrometry in the trace analysis of nonconducting materials. In order to avoid contamination by electrode preparation nonconducting high-purity glass samples or single crystals such as CaF_2 were analyzed directly with a conducting counter electrode (from high-purity tantalum) by so-called gliding SSMS as described in [133].

Recently, a powerful multielement analytical technique was developed in our laboratory using LA-ICP-MS for the sensitive determination of trace impurities in thin glass filaments used as reinforcing material in the construction industry or as optical fibers transmitting information via light pulses [125]. The trace analysis was carried out directly on very thin solid strands (without any sample preparation steps) by LA-ICP-MS by fixing a bundle of thin glass fibers (with a filament diameter of about 10–20 μm) on a thin special tape of a target holder. In order to verify the trace analytical data the ablated glass fibers were analyzed both by a quadrupole (LA-ICP-QMS) and by a double-focusing sector-field mass spectrometer (LA-ICP-SFMS). The simultaneous determination of 45 trace elements in glass fibers in the $\mathrm{\mu g\,g^{-1}}$ and $\mathrm{ng\,g^{-1}}$ range by LA-ICP-QMS was performed.

The detection limits of trace elements in glass fibers using the LA-ICP-MS with a quadrupole analyzer were in the sub-$\mathrm{\mu g\,g^{-1}}$ range whereas using a sector-field mass spectrometer (LA-ICP-SFMS) the detection limits could be improved by 3–4 orders of magnitude down to the low and sub-$\mathrm{ng\,g^{-1}}$ concentration range.

Because ultratraces of α-emitting, natural long-lived radionuclides (U and Th) disturb the electronic properties of electronic devices the determination of long-lived radionuclides in microelectronically relevant high-purity materials is required; e.g., the semiconductor industry needs new ultrasensitive analytical

Table 6
Selected application of inorganic mass spectrometry in trace analysis of high-purity conducting and semiconducting materials

Samples	Equipment	Analyzed elements	Limits of detection (LOD)	References
Tungsten, molybdenum	SIMS, SSMS, GDMS	20–30 elements	Low ng g^{-1} range	[9]
Aluminum, gallium	GDMS, SSMS	17 elements	0.0003–0.008 μg g^{-1}	[99]
Aluminum-based alloys	GDMS	33 elements	0.2 ng g^{-1} (U, Th)	[46]
Platinum powder	GDMS VG 9000	Mg, Al, Ca, Fe, Cu, Zn, Ru, Rh, Pd, Ag, Te, Ir, Pb, Au	3–30 ng g^{-1}	[96]
Gallium arsenide	GDMS, SSMS	23 elements	GDMS: 0.4 ng g^{-1} (Mn); SSMS: 0.8 ng g^{-1} (Mg)	[99]
Titanum	TIMS (THQ) isotope dilution	Cu, Pb, Cd, Ni, Fe, U, Th	0.07 ng g^{-1} (U, Th)–4 ng g^{-1} (Ni)	[104]
Cobalt	TIMS (THQ) isotope dilution	Fe, Zn, Tl, Cd, Th, U	0.007 ng g^{-1} (U)–1 ng g^{-1} (Tl)	[105]
Scandium	SSMS, ICP-QMS (Elan 5000)	43 elements, ICP-MS after trace–matrix separation	SSMS: 0.05 μg g^{-1} (Tb)–1 ng g^{-1} (B); ICP-QMS: 0.002 μg g^{-1} (Tb)–1.2 μg g^{-1} (Fe)	[106]
Au, Re, Pd, Pt	LA-ICP-QMS (Elan 6000)	56 elements, solution-based calibration	0.6 ng g^{-1} (Ho)–1.2 μg g^{-1} (Se)	[107]
Platinum	LA-ICP-QMS (Elan 6000)	Co, Ni, Cu, Zr, Ru, Rh, U, Ag, Pd, In, Sn, Hf, Ir, Pb	1 ng g^{-1} (Ir)–200 ng g $^{-1}$ (Sn)	[15]
Graphite	LA-ICP-QMS (Elan 6000)	Li, Sc, Ti, Cr, Mn, Co, Zn, Sr, Mo, Sn, Ba, Ce, Hf, Pt, Au	5 ng g^{-1} (Yb, Pr)–50 ng g^{-1} (Ce)	[77]
Ni alloy	ETV-ICP-QMS	Pb, Bi, Te	In solution: 2 pg g^{-1} (Bi)–4 pg g^{-1}	[108]
Gallium arsenide (matrix separation)	ICP-MS, SIMS, SSMS, rf GDMS,	Zn, B, Si, Ge, Sn, Sb P, S, Se, Te	ICP-MS: low ng g^{-1}; rf GDMS: 10 μg g^{-1} (Sn)	[66]
Silver alloy	LA-ICP-MS, ICP-MS	Zn, Cd, Sn, Sb, Au, Pb, Bi	Sub-μg g^{-1}–2 μg g^{-1}	[109]
Zirconium	LIMS	31 elements	Sub-μg g^{-1} range	[110]
Zircaloy	ICP-QMS (Elan 5000) (matrix separation)	34 elements, isotope dilution	0.05 μg g^{-1} (Rb, Sb)	[111]
Osmium	ICP-QMS (Elan 5000)	Na, Mg, Al, Ti, Cr, Ni, Zn, Sr, Zr, B, Mn, Fe, Co, Cu	1 ng g^{-1} range	[112]
Antimony (matrix separation)	ICP-QMS (PlasmaQuad3)	Se, Pd, Ag, In, Ta, W, Pt, Au, Hg, Tl	0.3 ng g^{-1} (Cd)–3.9 ng g^{-1} (Pb)	[113]
Copper	ICP-SFMS (Element)	9 elements, 49 LODs	0.1 ng g^{-1} (Ir)–2000 ng g^{-1} (P)	[17]
Indium	ICP-QMS (PlasmaQuad)	38 elements	0.03 μg g^{-1} (U)–6 μg g^{-1} (B)	[114]
Chromium	ICP-QMS (Elan 6100 DRC)	Nb, Zr	2 ng g^{-1} (Nb)–5 ng g^{-1} (Zr)	[82]
Tantalum (matrix separation)	ICP-QMS (Seiko SPQ 9000)	B, P	90 ng g^{-1} (10σ)–40 ng g^{-1} (10σ)	[115,116]
Tantalum (matrix separation)	ICP-MS (Element)	39 elements	1 ng g^{-1} (Lu, Tm)–6 ng g^{-1} (V)	[117]
Tantalum (matrix separation)	ICP-QMS (Elan 5000)	25 elements	10 ng g^{-1} (Ce)	[118]
Plutonium, beryllium	ICP-QMS (VG PlasmaQuadPQ2), SSMS “MS 702”	52 elements	For Pu matrix: 4 ng g^{-1} (Cu)–20 ng g^{-1} (Ca)	[119]
Gold	ICP-QMS (Elan 6000)	As (flow injection, hydride generation)	55 ng g^{-1}	[120]

