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Mass spectrometric methods for the direct elemental and isotopic analysis of solid materials †

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Methods for the direct analysis of solids have a number of undeniable advantages over the methods that require preliminary dissolution of samples. High sensitivity and selectivity make the direct mass spectrometric techniques the most in-demand. The review concerns spark source mass spectrometry, laser ionization mass spectrometry, laser ablation inductively coupled plasma mass spectrometry, secondary ion mass spectrometry, secondary neutral mass spectrometry and glow discharge mass spectrometry. Basic principles, analytical characteristics and trends in the development of these techniques are discussed. Particular attention is given to applications of the techniques as well as to their competitive advantages and drawbacks. The bibliography includes 123 references.

Contents

I.	Introduction	427
II.	Spark source mass spectrometry	428
III.	Laser ablation inductively coupled plasma mass spectrometry	428
IV.	Laser ionization mass spectrometry	431
V.	Secondary ion mass spectrometry	432
VI.	Glow discharge mass spectrometry	435
VII.	Conclusion	441

I. Introduction

Recently, there has been rapid progress in methods for the direct mass spectrometric analysis of solid materials, which do not require the sample preparation procedure including preliminary dissolution of samples. Relevant types of mass analyzers are in-demand in various fields of science and technology. Elimination of chemical sample preparation is an undisputed advantage of these methods over other (usually, multistep) methods of analysis of solid samples.

The review concerns main methods for the direct mass spectrometric analysis, *viz.*, spark source mass spectrometry (SSMS), laser ionization mass spectrometry (LIMS), laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS), secondary ion mass spectrometry (SIMS), secondary neutral mass spectrometry (SNMS) and glow discharge mass spectrometry (GD-MS).

Historically,[1] all these methods except LA-ICP-MS emerged within a rather short period of time, *viz.*, in the 1960s – 1970s, and developed almost concurrently, being aimed at performing highly sensitive elemental analysis of solid samples. Each method was characterized by a number of specific features. Since SSMS was proposed first and had a well-elaborated design, it became a widely

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used method for analyzing almost all types of samples (even dielectric ones, although this requires a specific sample preparation procedure). The SIMS technique is of limited use, being aimed at performing the local and elemental analysis of trace impurities in high-purity semiconductor materials. The next two methods, LIMS and GD-MS, were used for elemental analysis of metals and alloys. Laser ablation inductively coupled plasma mass spectrometry was developed in the 1990s in order to adapt inductively coupled plasma mass spectrometry (ICP–MS), a commonly recognized method of elemental analysis, to the direct analysis of samples.

We tried to describe modern trends in the development of the techniques in question as well as to consider and compare their advantages and drawbacks using the studies reported in the last decade. Since relevant publications date back to at least the early 2000s,[2,3] this review seems to be topical.

II. Spark source mass spectrometry

The technique utilizes a spark discharge between two electrodes as ion source. In most cases, a pulsed 1-MHz radiofrequency voltage of at most 100 kV is applied to electrodes. The discharge is accompanied by atomization and ionization of the sample which can either be supported on an electrode or be an electrode itself. Owing to high energy (a few keV) of ions produced in the spark ion source, it is mainly used in the sector instruments with a Mattauch–Herzog geometry. A sector mass analyzer is characterized by high resolution (to 10 000) ‡ and makes it possible to resolve almost all mass interferences, but is expensive and has a complex design and a much lower performance than the time-of-flight systems because of the scanning operating mode. As a rule, photographic plates are used as detector; electronic detectors are used more rarely.

Spark source mass spectrometry is used to analyze trace impurities in metals and alloys, high-purity materials, semiconductors, glasses, ceramics, radioactive samples, as well as geological and biological samples; however, the technique seems to be not timely now. A comprehensive review devoted to applications of SSMS is available.[4] It should be noted that analysis of non-conductive samples (unlike conductive ones, which are suitable for the direct analysis) requires an additional auxiliary electrode[5] or mixing with a conductive powder.[6]

Attempts to perform a depth profiling as well as local analysis of the surface have been reported. However, the spatial resolution achieved (1–10 and 10–100 μm, respectively) cannot compete with the resolution attained by other methods.

The characteristic features of SSMS include nearly the same sensitivity for all elements, low limits of detection (of the order of 10–100 ppb) and minimum sample preparation. Severe drawbacks of the technique consist in low accuracy and precision, as well as duration, complexity and high cost of analysis. Low accuracy is due to the selectivity of ionization processes occurring in the ion source, namely, these processes can be specific to each particular element, so even minor changes in plasma parameters may significantly influence the result. The systematic error can be as large as 30% and exceed the statistical error.

As an attempt to re-energize the SSMS technique, Jochum *et al.*[7] developed a multi-ion counting SSMS approach, which involves simultaneous counting of ions using a detector array consisting of 20 channeltrons. However, this method is also of limited use.

Labour-consuming and expensive analysis, the lack of actual or potential advantages over other methods, as well as progress in GD-MS, SIMS, ICP-MS and LA-ICP-MS predetermined cessation of the evolution of SSMS. At present, no SSMS spectrometers are produced and there are almost no studies on SSMS, while the available SSMS instruments (when in operation) are used for routine analysis.

III. Laser ablation inductively coupled plasma mass spectrometry

The technique involves pulsed sputtering of a microscopic volume of a sample under the action of laser radiation focused on the sample surface followed by transfer of aerosols with a stream of a gas (argon, helium) to the ICP torch and detection of ions thus produced using a mass spectrometer (Fig. 1). Most often, three types of mass spectrometers are utilized, namely, the quadrupole, magnetic sector and time-of-flight instruments. Recently, the last-mentioned type has taken up new positions owing to its high performance. Attempts to carry out LA-ICP-MS experiments using a double-focusing sector mass spectrometer with a Faraday detector array have been reported.[8,9] In fact, this type of mass spectrometers allows a few dozens of components of the mass spectrum to be detected simultaneously, which extends the operating range (compared to the sector mass spectrometers) when detecting rapidly changing

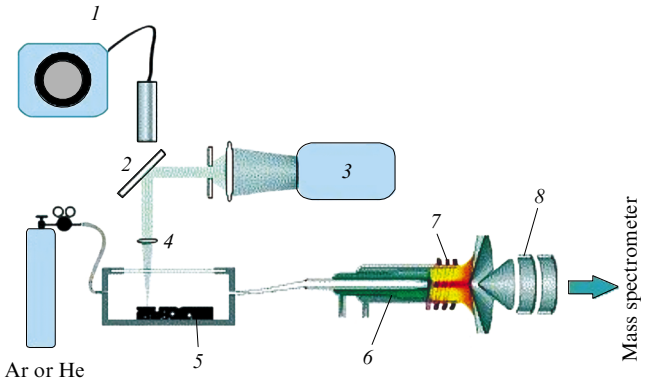


Figure 1. LA-ICP-MS: a schematic.
Video camera (*1*), mirror (*2*), laser (*3*), lens (*4*), ablation chamber (*5*), burner (*6*), high-frequency coil (*7*) and ion optics (*8*).

‡ At present, by high-resolution mass analyzers are meant instruments with a mass resolution of at least 20 000. Mass analyzers used for the elemental analysis of solids by SSMS have a mass resolution between 100 and 10 000; therefore, in the SSMS studies, a mass resolution > 5000 is considered high.

signals including the laser ablation signal. However, it should be noted that the resolution of this type of mass spectrometers (240 – 800) is too low to resolve the mass spectrometry interferences, whereas the resolution of a single-detector double-focusing mass spectrometer (to 10 000) is high enough to eliminate interferences.

Recently, LA-ICP-MS has been a routine technique that is widely used for the elemental and isotopic analysis of various solid samples. The fundamental advantages of LA-ICP-MS include almost no contamination of samples in the course of sample preparation and analysis, the possibility of direct sputtering of samples with any type of conductivity, rather low limits of detection (of the order of a few particles per million for the light elements and a few tens of particles per billion for the heavy elements), especially when using helium or helium/argon mixture as discharge gas, a local character of analysis and a wide range of elements to be determined.[10,11] Detailed description of the operating principles and specific features of the technique can be found in a collection of works [12] and in Refs 13 and 14.

Further progress in LA-ICP-MS implies the development of analytical procedures to investigate a wide range of systems including biological ones,[15,16] to solve the mass spectrometer calibration problems,[16] and to develop methods for two- (2D) and three-dimensional (3D) mapping of samples. LA-ICP-MS is finding expanding applications related to nuclear non-proliferation and analysis of nuclear materials.[17] The technique allows one to determine the isotopic abundance ratios of uranium and some other elements in soil and dust particles.[17,18] Using the measured isotopic abundance ratios of lead, uranium and thorium, one can date the age of rocks.[19] The method is improved by using short-wavelength femtosecond lasers, which enable production of smaller particles by sputtering, reduces fractionation of elements in the course of laser ablation and improves the accuracy of analysis.[20,21] Attempts are made to improve the depth resolution in the course of depth profiling through a decrease in the pulse energy at high repetition rate and formation of a 'flat-top' laser beam profile.[22]

Now we will consider the LA-ICP-MS investigation lines mentioned above in more detail.

III.1. The laser pulse: how to choose its duration and wavelength

The most widely used sources of laser radiation for LA-ICP-MS studies include Nd:YAG solid-state lasers operating at the fourth (266 nm) or fifth (213 nm) harmonic as well as excimer lasers, first of all, 193-nm ArF lasers. All of them are characterized by pulse durations of the order of a few nanoseconds.

There are also commercially available femtosecond lasers. In most cases, combined laser systems based on titanium – sapphire lasers (fundamental mode wavelength is 800 nm) with frequency multipliers are used. The 1030-nm radiation of a Nd:YAG laser is amplified using ytterbium-doped tungstate $KGd(WO_4)_2$ [from this point on, Yb:$KGd(WO_4)_2$ will be denoted as Yb:KGW]. As a rule, the third or fourth harmonic of a titanium – sapphire laser (266 and 200 nm, respectively) is used. A 200-nm wavelength can be obtained by parametric mixing of the fundamental wavelength of the titanium – sapphire laser with its third harmonic.