Table 7
Selected application of inorganic mass spectrometry in trace analysis of high-purity nonconducting materials

Samples	Equipment	Analyzed elements	Limit of detection	References
TiO_2	TIMS "THQ" IDA	Cu, Pb, Tl, Cd, Ni, Cr, Fe, U after matrix separation	1.8 ng g^{-1} (Tl)–2.5 μg g^{-1} (Fe)	[121]
ZrO_2	GDMS VG 9000	57 elements	0.006–185 μg g^{-1}	[52]
BN, BC_4, Si_3N_4, WC	LIMS, SSMS	F, Na, Mg, Al, P, S, Cl, K, Ca, Ti, Fe, Co, Zn, Cu	Low ng g^{-1} range	[122]
Silicon carbide	rf GDMS, LIMS	B, Al, Ti, V, Cr, Cu, Zr	rf GDMS and LIMS: 10 μg g^{-1} (Cr)	[123]
Al_2O_3	ETV-ICP-QMS (Elan 5000)	Ca, Fe, Ga, Mg, Mn, Na, Ni, V	0.07 μg g^{-1} (Ga)–1.1 μg g^{-1} (Na)	[124]
Glass fibers	LA-ICP-SFMS, Element	Sb, Cs, REE, Hf, Ta, Pb, Th, U	0.03 ng g^{-1} (U, Th)	[125]
SiO_2	LA-ICP-QMS (Elan 5000)	Li, B, Na, Mg, Al, K, Ca, Ti, V, Cr, Fe, Mn, Cu, Zr, Ba, Pb, 24 ng g^{-1} (Sb)	0.02 ng g^{-1} (Cu)–20 ng g^{-1} (Al)	[85]
Photoresist	LA-ICP-QMS (Elan 5000)	Al, Cu, Pt, Au, Th, U, Cu, Ga, As, In	20–285 ng mL^{-1}	[126]
SiC, ZrO_2, Al_2O_3 (matrix separation)	ICP-QMS VG PlasmaQuadPQ2	Li, B, Na, Mg, Al, Ca, Sc, Ti, V, Cr, Mn, Fe, Ni, Co, Cu, Zn, Ga, Sr, Y, Zr, Nb	5 ng g^{-1} (Co)–4.7 μg g^{-1} (Na)	[127]
Al_2O_3 (matrix separation)	ICP-SFMS, Element	V, Cr, Mn, Fe, Ga, Co, Ni, Cu, Zn	0.4 ng g^{-1}–1400 ng g^{-1}	[128]
La_2O_3 (matrix separation)	HPLC-ICP-MS	Ce, Pr, Nd, Sm	0.11 μg g^{-1} (Sm)–0.7 μg g^{-1} (Ce)	[129]
$La_{0.65}Sr_{0.3}MnO_3$	LA-ICP-MS, SSMS, ICP-MS (Elan 5000)	20 elements	Low μg g^{-1} range and below	[130]
$La_{0.65}Sr_{0.3}MnO_3$	rf GDMS	B, Mg, Al, Ni, Co, Zn	10 μg g^{-1}	[131]
$La_{0.65}Sr_{0.3}MnO_3$ layers Ni-cermet, YSZ	LA-ICP-MS, SSMS, ICP-MS (Elan 5000), rf GDMS, SIMS	B, Mg, Al, P, Si, Ti, Cr, Co, Ni, Cu, Zn, Zr, Ba, Ce, Pb	Low μg g^{-1} range	[132]

methods for the determination of long-lived radionuclides in so-called "low-α materials" (e.g., in low-α solder paste, SnPb alloys) with very low-α activity ($<0.02\,\mathrm{count\,cm^{-2}\,h^{-1}}$). ICP-MS and LA-ICP-MS could be the methods of choice for future application due to their high sensitivity and low detection limits, because α-spectrometry needs time-consuming sample treatment, enrichment procedures and long measurement times at this activity level. The analysis of uranium and thorium traces in $(Ba,Sr)TiO_3$ ferroelectrical materials by ICP-MS was described by Fukuda and Sayama [134].

The determination of trace impurities in high-purity zirconium oxide by ICP-MS is difficult due to the chemical resistance of the material. Therefore Kohl et al. [127] described a dissolution technique by means of fusion with ammonia sulphate. The problem with this fusion technique is the amount of impurities present in ammonia sulphate, which determines the detection limits of the analytical method used. In order to improve the detection limits we proposed a microwave-induced digestion and subsequent matrix separation. About 200 mg of sample was digested using a mixture of highest-purity fluoride acid, nitric acid and hydrogen peroxide in a microwave oven [135]. The sample was completely dissolved. After separation of matrix by liquid–liquid extraction with 50% HDEHP in toluene the organic phase was carefully separated and discarded and the aqueous phase was analyzed by ICP-SFMS. The detection limits were determined by ICP-SFMS for multielement trace element determination by ICP-SFMS down to $500\,\mathrm{pg\,g^{-1}}$.

Wende and Broekaert [124] described the trace analysis of contaminants in high-purity Al_2O_3 by electrothermal evaporation (ETV) ICP-QMS, which is an interesting alternative to LA-ICP-MS but only for special analytical problems. The detection limits for trace elements in ceramic powders, e.g., Al_2O_3 measured by sector-field ICP-MS and quadrupole-based ICP-MS with and without trace–matrix separation, were compared by Jakubowski et al. [128]. However, the danger of possible contamination during sample preparation is enormous. In order to minimize the risk of contamination on-line separation with ICP-MS, closed systems and lower consumption of chemicals are proposed by Broekaert [12]. ICP-MS and LA-ICP-MS could be the methods of choice for future application due to their high sensitivity and low detection limits in the low $\mathrm{pg\,g^{-1}}$ range in solid materials.

5.3. Characterization of layered systems and surface contamination

Jäger et al. [131] applied rf GDMS for the determination of trace elements (B, Mg, Al, Ni, Co, Zn, Cu, Ga, As, In) in ceramic perovskite layers $La_{0.65}Sr_{0.3}MnO_3$ of rf GDMS. For the quantification procedure by external calibration via calibration curves the preparation of synthetic laboratory standards from high-purity powdered initial materials doped with trace element concentrations from 20 to $500\,\mathrm{\mu g\,g^{-1}}$ (mixed and pressured to compact samples) was proposed. The detection limits in rf GDMS were below $10\,\mathrm{\mu g\,g^{-1}}$. As a surface analytical method, LA-ICP-MS is also able to directly determine trace impurities in thick ceramic layers and was also applied for the microlocal analysis of ceramic samples with lateral resolution of some μm [4,97]. LA-ICP-MS was demonstrated by Westheide et al. [81] for the determination of 11 and 26 trace elements in thick ceramic layers of solid oxide fuel cells ($La_{0.65}Sr_{0.3}MnO_3$ and yttria-stabilized ZrO_2 (YSZ), respectively). Because no standard reference materials exist for most ceramic materials matrix-matched synthetic lab standards were prepared from high-purity oxides doped with the trace elements of interest. At $0.1–2\,\mathrm{\mu g\,g^{-1}}$, the detection limits observed are 1 order of magnitude better than in rf GDMS.

In addition to sensitive trace element determination in high-purity materials LA-ICP-MS is able to perform depth profiling on thick nonconducting layers, which was investigated in [4] on a multilayer system consisting of $La_{0.65}Sr_{0.3}MnO_3$ and Ni-cermet on yttria-stabilized zirconia for the solid oxide fuel cell, on multilayered glass and metal materials by Mason and Mank [136], on a Ti-based layer deposited on steel and WC/Co substrates by Plotnikov et al. [137] and

Table 8
Application of ICP-MS in trace analysis of high-purity solutions

Samples	Equipment	Analyzed elements	Limits of detection	References
H_2O	ICP-QMS (HP 4500)	17 elements	0.6 ng L^{-1} (Li)–6 ng L^{-1} (Ca, Pb)	[144]
H_2O	ICP-QMS (Elan 6000)	21 elements	0.3 ng L^{-1} (U)–0.15 µg L^{-1} (As)	[73]
H_2O	ICP-SFMS PlasmaTrace	50 elements	Sub-pg L^{-1} (Ho)–10 ng L^{-1} (P, As)–0.1 µg L^{-1} (S)	[71]
H_2O_2	ICP-QMS (Elan 6100) DRC	25 elements	0.01 ng L^{-1} (Rh, In, U)–5 ng L^{-1} (Se)	[143]
Isopropyl alcohol (IPA)	ICP-SFMS, Element	Li, B, Na, Mg, Cr, K, Ca, Cu, Mn, Fe, Ni, Zn, Sn, Pb	0.01 pg L^{-1} (Li)–0.2 pg L^{-1} (Na, Mg, Cr, K, Cu, Mn, Zn)	[145]
H_3PO_4, H_2SO_4, HNO_3, $H_2S_2O_8$, HF, HCl, H_2O_2, H_2O	ICP-SFMS PlasmaTrace 2	Si, P, S, Cl, As, Se, Br	0.001 ng g^{-1} (As in H_2O)–2 µg g^{-1} (Cl in H_2SO_4)	[72]