The particle size is affected by the changes in the wavelength and pulse duration, whereas the stoichiometry of aerosols is mainly governed by the pulse duration. If the laser wavelength and pulse duration become smaller than the relaxation time of the temperature at the surface of a crater produced by the laser pulse (of the order of 200 fs),[20] the reproducibility and accuracy of analysis are improved owing to a decrease in the size of the sputtered particles from 100 nm – 100 μm to 0.1 – 100 nm and improved stoichiometry of aerosols whose compositions approach that of the sample.[20,22] As a consequence, thermal mechanism of vaporization and sputtering of samples is replaced by the mechanism of atom – atom bond cleavage with the formation of a plasma channel [23] under the action of the light field whose strength is comparable with that of the intra-atomic field. In this case, the laser plume contains a much lower amount of highly volatile components of the sample. The sensitivities of analyses of conductive and dielectric samples using femtosecond laser pulses become almost the same, which significantly simplifies the calibration procedure.[21,22]

However, a direct comparison of systems with a short-wavelength nanosecond laser (ArF excimer laser, 193 nm), femtosecond laser (UV titanium – sapphire laser, third harmonic, 265 nm), and femtosecond laser (near-IR titanium – sapphire laser, first harmonic, 795 nm) revealed a noticeable difference between the UV and IR systems (considerable fractionation was observed for a number of elements using the IR system); also, the analytical parameters of the nano- and femtosecond UV lasers used to analyze dielectric samples appeared to be close. It was concluded [20] that the more expensive and complicated femtosecond lasers should be used instead of nanosecond instruments only in the studies of a wide range of conductive and non-conductive samples.

III.2. Two- and three-dimensional mapping

The LA-ICP-MS technique was initially developed for the elemental and isotopic analyses of samples. Currently, it allows one to carry out point-to-point analysis, depth profiling, as well as the 2D elemental and isotopic mapping of samples. This feature is in-demand in biochemistry, ecotoxicology, archeology, geochemistry and in studies of various inhomogeneous materials.[21] For instance, the distribution of zinc and magnesium in frozen rat brain tissue sections was analyzed using 2D-mapping with a 100-μm spatial resolution.[24] The technique was calibrated using the rat brain samples mixed with zinc- and magnesium-containing compounds and then the metals were quantitatively imaged.

Two-dimensional mapping was used to study the distributions of platinum group elements (Ru, Rh, Os, Ir, Pt) as well as W, Re and Au in meteorites to obtain information on the crystallization history and to evaluate the cooling rates of the meteorite parent bodies.[21]

The potential of 2D- and 3D-mapping using a combination of laser ablation inductively coupled plasma time-of-flight mass spectrometry (LA-ICP-TOFMS) and laser-induced breakdown spectroscopy (LIBS) was analyzed [25] using a fifth-harmonic nanosecond Nd:YAG laser operating at 213 nm. When LA-ICP-TOFMS is coupled to a conventional low-resolution mass spectrometer (a TOF

mass spectrometer which allows one to acquire rapidly changing mass spectra of samples), a number of elements, such as F, O, H, N, Si, Se, As, Ca, S cannot be determined or the corresponding limits of detection are very high. The reasons are as follows:

— mass interferences of the major isotopes of Si, Se, As, Ca, S with various cluster components; and

— high concentration of certain elements (O, N, H) in the inductively coupled plasma plume.

Problems related to interferences can be to some extent solved using high-resolution mass spectrometers, but even in this case, *e.g.*, calcium is determined from its low-abundance isotope $^{44}Ca^+$ (2.086 at.%) because the major isotope, $^{40}Ca^+$, interferes with the major isotope of argon, $^{40}Ar^+$, which reduces the sensitivity and the limit of detection.[26] Besides, at high resolution the aperture of the mass spectrometer decreases and, correspondingly, the sensitivity with respect to the elements to be determined also decreases and the corresponding limits of detection increase. Combining LA-ICP-TOFMS and LIBS eliminates the mapping problem of calcium. The LIBS technique involves the detection of emission spectra from the same laser plume as that used to sputter the sample for the LA-ICP-TOFMS measurements. Two-dimensional mapping of calcium (using the $^{44}Ca^+$ isotope for LA-ICP-TOFMS and the Ca II 315.88 nm emission line for LIBS) revealed a better signal-to-noise ratio for LIBS compared to LA-ICP-TOFMS.

LIBS was used to construct the 2D distributions of Ca, Si and Al, while LA-ICP-TOFMS was utilized to construct the 2D distributions of $^{140}Ce^+$, $^{139}La^+$, $^{146}Nd^+$, $^{208}Pb^+$ and $^{55}Mn^+$ in a rare-earth ore sample.[25] Correlations between the content of the following groups of elements were found: Ce, La, Nd, Al and Mn, Fe (lead and calcium were located in other regions of the sample). It was assumed that combinations of these groups of elements are related to different ore phases. Three-dimensional mapping was performed for a total of four elements including Si, Ca (LIBS) and U, Ce (LA-ICP-TOFMS). The depth resolution was 3 μm (depth of analysis was 15 μm) and the in-plane resolution was nearly 10 μm. Future plans involve using high-resolution spectrometers operating in a wide spectral range in order to obtain information on the isotopic composition of a number of elements using laser ablation molecular isotopic spectrometry (LAMAIS).[27] Combining LA-ICP-TOFMS, LIBS and LAMIS will extend the analytical potential of the laser ablation techniques.

III.3. Depth profiling

Attempts to utilize LA-ICP-MS for depth profiling have been made for a long time.[22–24] However, the depth resolution of the technique (usually, 1 μm) is much lower than that of SIMS (< 1 nm) or GD-MS (a few nanometres). The low resolution is due to non-'flat-top' laser beam profile; as a result, a crater produced after application of a pulse also has a non-flat surface. In addition, application of a single, few nanoseconds long pulse produces a crater whose depth is a few hundreds of nanometres. Going to femtosecond lasers characterized by reduced power and low repetition rates (less than 1 Hz) led to significant improvement of the depth resolution, *e.g.*, 300 nm for metallic coatings on metallic substrates (500 nm of chromium on nickel substrate).[28] A similar depth resolution of 240 nm was obtained for metallic coatings on polymers.[29] However, this resolution is still too low to make LA-ICP-MS a routine depth profiling technique.

III.4. Calibration

As for other methods, the problem of calibration and the related problem of reference samples are key to the direct mass spectrometric analysis of solid samples. If these problems persist, quantification is in fact impossible. In some cases, *e.g.*, when analyzing dielectric samples, one can use the method of the relative sensitivity factors (RSF) which is also suitable in other direct methods of mass spectrometric elemental analysis. Calibration is performed using a kit of reference samples, usually, glasses. However, the RSF method is inapplicable to analysis of conductive materials, biological samples and complex composite materials. This is first of all due to the difference between the relative compositions of the sample and sputtered matter (*i.e.*, the concentration ratio of the elements in the sample is different from the concentration ratio of the same elements in the gaseous phase). Besides, a significant role is played by the matrix effects that are responsible for nonlinear character of the calibration curve.[18, 19, 22] Nevertheless, the RSF approach was successfully used for, *e.g.*, analysis of silicon carbide (calibration was performed with silicon reference samples)[30] using a Nd:YAG fifth harmonic laser operating at 213 nm and a quadrupole mass spectrometer. A comparison of the results obtained by the LA-ICP-MS and ICP-MS (using a dissolved sample) revealed good agreement between them.

A procedure for calibration of the LA-ICP-MS technique in the determination of europium- or protium-labelled proteins has been developed.[16] Using a conventional printer, a solution of indium (internal reference) was introduced into preliminarily supported proteins. The amount of indium introduced varied with the printing density. The results obtained by the LA-ICP-MS and ICP-MS methods were in good agreement.

III.5. Analysis of microparticles, microincusions, nuclear materials and minerals

Elemental and, which is more important, isotopic analysis of radioactive microparticles[31] to control nuclear activity of various countries has become an important application of the LA-ICP-MS. The technique offers a number of advantages over thermal ionization mass spectrometry (TIMS) and SIMS, namely, much lower limits of detection and a shorter time necessary to carry out the analytical procedure itself. Having preliminarily located microparticles on the target (using an electron microscope or from fission tracks upon irradiation of the target in a nuclear reactor), one can rapidly perform an isotopic analysis at a rate of a few minutes per particle. As an example, the problem was solved using a femtosecond diode-pumped Yb:KGW laser operating at 1030 nm (pulse duration was 360 fs) and conventional ICP-MS with a quadrupole mass spectrometer.[32] The pulse energy was low (100 μJ), while the pulse repetition rate was high (10 kHz). The accuracy of determination of the $^{235}U/^{238}U$ isotopic abundance ratio was ~4% (particle size was at most 1 μm and the particles contained from 10 to 200 pg of uranium). The absolute limit of

detection was 0.350 fg, which corresponds to an UO_2 particle size of 200 nm.

The LA-ICP-MS technique was also utilized for isotopic analysis of lead in microinclusions of melts [18] and liquids [19] in rocks. These studies were carried out using high-resolution magnetic sector mass spectrometers, which made it possible to eliminate the problem of interferences. For comparison, a quadrupole mass spectrometer was also used.[19] A sample was sputtered with a 193-nm ArF excimer laser (pulses were a few nanoseconds long). It was concluded that the magnetic sector mass spectrometer provided a higher signal-to-noise ratio than the quadrupole mass spectrometer at almost the same time taken to acquire data for the 20 elements chosen.

High accuracy of isotopic analysis was achieved in multicollector laser ablation inductively coupled plasma mass spectrometry (LA-MC-ICP-MS) studies [33–35] carried out using multicollector sector mass spectrometers. The technique is a version of LA-ICP-MS. It was used to determine the content of ^{10}B in steels.[33] The ^{10}B isotope is an efficient thermal neutron absorber, materials with high content of ^{10}B (90% – 97%) are used in nuclear reactors and in production of radioactive waste storage containers. Reprocessing of these materials may cause changes in the content of ^{10}B, so this parameter should be rapidly and exactly determined. This can be done by LA-MC-ICP-MS. Experiments were carried out using a Nd:YAG nanosecond laser (213 nm) and a femtosecond titanium – sapphire laser (795 nm). The relative standard deviation (S_r) of the ^{10}B content obtained using the nanosecond laser was rather high (in the range from 0.3% to 0.7%). The S_r value determined with the femtosecond laser was 0.1% – 0.2%, being comparable with the values obtained by TIMS.

Laser ablation inductively coupled plasma multicollector mass spectrometry was used to identify small particles of glasses of different origin from the lead isotopic ratio for forensic purposes.[34] As in Ref. 33, experiments were performed using a Nd:YAG laser (213 nm) with pulse durations of a few nanoseconds. To improve the accuracy, the isotopic abundance ratios were corrected using the $^{203}Tl/^{205}Tl$ intensity ratio. This made it possible to take into account the nonuniform transfer of different isotopes through the mass spectrometer. Eventually, the concentration ratios of the lead isotopes ^{206}Pb, ^{207}Pb, ^{208}Pb used as markers for identification of glasses of different origin were determined with a rather high accuracy (0.03% – 0.1%).

Multicollector LA-ICP-MS (a Neptun mass spectrometer) and single-collector LA-ICP-MS (an Element XR mass spectrometer) were used [35] to solve two problems, namely, to date rocks from the $^{206}Pb/^{238}U$ and $^{207}Pb/^{235}U$ concentration ratios and to carry out high-precision determination of the $^{176}Hf/^{177}Hf$ isotopic abundance ratio. Experiments were carried out using a nanosecond ArF excimer laser (193 nm). The cell with the sample was blown with helium. Since the intensity of the analytical signal from ^{235}U was low (this influenced the accuracy of determination of the $^{207}Pb/^{235}U$ ratio, the $^{207}Pb/^{238}U$ ratio was measured instead and then multiplied by a factor of 137.88 equal to the $^{238}U/^{235}U$ isotopic abundance ratio. The relative intensities of the lead and uranium isotopes were determined with high accuracy, which in turn made it possible to date the rocks studied with high accuracy (0.3% – 2.5%). Also, the accuracy of determination of the $^{176}Hf/^{177}Hf$ isotopic abundance ratio was high enough (error was 0.01% – 0.05%) to obtain information on crystallization processes in the minerals under study.

The LA-ICP-MS technique is of interest for the nuclear industry [36] because it is suitable for the direct elemental and isotopic analysis of various radioactive solid samples (including nuclear fuel) and allows one to significantly reduce the staff radiation load as well as to make the analytical procedure less expensive and simpler compared to the analysis of dissolved samples.

IV. Laser ionization mass spectrometry

The technique represents a version of laser ablation with direct ionization in a vacuum and is abbreviated as LIMS. It was proposed nearly five decades ago and is characterized by high sensitivity, performance and resolution. This is a promising method for analysis of solid samples which can be utilized in many fields of science and industry *e.g.*, metallurgy, geology, ecology and biology.

Unlike LA-ICP-MS, in LIMS atoms are ionized in the laser plume rather than the ICP torch; consequently, there is no need to use discharge gas, and various interferences manifest themselves to a lesser extent. The sample surface absorbs the laser energy, which leads to melting of the sample followed by vaporization owing to abrupt increase in temperature on a relatively small surface area. Phase transitions take $\sim 10^{-10}$ s to occur. Then, the remaining energy of the laser pulse (pulse duration is noticeably longer than 10^{-8} s) is absorbed by plasma thus produced; this is accompanied by atomization, excitation and ionization of atoms in the sample. As a result, the surface becomes surrounded by various species, *viz.*, differently excited atoms, electrons, ions and clusters. The ions formed are collected from plasma by the focusing electric field.

Since the lifetime of the laser plume is short, acquisition of a mass spectrum requires a very high-performance mass spectrometer; therefore, almost all studies are carried out using time-of-flight mass spectrometers. However, it should be noted that the scatter of the kinetic energies of ions produced under the action of high-energy laser beam is of the order of a few hundreds of electronvolts (*cf.* at most 20 eV for correct operation of TOFMS). In this connection, mass spectrometers with axial inlet geometry, which is unsuitable for compensation of broad ion energy distribution, are characterized by a low resolution from 30 to 60.[26] A number of mass spectrometers with linear axial inlet geometry have been designed, *e.g.*, LAMMA 500, LAMMA 1000, LIMA 2A. However, they are very rarely used for quantitative analysis, in particular, owing to low resolution. In this case, utilization of orthogonal inlet geometry is hampered by the low aperture of time-of-flight mass spectrometers in the case of large scatter of ion energies and a narrow mass sampling owing to different arrival times of different-mass ions to the action range of the ejecting pulse.

Sysoev *et al.*[37] proposed a version of laser ionization time-of-flight mass spectrometer (LI-TOFMS) known as LAMAS-10 where sectorial axially symmetrical electric field acting as an energy filter was used instead of a

traditional reflectron. This design enables high transmission of the mass spectrometer due to the lack of a decelerating grid and long effective ion path length (167 cm) in a small volume. Laser radiation was generated using a laser with a power density of $(1-2)\times10^9$ W cm^{-2}. The pulse duration was 7 ns and the focal spot was 70 μm in diameter. The analytical parameters of the mass spectrometer were as follows: the resolving power was 600–900; the limit of detection varied from 2×10^{-6} mass % to 1.7×10^{-5} mass % depending on the element, the dynamic range was $1-10^8$ and the relative standard deviation (a measure of the random error for the elements detected) varied from 0.4% (for major components) to 26% (for trace amounts of impurities present at a level between 10 and 100 ppb).§

To solve the problem of ion energy scatter, an energy filter to control the ion energies and a quadrupole ion trap (a kind of a storage device between the ion source and the TOF analyzer) were proposed and successfully used. Utilization of the ion storage device significantly reduced the scatter of ion energies and made it possible to improve the resolution to a value of 1500, although the absolute limit of detection was rather high, namely, of the order of 10 pg.[38,39]

An original approach in order to use LI-TOFMS with orthogonal inlet geometry was proposed.[38] The ion source was filled with helium, which abruptly cooled the sputtered ions. In addition, conventional ion optics was replaced by a radiofrequency hexapole or transportation of ions; this additionally reduced the scatter of ion energies. Such a modification made it possible not only to eliminate major problems of the orthogonal inlet of the TOFMS system (see above), but also to significantly reduce the intensities of doubly charged ions and, as a consequence, to achieve satisfactory sensitivity, resolution and reproducibility values. However, the authors of that study [38] faced with a problem characteristic of radiofrequency ion-transport devices, *viz.*, severe difficulties in transport of light ions because of scattering them away. In this connection, it was proposed to modify the LI-TOFMS system, namely, the radiofrequency ion-transport device was replaced by conventional ion optics.[39] The system was characterized by a resolution of 3000 and by the limits of detection of the order of 0.1–1 ppm. The drawback of the design is as follows. Residual oxygen in the ion source led to formation of oxides, so a large number (or even most) elements that form strong oxides (*e.g.*, Nb, Zr, Ta, rare-earth elements) were 'present' in the mass spectrum in the form of oxides (NbO^+, ZrO^+, TaO^+, *etc.*) rather than atomic ions (Nb^+, Zr^+, Ta^+) even in the analysis of metallic samples.

Intense formation of oxides was also observed in the absence of ballast gas.[40] In that study, ions were detected using a Fourier transform ion-cyclotron resonance mass spectrometer. The oxides sputtered were as follows: Y_2O_3, Mn_2O_3, CuO, ZnO. The mass spectra exhibited not only signals from the oxide ions, but also intense signals from the clusters MH^+, MOH^+, MOH_2^+, MH^+, MOH^+, MOH_2^+, MO_2H^+, M_2OH^+, $M_2O_2H^+$, $M_xO_y^+$, *etc.* (M = Y, Mn, Cu, Zn). Of course, this effect significantly deteriorates the analytical characteristics of the technique (the limits of detection, reproducibility and accuracy).

An attempt to modify LIMS for operation at atmospheric pressure was reported.[41] To this end, the laser ablation system was combined with the source of metastable atoms which is used in the direct analysis in real time (DART) for surface ionization of organic compounds. In this case, ionization of atoms mainly proceeded by the Penning mechanism through collisions with metastable helium atoms. That study was carried out using a high-resolution time-of-flight mass spectrometer with a mass resolution of 6000, which made it possible to use the mass defect to eliminate most interferences. However, low temperature plasma (relative to the temperatures in the ICP and glow discharge) causes the appearance of a large number of intense cluster components (FeOH, CuOH, FeO, FeO_2, $CuOH_2$, FeO_2H_2, *etc.*) in the mass spectrum. This of course significantly restricts the potential of the technique in the direct elemental and isotopic analysis of solid samples.

Undoubted advantages of LIMS include relative simplicity, the possibility to analyze gaseous components and very low consumption of ballast gas (helium). Also, LIMS is less influenced by the matrix effects than SIMS but loses out to GD-MS, LA-ICP-MS and SIMS in limits of detection. Yet another drawback of LIMS consists in that analysis of metals is accompanied by the presence of relatively intense analytical signals of oxide components of some elements (niobium, zirconium, rare-earth elements, *etc.*) in the mass spectra, while analysis of oxides is accompanied by the appearance of intense analytical signals from other cluster components. As to the depth profiling, the depth resolution of LIMS is comparable with that LA-ICP-MS but is much poorer than that of GD-MS or SIMS.

V. Secondary ion mass spectrometry

Secondary ion mass spectrometry (SIMS) is an efficient tool for the surface studies, first of all, for the surface studies of semiconductors. Main advances in SIMS achieved over a period of three decades are just associated with the analysis of semiconductors. Numerous studies on the application of SIMS in electronic industry are available. Recently, the field of application of the technique significantly extended.