on Ti-based coatings on steel by Bleiner et al. [138] using a 193 nm where a depth resolution of 0.2 μm was measured. Significantly better depth resolution was obtained in depth profiling by GDMS (>10 nm), SNMS (>3 nm) and SIMS (>5 nm) [132].

ICP-MS was used for the determination of the stoichiometry and a multitude of trace impurities in a small volume of thin $Ba_{0.7}Sr_{0.3}TiO_3$ layers (40 nm) after their dissolution in a small volume of HNO_3/H_2O_2 mixture [139,140].

Apart from the ultratrace analysis of high-purity material for microelectronics (metals, semioconductors or ceramics) especially surface contaminations must be determined because they influence the microelectronic properties of devices. For example, on silicon wafer surfaces for microelectronic applications a cleanness in respect to metallic impurities of $<10^{10}$ atoms cm^{-2} is required. Total reflection X-ray fluorescence analysis (TRXF) is mostly used in routine mode in the microelectronics industry for the determination of silicon surface impurities after vapor phase decomposition (VPD) [32]. In VPD the silicon wafer is deposited in a closed box and treated with HF vapor which etches the silicon oxide layer. A small droplet (e.g., 100 μL $H_2O/H_2O_2/HF$ as a scanning solution) is deposited on the wafer surface and scanned using a droplet scanner in order to dissolve surface contaminations. VPD is described by Horn [141], who determined the surface contamination of Al, Fe, Zn by ICP-QMS (e.g., Na—1.16 pg g^{-1} and Fe—0.29 pg g^{-1}) in a small amount of scanning solution. O'Brien et al. [142] analyzed surface contamination on silicon surface after VPD of silicon wafers using the ICP-QMS (Platform) with collision cell. Difficult-to-determine elements (Fe, Cr, Co, Cu, Mn, etc.) were analyzed in the concentration range of 30 ppt cm^{-2} (Mn)–600 ppt cm^{-2} (Al).

5.4. Application of ICP-MS for analysis of high-purity liquids

Water is a matrix which can be easily purified, low detection limits down to sub-fg g^{-1} for elements where no isobaric interference with atomic ions or molecular ions occur were measured by sector-field ICP-MS by Yamasaki et al. [71]. The limits of detection for microelectronic-grade deionized water to analyze elements by ICP-MS with dynamic reaction cells were between 1 ng L^{-1} for B, K, Ca and Zn down to 0.01 ng L^{-1} for Rh, In and U [129]. The trace analysis of high-purity hydrogen peroxide by ICP-MS with a dynamic reaction cell was performed by Völlkopf et al. [143]. The application of a gas-filled dynamic reaction cell allows the dissociation of disturbing molecular ions and a improvement of detection limits. In spike recovery studies the authors checked the accuracy of the analytical method.

Applications of ICP-MS in the trace analysis of high-purity solutions are summarized in Table 8.

6. Conclusions

Inorganic mass spectrometric techniques—and to an increasing extent ICP-MS and LA-ICP-MS—are powerful analytical techniques in determining very low element concentrations in high-purity materials due to their low detection limits. Besides the solid-state mass spectrometric techniques, which allow the direct multielement determination of analytes in the pg g^{-1} range with a minimum of sample preparation, ICP-MS with detection limits in the sub-fg mL^{-1} range in ideal aqueous solution is an excellent tool for the analysis of trace impurities of any liquids (solutions used for cleaning processes or digested and diluted solutions of solid samples). A further improvement of the detection limits of ultratrace contaminants is possible by the application of matrix separation and enrichments of analyte. In order to reduce the analysis time the digested solid samples were often diluted only and analyzed without matrix separation. Subsequently, matrix effects (influence of matrix on ion intensity of analytes or formation of disturbing polyatomic ions) were observed which must be taken into consideration.

Future trends for the trace and ultratrace analysis of high-purity materials focus on the development of analytical methods with multielement capability to obtain higher sensitivity and lower detection limits. The developed techniques should be highly effective and powerful and should also reduce experimental effort and costs. In this way, an improvement of coupling techniques (such as LA, CE and HPLC) could reduce the sample preparation steps and minimize the sample size analyzed. Due to lack of suitable high-purity standard reference materials the significance of absolute quantification techniques (such as isotope dilution analysis) will increase. The precision and accuracy of trace element determination by inorganic mass spectrometry should be improved by the analytical techniques developed and also the verification of trueness. In particular, the creation of valuable reference materials with a multitude of certified trace elements is necessary.