Popularity of SIMS is based on its advantages.[1,42,43] In particular, the technique makes it possible:

— to determine the depth distribution of elements with a resolution of down to 0.3 nm unique for an analytical method;

— to perform 2D-mapping of samples with a resolution from a few tens to a few hundreds of nanometres;

— to perform 3D-mapping of samples;

— to conduct isotopic analysis;

— to carry out qualitative elemental analysis;

— to determine a number of elements such as N, O, H, P, Se, F (detection of these elements by other direct mass spectrometric methods is impossible or problematic);

— to detect organic compounds using heavy clusters (Bi_3^+, C_{60}^+, *etc.*) for sputtering of samples.

Of course, SIMS has some drawbacks, namely:

— this is not a method for quantitative analysis because there is no one-to-one correspondence between

§ See also A A Sysoev, A A Sysoev *Eur. J. Mass Spectrom.* **8** 213 (2002).

the concentrations of elements in the sample and the intensities of corresponding signals in the mass spectrum;

— for certain elements, the intensities of signals from their oxides are higher than those of signals from the elements in the mass spectrum;

— the relative sensitivities for different elements differ by 3 – 4 orders of magnitude, which imposes limitations on the number of elements that can actually be determined;

— complexity and high cost of equipment, the need for ultrahigh vacuum; and

— the possibility to obtain information on the composition of sample at a depth of at most 100 – 200 nm because SIMS is the method for surface analysis.

Nevertheless, at present SIMS belongs to the most efficient and widespread methods for analysis of solid samples.

In this review we will dwell not only on the main fields of application of SIMS, *viz.*, depth profiling and spatial analysis, but also some new avenues of research, namely, isotopic analysis and the use of heavy clusters for the determination of organic compounds. Besides, we will try to compare the analytical potential of SIMS and other mass spectrometric methods for the direct elemental analysis of solid samples.

V.1. SIMS: the foundations

Physical principles underlying SIMS have been discussed repeatedly (see, *e.g.*, Refs 1, 42, 43); therefore, we will only briefly outline them.

The operating principle of SIMS is based on sputtering of a solid sample with an ion beam and subsequent formation of secondary ions through ion – ion collisions. It is usual to distinguish between 'static SIMS' and 'dynamic SIMS'. In the former case, one deals with low primary ion doses (less than 10^{12} ions per square centimetre) on the sample surface, which statistically provides such conditions that each ion arrives at an undamaged surface area. This creates prerequisites for sputtering of large molecular fragments. In the latter case, the ion dose is much higher and correspondingly, the degree of fragmentation is also higher. Therefore, dynamic SIMS is used for elemental analysis (depth profiling and mapping). The results obtained are presented in the form of mass spectra (static SIMS) or as depth profiles, 2D and 3D maps and mass spectra as well (dynamic SIMS). Usually, sputtering is done using O^+ and Cs^+ ions, which are suitable for high-resolution 2D-mapping; however, recent experiments are increasingly frequently performed with heavy clusters, *e.g.*, Au_2^+, Au_3^+, Bi_2^+, Bi_3^+, C_{60}^+. This allows one to sputter and analyze not only inorganic, but also organic samples. To improve the depth resolution, low-energy ions (about 250 eV) are used instead of conventionally used 10-keV ions.

Like LA-ICP-MS, in SIMS ions can be detected using three types of mass spectrometers, *viz.*, magnetic sector, quadrupole and time-of-flight instruments. The last-mentioned type has been used increasingly frequently because TOFMS enables not only fast acquisition of mass spectra (this is of particular importance for dynamic SIMS), but also high mass resolution (about 5000 – 6000). This is high enough to eliminate almost all interferences.

V.2. Depth profiling and imaging

Secondary ion mass spectrometry is most often used as a method for local analysis. It enables determination of the surface distribution and the depth profiles of elements, isotopes and molecular fragments and eventually detailed 3D-mapping of samples. The range of samples is very wide and includes inorganic, organic high-molecular-mass compounds, biological objects and rocks, thin films and coatings, nuclear materials, as well as micro- and nanoparticles.

The in-plane (surface) resolution of SIMS is less than 1 μm (down to 50 nm) while the depth resolution is less than 1 nm. The maximum attainable in-plane resolution is governed by the width of the primary beam.

A critical review[44] is devoted to detailed consideration of modern applications of SIMS in the surface analysis (2D-mapping) and in ecology, biology, biomedicine, geology, cosmochemistry and materials science. Therefore, we will not dwell on these issues. However, mention can be made that SIMS is not only characterized by the uniquely high spatial resolution among the LIMS, LA-ICP-MS, matrix-assisted laser desorption/ionization (MALDI) and desorption electrospray ionization (DESI) techniques, but also competes in this parameter with other methods of surface analysis (electronic, X-ray, vibrational and fluorescence spectroscopy), being second only to transmission electron microscopy electron energy loss spectroscopy (TEM-EELS). An image formation model for SIMS imaging was reported.[45]

The emergence of a new application field of SIMS, analysis of microparticles, is due to a combination of high in-plane resolution and the possibility to perform isotopic and elemental analyses. Relevant software for fast monitoring of the surface in order to locate the particles under study and analyze them is available. This made SIMS a highly efficient method for control of the origin of uranium contaminations. It was proposed[46] to identify different stages of nuclear fuel processing by simultaneous determination of the isotopic composition of uranium and the content of elemental fluorine in microparticles.

The next application of SIMS is analysis of nanoparticles (dust particles and aerosols of different nature) for environmental safety, biomedicine and geology. A number of studies (see, *e.g.*, Refs 47 and 48) are devoted to analysis of nanoparticles encapsulated within living cells.

The degradation of resolution with depth is a key issue in depth profiling. To solve the problem, various corrections are applied. An original approach[49] involves deconvolution of the depth profile of carbon atoms using the available profile of a superlattice composed of alternating diamond layers containing different isotopes of carbon (^{12}C and ^{13}C). In this case, one can obtain an almost exact response because the sputtered atoms have the same mass, ionization energy and binding energy in the lattice. The procedure allowed the spatial resolution to be improved by a factor of 5 to 7.

It was proposed[50] to obtain the depth profiles of helium in high-purity iron using $CsHe^+$ molecular ions (produced upon bombardment of the sample surface with primary Cs^+ ion beam) rather than helium ions, which

can hardly be produced owing to high ionization energy of helium. This approach allowed one to determine the helium concentration at a level of 60 ppm.

V.3. Isotopic analysis

An analysis of the isotopic composition of uranium, thorium, plutonium, americium and some other transuranium elements in deposited microparticles is an important method for controlling nuclear activity of different countries. In this case, a key problem is to find particles containing high concentrations of radioactive elements, first of all, ^{235}U. Usually, the problem can be solved by detecting fission tracks emerging in the substrate near the radioactive target [32, 51] upon its irradiation with a neutron beam in a nuclear reactor.

This approach was used to locate radioactive particles [51] using SIMS for isotopic analysis of these species. Experiments with a low-resolution mass spectrometer (mass resolution was set to 300) faced with a number of problems including the mass spectrometry interference of $^{236}U^+$ with $^{235}U^1H^+$ in the determination of the relative concentration of ^{236}U (detection of this isotope indicates that the material the particle is made of is involved in nuclear processes in the reactor). Having applied a correction for the relative concentration of $^{235}U^1H^+$ from the relative concentration of $^{238}U^1H^+$, the relative concentrations of uranium isotopes in microparticles were determined correctly. Eventually, the technique was used to determine the $^{235}U/^{238}U$ isotopic abundance ratio in real samples. However, it was concluded [51] that correct quantitative determination of uranium isotopes in microparticles requires the use of high-resolution mass spectrometers.

A drawback of SIMS, namely, domination of the intensities of oxide ions over the intensities of element ions (including actinides) was used to resolve the interference of $^{241}Pu^+$ with $^{241}Am^+$ and thus to determine the content of ^{241}Am in nuclear fuel.[52]

V.4. Analysis of organic compounds using heavy clusters

Analysis using heavy clusters is one of the most promising and rapidly progressing applications of SIMS. A detailed description of the approach can be found in the literature.[53, 54]

A beam of heavy clusters Bi_3^+ produced in a low-energy ion gun was used to determine mineral and organic pigments, various additives and decomposition products in the painting materials of the 'Portrait of Nicolaes van Bambeeck' painted by Rembrandt.[55] A TOF-SIMS combination was used [56] for the direct analysis of green pigment in Renaissance paintings. It was established that this layer is composed of two different pigments, *viz.*, atacamite and copper carboxylate.

SIMS (25-keV Bi_3^+ ions) was used with high-resolution TOFMS (mass resolution 5000) for the direct analysis of a human skin sample from a mummy.[57] The skin samples were cut with a diamond knife into small pieces 1×1 mm in size and 7 mm thick, implanted into a silicon matrix, frozen and transferred to the mass spectrometer. The instrument was used in two modes, (i) with high mass resolution and a relatively low spatial resolution (2 μm) and (ii) with low resolution (1000) and relatively high spatial resolution (400 nm). This made it possible to distinguish between dermis and epidermis based on the composition of amino acids present in two main proteins. It was concluded that TOF–SIMS can be successfully used in studies of various arhcaeological biomaterials.

V.5. Secondary neutral mass spectrometry

The technique is a version of SIMS. Here, the sputtered atoms are ionized under the action of magnetron discharge, unlike conventional SIMS where ionization occurs within the surface layer of the sample. In some cases, the use of atoms instead of ions makes it possible to go from qualitative to quantitative analysis upon layer-by-layer sputtering because the relative content of sputtered atoms of the elements to be detected in the gaseous phase to a first approximation corresponds to the relative abundance of these elements in the sample. Conventional SIMS with detection of ions produced upon bombardment of the sample surface shows no such correspondence. Also, changes in the properties of the sample surface upon bombardment with O_2^+ and Cs^+ ions (this improves the depth resolution) cause changes in the sputtering rate and ionization probability.[43] Note that, in spite of high potential of SNMS, the technique is almost not used for quantitative analysis of the composition of samples owing to low performance and high cost of analysis and equipment.

Conventional SNMS involves the use of a low-pressure discharge system coupled to an ion-cyclotron resonance mass spectrometer and extraction of low-energy ions by a constant electric field applied to the sample. However, this is only applicable to conductive samples. Dielectric samples are sputtered using two modifications of SNMS with ionization in high-frequency, low-pressure discharge with a conventional ion gun (ion energy is ~ 1 keV) and with no ion gun. Electrons that compensate the surface charge and ions to sputter the sample arrive at the sample surface during different parts of the high-frequency discharge period.[43] Note that the main physical principles underlying SNMS and GD-MS are similar.