References

[1] J.R. De Laeter, Application of Inorganic Mass Spectrometry, Wiley, New York, 2001.
[2] C.M. Barshik, D.C. Duckworth, D.H. Smith (Eds.), Inorganic Mass Spectrometry, Wiley, New York, 2000.
[3] F. Adams, R. Gijbels, R. Van Grieken (Eds.), Inorganic Mass Spectrometry, Chemical Analysis, vol. 95, Wiley, New York, 1988.
[4] J.S. Becker, H.-J. Dietze, Int. J. Mass Spectrom. 195/196 (2000) 1.
[5] S.K. Aggarwal, H.C. Jain, Introduction to Mass Spectrometry, Indian Society for Mass Spectrometry, 1997.
[6] J.S. Becker, H.-J. Dietze, Spectrochim. Acta B 53 (1998) 1475.
[7] C. Brunnée, Int. J. Mass Spectrom. Ion Process. 76 (1987) 121.
[8] M. Grasserbauer, Mikrochim. Acta 1 (1987) 291.
[9] M. Grasserbauer, Pure Appl. Chem. 60 (1988) 437.
[10] J.S. Becker, J. Westheide, A.I. Saprykin, H. Holzbrecher, U. Breuer, H.-J. Dietze, Mikrochim. Acta 125 (1997) 153.
[11] P. De Bièvre, Adv. Mass Spectrom. 7A (1978) 396.
[12] J.A.C. Broekaert, Analytical Atomic Spectrometry with Flames and Plasmas, Wiley-VCH, Weinheim, Berlin, 2002.
[13] J.S. Becker, H.-J. Dietze, J. Anal. Atom. Spectrom. 14 (1999) 1493.
[14] S. Kozono, S. Takahashi, H. Haraguchi, Anal. Bioanal. Chem. 372 (2002) 542.
[15] J.S. Becker, C. Pickhardt, H.-J. Dietze, J. Anal. Atom. Spectrom. 16 (2001) 603.
[16] S.D. Durrant, J. Anal. Atom. Spectrom. 14 (1999) 1385.
[17] S. Pattberg, R. Matschat, Fresenius J. Anal. Chem. 364 (1999) 410.
[18] F.D. McDaniel, in: E. Kaufmann (Ed.), Methods in Materials Research, Unit 12a.5, Wiley, New York, 2001
[19] R. Matschat, M. Czerwensky, M. Hamester, S. Pattberg, Fresenius J. Anal. Chem. 359 (1997) 418.
[20] G.M. Hieftje, G. Gamez, M. Huang, S.A. Lehn, in: Proceedings of the 29th Federation of Analytical Chemistry and Spectroscopy Societies (FACSS 2002), Providence, 13–17 October 2002, Book of Abstracts, p. 111.
[21] R.S. Houk, N. Praphairaksit, Spectrochim. Acta B 56 (2001) 106.
[22] B. Welz, Atom Absorptions Spektrometrie, Wiley-VCH, Weinheim, Berlin, 1997.
[23] T. Itagaki, T. Ashino, K. Takada, Fresenius J. Anal. Chem. 368 (2000) 344.
[24] A. Montaser, D.W. Golightly (Eds.), Inductively Coupled Plasma Emission Spectrometry, VCH, New York, 1992.
[25] I. Kardjova, S. Arpadjan, L. Jordanova, Fresenius J. Anal. Chem. 367 (2000) 146.
[26] U. Schäffer, V. Krivan, Fresenius J. Anal. Chem. 371 (2001) 859.
[27] D. Wildhagen, V. Krivan, Fresenius J. Anal. Chem. 359 (1997) 239.
[28] L. Moens, R. Dams, J. Radioanal. Nucl. Chem. 192 (1995) 29.
[29] I.E. De Vito, R.A. Olsina, A.N. Masi, Fresenius J. Anal. Chem. 368 (2000) 392.
[30] H. Aiginger, C. Streli, Spectrosc. Eur. 9 (1997) 16.
[31] C. Weiss, J. Knoth, H. Schwenke, H. Geisler, J. Lerche, R. Schulz, H.-J. Ullrich, Mikrochim. Acta 133 (2000) 65.
[32] L. Fabry, S. Pahlke, L. Kotz, P. Wobrauschek, S. Strehli, Fresenius J. Anal. Chem. 363 (1999) 98.
[33] I.T. Platzner, Modern Isotope Ratio Mass Spectrometry, Wiley, New York, 1997.
[34] J.S. Becker, J. Anal. Atom. Spectrom. 17 (2002) 1172.
[35] J.S. Becker, H.-J. Dietze, Fresenius J. Anal. Chem. 368 (1999) 23.
[36] K.G. Heumann, S. Gallus, G. Rädlinger, J. Vogl, J. Anal. Atom. Spectrom. 13 (1998) 1001.
[37] G. Tölg, P. Tschöpel, in: Z.B. Alfassi (Ed.), Determination of Trace Elements, VCH, New York, 1994.
[38] H.-J. Dietze, Massenspektrometrische Spurenanalyse, Akademische Verlagsgesellschaft, Geest & Portig K.G., Leipzig, 1975.
[39] H.-J. Dietze, Analytikertaschenbuch 19 (1991) 249.
[40] R. Gijbels, Talanta 37 (1990) 363.
[41] K.P. Jochum, B. Stoll, J.A. Pfänder, M. Seufert, M. Flanz, P. Maissenbacher, M. Hoffmann, A.W. Hoffmann, Fresenius J. Anal. Chem. 370 (2000) 647.
[42] R.E. Honig, J.R. Woolsten, Appl. Phys. Lett 2 (1963) 138.
[43] H.-J. Dietze, J.S. Becker, Fresenius J. Anal. Chem. 302 (1985) 490.
[44] H.-J. Dietze, J.S. Becker, Laser Ionization Mass Analysis, Chemical Analysis Series, vol. 124, Wiley, New York, 1993, p. 453.
[45] H.J. Heinen, R. Wechsung, H. Vogt, F. Hillenkamp, R. Kaufmann, in: W. Demtröder (Ed.), Laserspektroskopie, Springer-Verlag, Berlin, Heidelberg, New York, 1979, p. 257.
[46] C. Venzago, M. Weigert, Fresenius J. Anal. Chem. 350 (1994) 303.
[47] R.K. Marcus (Ed.), Glow Discharge Spectroscopies, Plenum Press, New York, London, 1993, p. 1.