Quantitative SNMS studies of thin conductive layers (Pd/Cu, Si/Cu) and combined, conductive and non-conductive layers ($Si/TaO_x/Cu$, $Si/Ta-TaO_x/Cu$) from a few to a few tens of nanometres thick are well documented (see, *e.g.*, Refs 43 and 58–61). As a result, qualitative depth profiles of the elements with sharp inter-layer boundaries were obtained.

To reveal how matrix effects influence the probability of ionization of sputtered atoms, titanium atoms were ionized using a resonant laser ionization process with laser one-colour (319.99 nm) two-step ionization through their resonant and auto ionization states, *viz.*, $a^3F_4 \rightarrow w3G^0_5 \rightarrow$ auto ionization.[61] The system studied was multilayered Si/Ti, each layer being 10 nm thick; a beam of 1.0-keV Ar^+ ions was used. The depth profile of $^{50}Ti^+$ obtained by conventional SIMS exhibited a decrease rather than increase in the $^{50}Ti^+$ signal upon sputtering the titanium layer. This matrix effect originates from significant changes in the ionization probability and sputtering rate of titanium on going from the silicon layer to the titanium layer.

A laser-enhanced SNMS study of the Si/Ti structure gave much better results, namely, a correct depth profile of Ti was measured.

VI. Glow discharge mass spectrometry

Glow discharge is an electric discharge between two electrodes in a discharge cell filled with a low-pressure (10 – 1300 Pa) noble gas (see Fig. 2). The voltage applied to the electrodes varies from 100 V to a few kV and the electric current is of the order of a few mA. Initially, glow discharge was used for analytical purposes in emission spectrometry. In 1971, Coburn and Kay [63] presented the first glow discharge mass spectrometry system. Currently, various analytical GD-MS systems for research and commercial applications are available. There has been a trend towards the use of radiofrequency discharge and pulsed discharge instead of DC discharge as well as increased interest in time-of-flight mass analyzers.

By and large, GD-MS is a universal mass spectrometric technique. It features high sensitivity, accuracy, reproducibility, depth resolution and fast depth profiling. Wide use of GD-MS is also favoured by the relatively cheap equipment and low operating cost. The major drawback of the method is the lack of lateral (surface) resolution.

VI.1. Types of discharges and mass analyzers

There are four main types of discharge for GD-MS:

— direct current glow discharge (DC GD);
— radiofrequency glow discharge (RF GD);
— pulsed glow discharge (PGD) and
— pulsed RF GD.

The most widespread type of discharge cell is the Grimm cell. It represents a flat sample pressed to an air seal ring with a hollow anode at the centre, at a short distance from the sample.[64] Experiments with Grimm cells impose stringent requirements on the sample, *viz.*, it should have a smooth surface and be vacuum-tight. This reduces the range of suitable analytes. Recently, a study carried out using a modified Grimm cell was reported;[65] the sample was placed in a pre-chamber where the pressure was maintained equal to the pressure in the discharge cell.[65] However, since in this case there is a poorly evacuated additional volume, the mass spectrum exhibits more intense signals of parasitic components, in particular, NO^+, NH_2^+ and NH_3^+. Bubbling argon allows one to some extent reduce the intensities of these components.[65] Yet another type of the Grimm cell features ion transportation through a hollow anode by argon flow in order to reduce the loss of ions on the anode walls through ambipolar diffusion of ions to the wall and, consequently, to improve the sensitivity.[66] There are also discharge cells with a thin rod or a wire as the cathode, with the secondary cathode (to analyze non-conductive samples) and cells with a monolithic hollow cathode.

A discharge cell with combined hollow cathode to optimize the operating parameters of time-of-flight mass spectrometers was designed.[67 – 72] It consists of a flat sample pressed to an auxiliary hollow cathode made of high-purity and, usually, monoisotopic metal (first of all, aluminium or niobium). The hollow cathode allows one to increase the sputtering and ionization rates of the sample. Besides, discharge in the hollow cathode exists irrespective of the type of the sample (conductor or dielectric), whereas DC discharge in the Grimm cell requires a specific procedure in the case of dielectric samples. Yet another advantage of the modified Grimm cell consists in the possibility to use samples with rough surface and non-vacuum-tight samples.

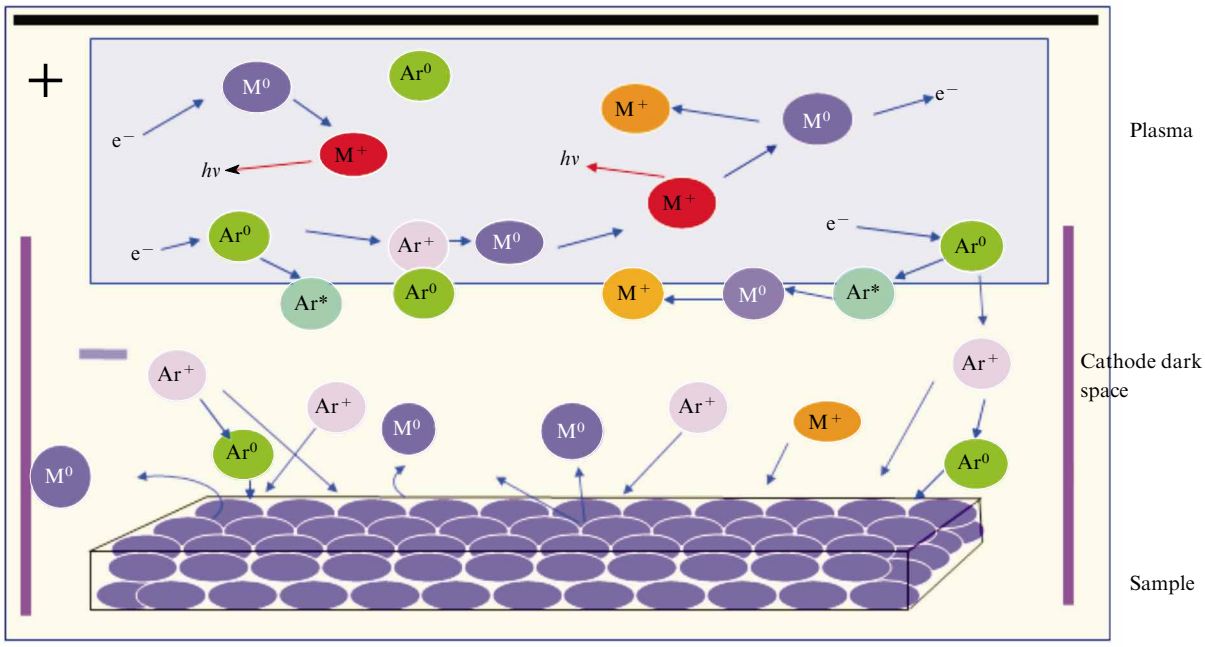


Figure 2. DC glow discharge: a schematic.[62]
M^0 and M^+ are respectively atoms and ions of sample material; Ar^0, Ar*, Ar^+ are respectively neutral, excited and ionized argon atoms.

Most often, GD systems are coupled to high-resolution sector mass spectrometers (mass resolution 300–10 000), while the quadrupole (mass resolution 300–800) and time-of-flight (mass resolution 400–3000) instruments are used more rarely. Attempts to use Fourier transform ion-cyclotron resonance mass spectrometry[73] featuring extremely high resolution ($n \times 100\,000$) failed because of difficulties in maintaining a very low pressure (10^{-6} Pa) in the chamber of the mass spectrometer, low signal-to-noise ratio and narrow dynamic range of concentrations to be determined.

VI.1.a. Direct current GD-MS with high-resolution magnetic sector mass spectrometers

Commercially available magnetic sector mass spectrometers for GD-MS studies are equipped with DC discharge cells only. This type of instruments, in particular, the Element GD mass spectrometer ('Thermo FIsher Scientific Inc.', USA), has a mass resolution of up to 10 000, which makes it possible to eliminate most part of interferences of the isotopes to be determined. Note that DC GD systems are inappropriate for the direct analysis of semiconductors and dielectric samples. This problem can be solved as follows. A traditional procedure involves mixing of pre-ground non-conductive samples with a well-compressible, high-purity conductive material (metal, graphite).[74] Otherwise, one can employ a flat secondary (usually, tantalum) cathode.[75] Both approaches have some drawbacks, *viz.*, lower sensitivity due to (i) dilution of the samples in the former case and (ii) greater power consumption for sputtering of the secondary cathode in the latter case, as well as contamination of samples and the appearance of interfering peaks from impurities and clusters in the mass spectrum.

VI.1.b. Pulsed GD-MS with time-of-flight mass spectrometers

The sputtering rate, the degree of ionization of the sample and, as a consequence, the sensitivity and limits of detection depend on the discharge power. As it increases, the sensitivity rapidly increases and the limit of detection decreases. However, the DC discharge cells can operate at power of at most 100 W even if the cathode is cooled. At higher power, one deals with strong overheating which can cause structural and compositional changes in and even destruction of the sample. A more efficient way to improve the sensitivity is to use pulsed discharge. The peak power during the pulse length exceeds 1 kW (*cf.* a few tens of Watt for the average power). These general considerations gave an impetus to a series of studies on the key features and advantages of pulsed Grimm glow discharge as source for time-of-flight mass spectrometry reported by Harrison and co-workers.[76, 77]

Time-of-flight mass spectrometers are efficient when coupled to pulsed ionization systems. Unlike the quadrupole or double-focusing sector mass spectrometers, time-of-flight mass spectrometers enable acquisition of the entire mass spectrum rather than its fragments upon application of every single pulse; this improves the accuracy and reproducibility of analysis. Also, ions produced in the source are consumed much more efficiently (the duty cycle, *i.e.*, the proportion of ions used in the mass spectrometer increases), thus improving the sensitivity of the technique. Yet another point concerns the depth profiling. Owing to a relatively high rate of film sputtering, sequential mass spectrometers (quadrupole and double-focusing sector instruments) used to analyze thin layers allow one to detect only a small number of elements, whereas the time-of-flight mass spectrometers are free from this drawback.