[48] R. Gijbels, M. van Straaten, A. Bogaerts, Adv. Mass Spectrom. 13 (1995) 241.
[49] W.W. Harrison, W. Hang, X. Yan, K. Ingeneri, C. Schilling, J. Anal. Atom. Spectrom. 12 (1997) 891.
[50] St. De Gent, R. Van Grieken, W. Hang, W.W. Harrison, J. Anal. Atom. Spectrom. 10 (1995) 689.
[51] W. Schelles, St. De Gent, V. Müller, R. Van Grieken, Appl. Spectrosc. 49 (1995) 939.
[52] W. Schelles, R. Van Griecken, J. Anal. Atom. Spectrom. 12 (1995) 49.
[53] A.I. Saprykin, J.S. Becker, H.-J. Dietze, Fresenius J. Anal. Chem. 364 (1999) 763.
[54] A.I. Saprykin, J.S. Becker, H.-J. Dietze, J. Anal. Atom. Spectrom. 10 (1995) 897.
[55] J.S. Becker, A.J. Saprykin, H.-J. Dietze, Int. J. Mass Spectrom. Ion Process. 164 (1997) 81.
[56] G.M. Hieftje, J.H. Barnes IV, P. Roger, M. Sperline, B. Denton, D.W. Koopenaal, C.J. Barinaga, in: Proceedings of the 29th Federation of Analytical Chemistry and Spectroscopy Societies (FACSS 2002), vol. 201, Providence, 13–17 October 2002, Book of Abstracts, p. 117.
[57] W. Hang, X. Yan, D.M. Waye, J.A. Olivares, W.W. Harrison, V. Majidi, Anal. Chem. 71 (1999) 3231.
[58] J. Pisonero-Castro, J.M. Costa-Fernandez, R. Pereiro, N. Bordel, A. Sanz-Medel, J. Anal. Atom. Spectrom. 17 (2002) 786.
[59] K.G. Heumann, S. Eisenhut, S. Gallus, E.H. Hebeda, R. Nusko, A. Vengosh, T. Walczyk, Analyst 120 (1995) 1291.
[60] K.G. Heumann, Mass Spectrom. Rev. 11 (1992) 41.
[61] J. Vogl, in: Presented at DGMS Workshop on New Developments in Inorganic Mass Spectrometry on 35th Conference of German Society of Mass Spectrometry, 3 March 2002.
[62] P. Sigmund, in: R. Behrisch (Ed.), Sputtering by Particle Bombardment I, Springer-Verlag, Berlin, 1981, p. 18.
[63] A. Benninghoven, K.T.F. Janssen, J. Tümpner, H.W. Werner (Ed.), Secondary Ion Mass Spectrometry, SIMS VIII, Wiley, New York, 1992, p. 3.
[64] H. Jenett, Analytikertaschenbuch, vol. 16, Springer-Verlag, Berlin, Heidelberg, 1997, p. 43.
[65] H. Bubert, H. Jenett, Surface and Thin Film Analysis, Wiley-VCH, Weinheim, Berlin, 2002.
[66] J.S. Becker, R.S. Soman, Th. Becker, V.K. Panday, H.-J. Dietze, J. Anal. Atom. Spectrom. 13 (1998) 983.
[67] J.S. Becker, H.-J. Dietze, J.A. McLean, A. Montaser, Anal. Chem. 71 (1999) 3077.
[68] A. Montaser, M.G. Minnich, J.A. McLean, J.A. Lui, J.A. Caruso, C.W. McLeod, in: A. Montaser (Ed.), Inductively Coupled Plasma Mass Spectrometry, Wiley, New York, 1998.
[69] J.A. McLean, J.S. Becker, S.F. Boulyga, H.-J. Dietze, A. Montaser, Fresenius J. Anal. Chem. 208 (2001) 193.
[70] A. Montaser (Ed.), Inductively Coupled Plasma Mass Spectrometry, Wiley, New York, 1998.
[71] S.-I. Yamasaki, A. Tsumura, Y. Takaku, Mikrochem. J. 49 (1994) 305.