By appropriately choosing the time delay of the ejecting pulse of the time-of-flight mass spectrometer relative to the discharge pulse one can not only improve the efficiency of sputtering and ionization, but also discriminate some parasitic gaseous components, such as Ar^+, ArH^+, N^+, O^+, H_2O^+, OH^+, Ar_2^+, Ar^{2+} (see Refs 69–71, 78). Temporal discrimination of these components can be explained by different ionization mechanisms of various gaseous ions and the sample ions.[79]

Pulsed GD systems are characterized by much lower (by 2–3 orders of magnitude) background of scattered ions compared to DC GD systems,[80] whereas the sensitivities of both types of systems, expressed in counts per second per ppm, are comparable[80, 81] owing to a decrease in the duty cycle and an abrupt increase in the efficiency of sputtering and ionization during the discharge time on going from DC discharge to pulsed discharge. To a first approximation, both factors compensate each other. Low background at relatively high sensitivity is a significant advantage of pulsed systems because it allows one to attain low limits of detection.

In addition to temporal discrimination using time-of-flight mass spectrometers, there exists yet another method for reducing various interferences. The intensities of gaseous components can be diminished by diluting the discharge gas with small amount of hydrogen (0.3 vol.%–0.5 vol.%).[71, 78] In this case, the afterglow is accompanied by a number of charge-transfer reactions between some gaseous components and (mainly) H_3^+.[78] As a result, the intensities of the gaseous components decrease by 1–2 orders of magnitude, whereas the intensities of the sample components increase by a factor of 1.5 to 2. The addition of hydrogen allows one to significantly reduce some interferences, in particular, calcium in silicon samples can be determined from its major isotope, ^{40}Ca.[82] Besides, hydrogen decreases the intensities of Ar^+ and ArH^+ and thus noticeably reduces the background of scattered ions.

It was assumed[83] that water and oxygen can be removed from the discharge cell through reactions with participation of the elements with gettering ability, *e.g.*,

$$Ta + O \longrightarrow TaO \longrightarrow \text{wall}$$

$$Ta + H_2O \longrightarrow Ta\cdot[H_2O] \longrightarrow \text{wall}$$

The getter properties of samples prepared from compacted Ti, Ta, W, Ag, C and La_2O_3 powders were studied. The samples were placed in a hollow copper cathode and the mass spectra were acquired using a quadrupole mass spectrometer. The getter properties of the elements were evaluated using the La/LaO intensity ratio. The most efficient getters were titanium and tantalum. However, it is impossible to use the described discharge cell[83] for actual analysis. Also, the getter properties of these elements cannot be utilized in the case of Grimm cells because of the absence of the atomic ion source and the surface covered by a layer of the getter element.

The getter properties of powdered metals (Ti, Ta, Ag) mixed with powdered dielectrics (uranium oxide or plutonium oxide) and a tantalum secondary cathode (flat diaphragm with an internal diameter of 4 mm) were studied.[84] The secondary cathode enabled two modes of sputtering dielectric samples, DC GD or pulsed GD. The use of tantalum as filler and as secondary cathode made it possible to minimize the U/UO and Pu/PuO ratios; this is indicative of good getter properties of tantalum.

A PGD-TOF-MS study using a combined hollow cathode and niobium and tantalum auxiliary cathodes as getters was carried out.[85] For comparison, an aluminium cathode was also used. Experiments with the tantalum cathode revealed the absence of signals from OH^+, OH_2^+, OH_3^+ as well as CH_2^+, CH_3^+ and $^{16}O^+$ in the mass spectrum. The mass spectrum acquired using the niobium cathode exhibited signals from all these components, the signals from OH^+ being the strongest among OH^+, OH_2^+ and OH_3^+. A similar picture was observed for the other two pairs, Al (cathode) – Si (sample) and Al (cathode) – Cu (sample). Nevertheless, tantalum also stood apart based on the NbO^+/Nb^+ intensity ratio (niobium was present in tantalum as impurity). The relative intensity of niobium oxide in Ta was minimum. It follows that tantalum is a much more efficient getter compared to all other elements used in the experiments; this is in good agreement with the published data.[83,84]

The afterglow of PGD is characterized by almost no ionization of atoms of the elements whose ionization energies are higher than the excitation energy of the resonant (metastable) level of argon (11.62 eV). These are nitrogen (14.53 eV), chlorine (13.01 eV), fluorine (17.41 eV), oxygen (13.61 eV) and hydrogen (12.47 eV). To improve the efficiency of their ionization, it was proposed to dilute the discharge gas with helium (30% v/v).[86] Indeed, helium is able to ionize all these elements because the energy of its metastable level (20.61 eV) exceeds the ionization energies of all elements in the periodic table except neon. Using a gas mixture containing argon, helium and hydrogen (0.3 vol.%), one can employ pulsed discharge and time-of-flight detection of ions for the direct determination of nitrogen in steels. Note that the addition of helium to the discharge gas causes the intensities of components of the sample to increase by a factor of 2 or 3 for both DC discharge[87,88] and pulsed discharge.[71] This effect is due to the emergence of an additional channel of Penning ionization of the atoms M in the sample by metastable helium atoms:

$$M + He^* \longrightarrow M^+ + He + e$$

The limits of detection in the case of PGD (10 – 40 ppb) are governed by the background of scattered ions in the mass spectrometer. The sensitivity is 5 – 15 cps ppm^{-1} at pulse repetition rates between 5 and 10 kHz.

Note that analysis of non-conductive samples using a combined hollow cathode is possible, but at heavy cost, namely, enhanced memory effect owing to redeposition of atoms of the sample on the surface of the auxiliary cathode. Besides, the auxiliary cathode should be made of high-purity metals. Currently, these problems can be solved successfully. To eliminate the memory effect, interchangeable high-purity aluminium or niobium cathodes are employed, the cathodes can be multiply used upon cleaning. Also, the sputtering rate of aluminium is much lower than that of almost all metals and alloys, thus making the influence of impurities present in the auxiliary cathode on the results of analysis less pronounced.

VI.1.c. Pulsed RF GD-MS with time-of-flight mass spectrometers

The thermal load on the discharge cell can be reduced using not only PGD systems, but also the RF GD mode.[81,89] On the one hand, this approach makes it possible to analyze non-conductive samples in the Grimm cell. On the other hand, it enables utilization of the dynamic effects accompanying PGD to improve the sensitivity and to reduce the background of scattered ions. As for short-pulse PGD, in this case the maximum intensities of the sample components in the mass spectrum are observed with some time delay (τ) relative to the trailing edge of pulse, whereas the intensities of gaseous components rapidly decrease upon application of the pulse. However, whereas for PGD the τ value is determined by the time of atomic diffusion from the sample surface to the anode (time delay τ for the heavier atoms is longer than for the light ones), for pulsed RF discharge the processes responsible for particular τ values are still to be clarified,[81] although, as in the preceding case, the τ values for heavier atoms are usually larger than for the light ones. Most probably, switching off RF field facilitates transport of ionized atoms from the sample to the anode.

Temporal discrimination of some gaseous components and sample components allows reduction of various interferences as in the case of PGD.[81] The limits of detection calculated from the background intensity fluctuations in the vicinity of the mass to be determined were between 0.2 and 2 ppm (*cf.*, 0.5 to 40 ppm for non-pulsed RF discharge). However, the limiting factor for the background remains unclear, although in this case it is the background intensity and related fluctuations that governed the limits of detection. Note that the background can be composed of two components only, *viz.*, additive noise of data acquisition system (analog-to-digital converter noise, pre-amplifier noise, power line noise, dark-current noise of microchannel plates) and ions scattered in the mass spectrometer. The former component can be eliminated by amplitude discrimination, while the latter one can be reduced to a value of $10^{-8} – 10^{-9}$ of the intensities of the matrix components using an energy filter in the time-of-flight mass spectrometer. Therefore, the limits of detection of the order of a few ppb seem not to be unattainable in this case. Probably, the much higher limits of detection obtained[81] at rather high sensitivity ($n \times 10$ cps ppm^{-1}) are due to the lack of attention to discrimination of the background.

VI.1.d. The sensitivity and limits of detection in different versions of GD-MS

For all types of GD systems the limits of detection obtained in the analysis of real samples usually depend on three parameters, that is, the sensitivity, the magnitude of the background of scattered ions in the mass spectrometer and interference with the cluster components (the influence of this parameter cannot be elimi-

Table 1. The limits of detection (*I*/ppb) and sensitivity values (*II*/cps ppm^{-1}) for different types of GDMS.

Analyte	DC or RF + sector mass spectrometer (Grimm cell)		RF + time-of-flight mass spectrometer (Grimm cell)		PRF + time-of-flight mass spectrometer (Grimm cell)		PEG + time-of-flight mass spectrometer (Grimm cell)		PGD + time-of-flight mass spectrometer (combined hollow cathode)		Ref.
	I	*II*	*I*	*II*	*I*	*II*	*I*	*II*	*I*	*II*	
Metals and alloys	10–1000 [a]	300 (DC)	500–40 000	3–40	200–2000	5–50	40–200	2–30	10–50	5–15	81, 87
Semiconductors	50–10 000 [a]	10 (RF)	–	–	20–300	2–20	–	–	20–100	1–10	93
Dielectrics	10–200 [a] (with secondary cathode)	10–1000	400–5000	0.01–5	200–2000	5–100	–	–	100–400	2–10	74

[a] For the detection of the entire mass spectrum at moderate mass resolution. For a single component detection with no interferences at low mass resolution and long data acquisition time, the limits of detection are less than 1 ppt.

nated even using magnetic sector mass spectrometers with a mass resolution of 10 000).[82–92]

From the data in Table 1 it follows that the sensitivities of various pulsed GD-MS techniques are comparable and that differences between the limits of detection are first of all due to different magnitude of the background. At the same time, the sensitivity of a magnetic sector mass spectrometer with the Grimm cell is much higher while the limits of detection are lower. This can be explained by a high aperture and larger duty cycle of this type of mass spectrometers. However, this simultaneously occurs only for a small number of isotopic components. If the entire mass spectrum should be acquired, the sensitivity of the system abruptly decreases due to the decrease in the integration time for each channel used and becomes comparable or even lower than the sensitivity of pulsed systems coupled to the TOF mass spectrometers (1–10 cps ppm^{-1}). In this case, the limits of detection significantly increase.