[72] H. Wildner, J. Anal. Atom. Spectrom. 13 (1998) 573.
[73] E. Wolf, Z.A. Grosser, At. Spectrosc. 18 (1997) 145.
[74] S.D. Tanner, V.I. Baranov, D. Bandura, Spectrochim. Acta B 57 (2002) 1361.
[75] C. Pickhardt, J.S. Becker, H.-J. Dietze, Fresenius J. Anal. Chem. 368 (2000) 173.
[76] J.S. Becker, C. Pickhardt, H.-J. Dietze, J. Anal. Atom. Spectrom. 16 (2001) 603.
[77] C. Pickhardt, J.S. Becker, Fresenius J. Anal. Chem. 370 (2001) 534.
[78] R.E. Russo, X. Mao, J.J. Gonzalez, S.S. Mao, J. Anal. Atom. Spectrom. 17 (2002) 1072.
[79] G.C.-Y. Chan, W.T. Chan, X. Mao, R.E. Russo, Spectrochim. Acta 55B (2000) 221.
[80] C. Pickhardt, I. Brenner, J.S. Becker, H.-J. Dietze, Fresenius J. Anal. Chem. 368 (2000) 79.
[81] J.Th. Westheide, J.S. Becker, R. Jäger, H.-J. Dietze, J.A.C. Broekaert, J. Anal. Atom. Spectrom. 11 (1996) 661.
[82] B. Hattendorf, D. Günther, M. Schönbächler, A. Halliday, Anal. Chem. 73 (2001) 5494.
[83] C. Pickhardt, J.S. Becker, M. Mertig, W. Pompe, Trace and ultratrace analysis on small amounts of platinum and palladium clusters by LA-ICP-MS, in: Proceedings of the Winter Conference on Plasma Spectrochemistry, Scottsdale, AZ, 6–12 January 2002, Book of Abstracts, p. 175.
[84] H. Lui, X. Mao, R.E. Russo, J. Anal. Atom. Spectrom. 17 (2002) 1115.
[85] J.S. Becker, D. Tenzler, Fresenius J. Anal. Chem. 370 (2001) 637.
[86] P.D. Mason, A.J.G. Mank, J. Anal. Atom. Spectrom. 16 (2001) 1381.
[87] D. Günther, I. Horn, B. Hattendorf, Fresnius J. Anal. Chem. 368 (2000) 4.
[88] J.S. Becker, C. Pickhardt, H.-J. Dietze, Int. J. Mass Spectrom. 202 (2000) 280.
[89] M. Guillong, I. Horn, D. Günther, J. Anal. Atom. Spectrom. 17 (2002) 8.
[90] C. Latkoczy, D. Günther, J. Anal. Atom. Spectrom. 17 (2002) 1264.
[91] J.T. Westheide, Rep. Res. Centre Juelich 3431 (1997) 1.
[92] P.R.D. Mason, W.J. Kraan, J. Anal. Atom. Spectrom. 17 (2002) 858.
[93] M. MotelicaHeino, P. Le Coustumer, O.F.X. Donard, J. Anal. Atom. Spectrom. 16 (2001) 542.
[94] M. Guillong, D. Günther, J. Anal. Atom. Spectrom. 17 (2002) 831.
[95] A.W. Leach, G.M. Hieftje, J. Anal. Atom. Spectrom. 17 (2002) 852.
[96] M. van Straaten, K. Swenters, R. Gijbels, J. Verlinden, E. Adriaenssens, J. Anal. Atom. Spectrom. 9 (1994) 1389.
[97] J.S. Becker, Spectrochim. Acta B 57 (2002) 1805.
[98] DOWA MINING CO., LTD., www.dowa.co.jp.
[99] A.P. Mykytiuk, P. Semeniuk, S. Berman, Spectrochim. Acta Rev. 13 (1990) 1.
[100] B. Wiedemann, K. Bethge, W. Schütze, U. Lambert, S. Pahlke, T. Reinhold, B. Weinert, T. Flade, Fresenius J. Anal. Chem. 350 (1994) 319.
[101] B. Wiedemann, J.D. Meyer, D. Jockel, H.C. Freyhardt, B. Birkmann, G. Müller, Fresenius J. Anal. Chem. 370 (2000) 541.