When carrying out the direct analysis of solid samples, traditional calibration using standard reference samples is often impossible because of the lack of the reference samples for most systems to be analyzed. However, for GD-MS the relative sensitivity factors (RSF) [2] are usually of the same order of magnitude; this allows one to carry out semiquantitative analysis without reference samples. The RSF values achieved using different DC GD mass spectrometers are in reasonable agreement.[90] This also holds for the RSF values obtained using DC GD and RF GD.[91] The ionization processes for pulsed and non-pulsed GD are different, namely, Penning ionization dominates in PGD, whereas two more processes (electron impact and asymmetric charge transfer) should also be taken into account for DC GD and RF GD. As a consequence, in the former case, the average scatter of RSF values appeared to be two times narrower than in the latter, thus making PGD more convenient with respect to calibration.[92]

VI.2. Analysis of semiconductors, dielectrics and polymers

Studies of conductive samples using any types of glow discharge systems face no severe difficulties. Analysis of semiconductors and dielectrics is more problematic; therefore, we will consider them in more detail.

Semiconductors were analyzed by the following modifications of GD-MS: RF GD-HRMS (HRMS is high-resolution MS), PGD-TOFMS and RF PGD-TOFMS. As mentioned above, all of them enable the direct analysis of non-conductive and poorly conductive samples using no auxiliary devices. Gallium arsenide and silicon carbide were analyzed by RF GD-HRMS;[93] metallurgical-grade silicon and pure silicon were analyzed by PGD-TOFMS,[82] while solar-grade silicon was analyzed by RF PGD-TOFMS.[94] The mass spectrum of SiC exhibited carbon clusters, C_n^+, up to $n = 7$.[93] Meanwhile, significantly higher relative intensities of such clusters were reported in the LIMS and SSMS studies. No such clusters were observed when SiC was analyzed by PGD-TOFMS; the mass spectrum exhibited a minimum number of cluster components (Fig. 3).

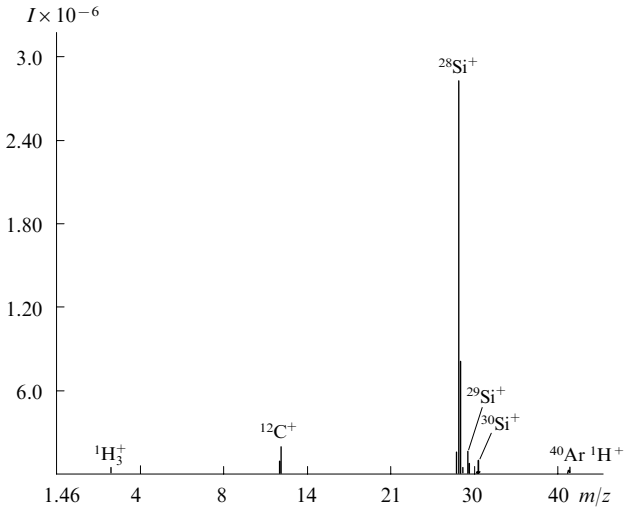


Figure 3. Fragment of the mass spectrum of SiC obtained by PGD-TOFMS.

It was found [93] that the energy of ions of the sample material is ~10 eV higher than that of gaseous ions. This made it possible to significantly reduce the relative intensities of gaseous components by adjusting the ion transfer optics. In most cases, the limits of detection were in the range from 1 to 100 ppm, being much lower (less than 0.1 ppm) for light elements including Li, Be and B. High limits of detection are probably due to low efficiency of ion transfer in continuous glow discharge.[81] The use of PGD-TOFMS for analysis of silicon [82] led to a considerable decrease in the limits of detection that spanned the range from 30 to 80 ppb for B, Zr, Ag, Ti, Cd, Mn and Sb; this is sufficient for the analysis of solar-grade silicon and moreover metallurgical-grade silicon.[82] The RF PGD-TOFMS study [94] was aimed at measuring the distribution profile of boron in solar-grade silicon. The profile thus obtained was in good agreement with the profile measured by SIMS; however, the limit of detection for boron was not reported.

Direct determination of radionuclides in soils, sea sediments and plants is an important application of GD-MS. An example is provided by the determination of radioactive isotopes of caesium, strontium, uranium, thorium and plutonium using a VG9000 GD high-resolution sector mass spectrometer equipped with a DC discharge cell.[95] Since all samples were dielectrics, experiments with DC discharge were carried out using two different analytical procedures, namely, mixing of samples with high-purity silver powder (1 : 10) and the use of a secondary cathode. In the former case, the sensitivity significantly reduced due to dilution of the sample and additional interferences appeared in, *e.g.*, the determination of thorium, $^{107}Ag^{109}Ag^{16}O^+$ and $^{232}Th^+$. To avoid dilution of the sample in the determination of ^{236}U, a tantalum secondary cathode was used initially. However, this was accompanied by interferences between $^{180}Ta^{40}Ar^{16}O^+$ and $^{236}U^+$. To eliminate them, it is necessary that the mass resolution be about 2000; however, an increase in the mass resolution of a magnetic sector mass spectrometer causes a proportional decrease in sensitivity.[95] As a result, attempts to attain the desired limits of detection at a level of a few pg per gram failed and subsequent experiments were carried out using a gold secondary cathode. Ultralow limits of detection (< 1 pg g^{-1}) of radionuclides were obtained with the secondary cathodes at a low mass resolution of 100 and an integration time of 1 h; the reproducibility was in the range 3% – 10%. Meanwhile, the low limits of detection are only attainable for a number of heavy elements at long data acquisition times, single-element analysis and very low mass resolution which cannot be used for moderate and light masses owing to numerous interferences. In the case of multi-element analysis with moderate mass resolution and integration times of the order of 10 min, the limits of detection were in the range from 0.02 to 1 ppm.

In PGD – TOFMS studies with a combined hollow cathode, short-pulse discharge allows one to avoid a severe problem that appeared in the analysis of non-conductive samples, namely, charge accumulation on the sample surface, because electrons from the glow discharge plasma compensate the surface charge.[96] It was found [86, 97, 98] that pulsed discharge in a combined hollow cathode causes sputtering of samples with high surface resistance. The effective surface resistance of sputtered GaN was higher than 10^7 Ω; in this case, the sputtering rate and the intensities of elements from the sample material in the mass spectrum should decrease appreciably. However, the intensity of gallium was comparable with the intensity of iron in the analysis of the steel reference sample. In this case, one deals with the onset of the surface conductivity in the course of sputtering of the sample material. The sputtering coefficient of nitrogen is larger than that of gallium; therefore, the surface layer of gallium nitride a few monatomic layers thick becomes enriched with gallium and the surface conductivity increases dramatically. A similar effect was also observed during the sputtering of a sapphire with a wide bandgap (9.5 eV) and, as a consequence, very low conductivity.[97, 98] The mechanism of sputtering of non-conductive samples in a pulsed glow discharge in combined hollow cathode was studied.[99] It was shown that two sputtering mechanisms are in operation simultaneously, namely, redeposition of the conductive layer of the auxiliary cathode material and formation of a specific layer enriched with the less volatile component.

An experimental RF GD-TOFMS system was utilized [100] for the direct analysis of both bulk and thin-coated glasses. Not only continuous RF discharge (as in Ref. 81), but also pulsed RF discharge was used, the sensitivity of analysis of conductive samples being much higher in the latter case. The sensitivity of the RF PGD-TOFMS analysis of dielectric samples and, therefore, the limits of detection appeared to be close to those achieved in the detection of metals;[81] this is probably due to the formation of a specific surface conductive layer (see above).

Main methods for analysis of polymers and polymer films include IR spectroscopy,[101] Raman spectroscopy [102] and gas chromatography.[103] Among the title mass spectrometry techniques, SIMS is used for polymer studies. The energy of sputtered ions in GD is much lower than the ion energy in the SIMS ion beam (*cf.* 100 – 200 eV for DC GD and 50 eV for RF GD *vs.* a few keV in SIMS). Therefore, GD-MS is a much less destructive method for analysis of polymers and one can obtain qualitative information on the polymer composition and carry out depth profiling. But until recently, GD was almost not applied to the analysis of polymers. The case in point is that polymers are usually very sensitive to thermal load and can degrade in conventional GD. On the other hand, the intensities of analytes in the mass spectrum acquired using a low-power discharge (no thermal effects) are low and their identification is difficult. Nevertheless, RF GD-TOFMS was used for, *e.g.*, analysis of polymer membranes based on polyphosphazene.[104]

The informativity and sensitivity of analysis of the composition of polymers were significantly improved upon going to pulsed techniques, in particular, RF PGD-MS.[105] Besides, that study demonstrated the possibility to analyze poly(methyl methacrylate), polystyrene and some other polymer thin films on silicon wafers (films were 300 – 400 nm thick). It was shown that polymers can be identified with certainty using the intensity ratio of the spectral components.

Fluorine- and chlorine-containing polymers were analyzed [106] by RF PGD-TOFMS with detection of negative ions. This made it possible to eliminate signals from Ar^+

and ArH^+, to significantly reduce the background and to increase the intensities of certain spectral components.