[102] J.S. Becker, A.I. Saprykin, H.-J. Dietze, Int. J. Mass Spectrom. 164 (1997) 81.
[103] P. Herzner, K.G. Heumann, Microchim. Acta 106 (1992) 127.
[104] B. Beer, K.G. Heumann, Anal. Chem. 65 (1993) 3199.
[105] B. Beer, K.G. Heumann, Fresenius J. Anal. Chem. 347 (1993) 351.
[106] V.K. Panday, J.S. Becker, H.-J. Dietze, Fresenius J. Anal. Chem. 352 (1995) 327.
[107] S.F. Boulyga, C. Pickhardt, J.S. Becker, Int. J. Mass Spectrom., in preparation.
[108] M.H. Hinds, D.C. Gregoire, E.A. Ozaki, J. Anal. Atom. Spectrom. 12 (1997) 131.
[109] W. Devos, Ch. Moor, P. Linemann, J. Anal. Atom. Spectrom. 14 (1999) 621.
[110] J.S. Becker, H.-J. Dietze, Fresenius J. Anal. Chem. 344 (1992) 69.
[111] V.G. Panday, J.S. Becker, H.-J. Dietze, At. Spectrom. 16 (1995) 97.
[112] J.S. Becker, H.-J. Dietze, Mikrochim. Acta 118 (1995) 103.
[113] M.V. Balarama Krishna, D. Karunasagar, J. Arunachalam, Fresenius J. Anal. Chem. 363 (1999) 353.
[114] S. Grazhulene, V. Karandashew, I. Zadnepruk, V. Orlova, Fresenius J. Anal. Chem. 355 (1997) 297.
[115] S. Kozono, S. Takahashi, H. Haraguchi, Analyst 127 (2002) 930.
[116] S. Kozono, S. Takahashi, H. Haraguchi, Anal. Bioanal. Chem. 372 (2002) 542.
[117] J.S. Becker, G. Küppers, F. Carsugi, W. Kerl, W. Schaal, F. Ullmaier, H.-J. Dietze, Rep. Res. Centre Juelich 3272 (1996) 143.
[118] V.K. Panday, J.S. Becker, H.-J. Dietze, Anal. Chim. Acta 329 (1996) 153.
[119] F. Pilon, S. Lorthioir, J.-C. Birolleau, S. Lafontan, J. Anal. Atom. Spectrom. 11 (1996) 759.
[120] P. Becotte-Haigh, J.F. Tyson, E. Denoyer, M.W. hinds, Spectrochim. Acta 51B (1996) 1823.
[121] K. Beer, K.G. Heumann, Fresenius J. Anal. Chem. 350 (1994) 284.
[122] J.S. Becker, H.-J. Dietze, Fresenius J. Anal. Chem. 346 (1993) 134.
[123] R. Jäger, J.S. Becker, H.-J. Dietze, J.A.C.V. Broekaert, Fresenius J. Anal. Chem. 358 (1997) 214.
[124] M.C. Wende, J.A.C. Broekaert, Fresenius J. Anal. Chem. 370 (2001) 513.
[125] J.Su. Becker, C. Pickhardt, N. Hoffmann, H. Höcker, J.Sa. Becker, Atom. Spectrosc. 23 (2002) 1.
[126] P.-H. Chi, F.-H. Ko, C.-R. Hsu, H.-L. Chen, C.-K. Yang, Y.-C. Sun, M.-H. Yang, J. Anal. Atom. Spectrom. 17 (2002) 358.
[127] F. Kohl, N. Jakubowski, R. Brand, C. Pilger, J.A.C. Broekaert, Fresenius J. Anal. Chem. 359 (1997) 317.
[128] N. Jakubowski, W. Tittes, T. Pollmann, D. Stuewer, J.A.C. Broekaert, J. Anal. Atom. Spectrom. 11 (1996) 797.
[129] S. Quin, Z. Jiang, B. Hu, Y. Qin, S. Hu, Fresenius J. Anal. Chem. 367 (2000) 250.
[130] J.S. Becker, U. Breuer, J. Westheide, A.I. Saprykin, H. Holzbrecher, H. Nickel, H.-J. Dietze, Fresenius J. Anal. Chem. 355 (1996) 625.
[131] R. Jäger, A.I. Saprykin, J.S. Becker, H.-J. Dietze, J.A.C. Broekaert, Mikrochim. Acta 125 (1997) 41.
[132] J.S. Becker, J. Westheide, A.I. Saprykin, H. Holzbrecher, U. Breuer, H.-J. Dietze, Mikrochim. Acta 123 (1997) 153.
[133] A.I. Saprykin, J.S. Becker, H.-J. Dietze, Fresenius J. Anal. Chem. 364 (1999) 763.
[134] M. Fukuda, Y. Sayama, Fresenius J. Anal. Chem. 357 (1997) 169.
[135] J.S. Becker, H.-J. Dietze, J. Anal. Atom. Spectrom. 13 (1998) 1057.
[136] P.R.D. Mason, A.J.G. Mank, J. Anal. Atom. Spectrom. 26 (2001) 1381.
[137] A. Plotnikov, C. Vogt, V. Hoffmann, C. Täschner, K. Wetzig, J. Anal. Atom. Spectrom. 16 (2001) 1290.
[138] D. Bleiner, A. Plotnikov, C. Vogt, K. Wetzig, D. Günther, Fresenius J. Anal. Chem. 368 (2000) 221.
[139] J.S. Becker, S.F. Boulyga, Fresenius J. Anal. Chem. 370 (2001) 527.
[140] S.F. Boulyga, H.-J. Dietze, J.S. Becker, J. Anal. Atom. Spectrom. 16 (2001) 598.
[141] M. Horn, Fresenius J. Anal. Chem. 364 (1999) 385.
[142] S.E. O'Brien, B.W. Acon, S.F. Boulyga, J.S. Becker, A. Montaser, J. Anal. Atom. Spectrom. 18 (2003) 230.
[143] U. Völlkopf, K. Klemm, M. Pfluger, Atom. Spectrosc. 29 (1999) 53.
[144] R. Hoelzl, L. Fabry, L. Kotz, S. Pahlke, Fresenius J. Anal. Chem. 366 (2000) 64.
[145] J. Wills, et al., in: Proceedings of the 1999 European Winter Conference on Plasma Spectrochemistry, Pau, France, 10–15 January 1999.