The determination of bromine in acrylonitrile butadiene styrene (ABS) by RF PGD-TOFMS involved a direct analysis of ABS and compacted mixture of ABS and silver powders (18 : 1 by mass).[107] The sensitivity of direct analysis using argon as discharge gas was very low. Like in the determination of nitrogen (see Section VI.1.b), this is due to the fact that the ionization energy of bromine (11.81 eV) is higher than the excitation energy of argon (11.62 eV). Experiments with compacted powders, although made it possible to improve the efficiency of sputtering, did not lead to noticeable increase in sensitivity owing to dilution of the sample. When helium was used instead of argon, the ionization efficiency abruptly increased, but the sputtering efficiency reduced because helium atoms are much lighter than argon ones. The limits of detection attained were rather high, *viz.*, 0.2 mass % for argon and 0.5 mass % for helium. Much lower limits of detection (about 0.04 mass %) were obtained in the determination of bromine in polymers by the same technique, RF PGD-TOFMS.[108] The difference between these results seems to be due to higher resolution of the mass spectrometer and better frequency characteristics of the GD unit used by the authors of Ref. 108 compared to those of the instrument described in Ref. 107.

An interesting system for analysis of polymers[109] includes a module for laser ablation of polymer samples and a tailor-made interface (in this case, a hollow cathode) for transfer of the species and atoms thus produced to glow discharge plasma. Helium was used as discharge gas to allow Penning ionization of fluorine and chlorine atoms. A number of polymers were identified from the relative intensities of the characteristic components in the mass spectrum, but the sensitivity of the system was too low to determine impurities.

Emphasize that only pulsed GD systems coupled to TOFMS have the operating characteristics suitable for commercial use of GD-MS in the analysis of polymers in the nearest future.

VI.3. Depth profiling

Glow discharge mass spectrometry becomes increasingly more popular as depth profiling technique.[100, 110, 111] Its main advantages include high performance and the ability to analyze rather thick (a few micrometres), thin (100 nm) and ultrathin (1 nm) films.[110–113] Earlier,[114–116] only thick films were analyzed by GD-MS; however, recent advances enabled analysis of increasingly thinner samples. The potential of DC GD-MS in depth profiling of solar-grade silicon can be illustrated by the results of a study[117] on the distribution of Fe, B, Cu, Ti and P up to a depth of 10 μm. The DC GD-MS and SIMS studies demonstrated good agreement between the concentration profiles obtained for most elements.

Recently, RF PGD-TOFMS systems have been increasingly frequently used for depth profiling. Such systems allow one to sputter both conductive and nonconductive samples and have a relatively high sensitivity. Besides, a rather high mass resolution of time-of-flight mass spectrometers (2500–3000) makes it possible to eliminate a large number of interferences.[110, 115] Unlike SIMS, RF PGD-TOFMS systems are suitable for measuring quantitative concentration profiles of elements in ultrathin layers, *e.g.*, profiles of boron and arsenic in silicon.[110] This can be done having known the sputtering rate of a silicon reference sample and using silicon as internal sandard. Quantitative profiles of cobalt in Nb/Al/Co ultrathin layers were obtained.[116] It was concluded that, in spite of somewhat lower depth resolution compared to SIMS, RF PGD-TOFMS is at least a competitive technique because of much higher performance and much lower cost.

An interesting combination of several methods for mass spectrometric analysis of elements, that is, LIMS, LA-PGD-TOFMS and PGD-TOFMS was reported.[118] In principle, by coupling an LA unit and a GD module to a TOF mass spectrometer one gets an LA-GD-TOFMS system with high in-depth and in-plane resolution. Indeed, such a system[118] provided almost a tenfold increase in the analyte intensities compared to the intensities measured by LIMS. However, this is still insufficient for efficient operation because one deals with poorer depth resolution (compared to GD) and in-plane resolution (compared to LA). In this case, a strategy with separate use of LIMS and GD-MS seems to be more promising.

VI.4. Isotopic analysis

There are a few studies on the isotopic analysis by GD-MS.[95, 119–121] The isotopic composition of boron and lithium in the samples of materials for nuclear industry was determined[95] by DC GD-HRMS with the secondary cathode (ICP-MS is inefficient because of low sensitivity for light elements). Like in ICP-MS, the main problem comes from various interferences, first of all, with multiply charged ions. In particular, $^{10}B^+$ interferes with $^{40}Ar^{4+}$, $^{40}Ca^{4+}$ and $^{30}Si^{3+}$. These interferences can be eliminated using mass spectrometers with a relatively low mass resolution (500). No higher mass resolution is also necessary to distinguish between the $^6Li^+$ and $^7Li^+$ isotopes and between doubly charged ions $^{12}C^{2+}$ and $^{14}N^{2+}$. The isotopic abundance ratio of $^{10}B^+$ and $^{11}B^+$ in ZrB solid samples was determined.[120] The reproducibility was 0.2%–0.5% at an instrumental discrimination of 1.4% (it can be removed by isotopic calibration). Like in Ref. 119, $^{40}Ar^{4+}$ ion was one of the main interfering components. In the isotopic analysis of silicon by HR-GDMS a mass resolution of 2000 appeared to be high enough to eliminate interferences between the silicon isotopes $^{28}Si^+$, $^{29}Si^+$, $^{30}Si^+$ and $^{27}AlH^+$, $^{12}C^{16}O^+$, $^{14}N_2^+$, $^{28}SiH^+$, $^{27}AlH_2^+$, $^{12}C^{16}OH^+$, $^{29}Si^+$, $^{14}N^{16}O^+$ (Ref. 121). The accuracy of determination was 0.2%–1%.

The results of determination of the isotopic abundance ratios of uranium[119] were in good agreement with those obtained by TIMS. The published accuracy values[119–121] fall in the range from 0.2% to 1%, being much poorer than the results obtained using multicollector systems. However, for single-collector HR-GDMS this accuracy is more a rule than exception because instabilities of the ion source for sequential mass spectrometers (a single-collector HR-GDMS is a sequential mass spectrometer) immediately influence the accuracy of analysis. Better accuracy can be achieved using TOF mass spectrometers which in fact simultaneously acquire the entire mass spectrum. For a PGD-TOFMS system, the accuracy in determination of the isotopic composition of an ele-

Table 2. Parameters of the analytical methods considered in this review: a comparison.

Parameter	LA-ICP-MS (see Refs 1, 10 – 14, 21 – 28)	LIMS (see Refs 37 – 40)	SIMS (see Refs 1, 42 – 48, 52)	GD-MS	
				DC GD or RF GD + sector mass spectrometer (Grimm cell) (see Refs 1, 74, 75, 84, 90, 95, 119)	PGD and RF GD + time-of-flight mass spectrometer (see Refs 80, 81, 89, 105)
Limit of detection /ppm	0.1,[a] 100,[b] 0.01,[c] 10 [d]	0.1 – 1	10^{-5} – 0.1	0.001 – 1	0.010 – 1
Performance /sample per hour	1 – 5	0.3 – 4	0.1 – 0.3	5 – 10	5 – 10
Reproducibility (%)	20 – 30	10 – 50	–	1 – 10	2 – 10
Systematic error (%)	10 – 20	–	–	5 – 20	5 – 20
Spatial resolution					
in-depth /nm	300 – 1000	1000	0.2 – 1	3 – 10	1 – 5
in-plane /μm	10 – 30	10 – 30	0.05 – 1	3000 – 4000	3000 – 6000
Intensities of cluster components MO_mH_n in the mass spectrum	–	+	+	–	–

[a] For argon, heavy elements; [b] for argon, light elements; [c] for helium, heavy elements; [d] for helium, light elements.

ment is first of all determined by the statistical error, *i.e.*, by the number of ions counted.[122] Having detected a sufficiently large number of $^{52}Cr^+$ ions, an accuracy of 0.1% was achieved.

Multicollector mode for almost all analyte isotopes was implemented using a detector representing Faraday-strip array.[123] As a result, the accuracy in determination of the relative abundance of isotopes by DC GD-MS with a magnetic sector mass spectrometer with a 50-μm slit was 0.1% – 0.04%. The limits of detection of the elements were much poorer (0.2 – 1.7 ppm) than those attained in HR-GDMS studies owing to relatively high pre-amplifier noise. To reduce the intrinsic thermal noise, the detector was cooled to −40 °C.

Summing up, the potential of the direct isotopic analysis of solids by GD-MS is far from being exhausted. Much lower level of interfering components and clusters compared to ICP-MS often allows one to exclude preliminary separation of analyte elements by, *e.g.*, chromatography or electrophoresis (in other words, this means no labour-consuming sample preparation).

For better visualization of the potential of the methods in question, one can compare their parameters, *e.g.*, the limits of detection, performance, depth resolution and in-plane resolution, reproducibility and the presence or absence of intense cluster components MO_mH_n (Table 2). Note that this comparison is to some extent conditional because the values listed are to a great extent determined by not only main principles underlying a particular technique, but also by the type of the sample and by the parameters of the analytical system in hand.

VII. Conclusion

Currently, there has been a rapid progress in the methods for direct mass spectrometric analysis. Some of them compete with other techniques, which also facilitates their development. SIMS, LA-ICP-MS and GD-MS rank first from the standpoint of applicability and versatility of analytes. Often, they are combined with other methods of analysis of solids, namely, Auger electron spectroscopy, X-ray photoelectron spectroscopy, Rutherford backscattering spectrometry, *etc.* It seems likely that in the nearest future one should expect the emergence of new versions of the methods considered, which should enhance their analytical potential.

New types of analytical problems and progress in mass spectrometry techniques cause significant changes in the capabilities of the techniques and in the corresponding application fields. For instance, SSMS became uncompetitive and stopped development in scientific terms; SIMS is to a great extent aimed at (i) mapping and depth profiling of mainly organic coatings and biological samples and (ii) performing isotopic analysis, whereas inorganic elemental analysis now does not play a leading role. The application fields of LA-ICP-MS and GD-MS significantly extended. Indeed, LA-ICP-MS is now used for analysis of biological samples and for isotopic analysis. As to GD-MS, it is employed to analyze semiconductor and non-conductive materials, thin films and coatings, as well as polymeric materials. Considerable advances have also been made in isotopic analysis. By and large, the technique becomes increasingly more versatile.

Summing up, mass spectrometry methods progress in diverse directions and now compete not only with one another, but also with other, non-mass spectrometry methods, although a number of common avenues of research, *e.g.*, isotopic analysis (SIMS, LA-ICP-MS and GD-MS), depth profiling (SIMS and GD-MS) and mapping of coatings and biological samples (SIMS and LA-ICP-MS) persist.

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