

Inorganic mass spectrometry of solid samples

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Summary. In this review some recent developments in the field of inorganic mass spectrometry of solids are described with special emphasis on the actual state of understanding of the ionization processes. It concentrates on the common characteristics of methods such as spark source-, laser-, secondary ion-, inductively coupled plasma- and glow discharge mass spectrometry.

Introduction

Within the field of instrumental inorganic trace analysis the use of mass spectrometry is enjoying at present a resurgence of interest [1, 2]. Existing and sometimes long established methods such as spark source mass spectrometry and thermal ionization mass spectrometry are at present finding new fields of applications. Also, developments of new methods are appearing rapidly, which become quickly commercialized as their market potential is realized, such as inductively coupled plasma mass spectrometry and glow discharge mass spectrometry.

This new wave of interest and the diversification of the methodology are driven for a large part by materials science which requires characterization of purity with increased sensitivity and accuracy for elemental impurities, in a rapidly expanding range of technologically important materials. Indeed, many of the complex new materials being developed and used today derive their unique properties from either a previously unobtainable purity or else from the presence of multiple phases or local variations in elemental concentration within heterogeneously constructed materials. Controlled impurity doping, segregation effects at interface, grain boundary migration and recrystallization effects, lead to needs for analytical problem solving with increasingly complex analytical instrumentation. Simply performing bulk analyses of a restricted number of impurities on such materials is, in general, not sufficient to achieve understanding of their nature and their properties. Localized analysis within composition gradients, even the precise determination of three dimensional distributions of impurities is now often required. In many problem areas it is mandatory that the full elemental range is adequately covered, or that spatially resolved information from the surface layer or from specific subsurface regions can be obtained.

This paper attempts to concentrate on a number of common features of a selected number of the now available

methods: spark source mass spectrometry, laser mass spectrometry, secondary ion mass spectrometry and ion imaging, inductively coupled plasma and glow discharge mass spectrometry. The common characteristic features of all these methods will be emphasized especially as far as they relate to the ion source and the mass spectrometry equipment. Indeed, the ion source in which energy is deposited into the sample for the atomization and the ionization of a representative part in a vacuum environment for subsequent extraction and analysis in the mass spectrometer, overwhelmingly determines both the type and the instrumental complexity of the mass spectrometric equipment and the eventual characteristics of mass spectra in particular. These, in turn are responsible for the ease of calibration and the general quality of the analytical data that can be obtained.

A few examples of state of the art performance concerning accuracy of several types of mass spectrometric techniques as now routinely available will be selected from the author's laboratory experience.

Methods for mass spectrometry of solids

Ionization processes in mass spectrometry of solids

To determine the elemental composition of a solid in a mass spectrometry, its crystalline and molecular structure must be destroyed, i.e. the substance is to be vaporized, atomized and finally ionized. This is generally achieved either by plasma solid interaction or by particle bombardment. A classification of some presently predominant and suggested methods is outlined on Fig. 1.

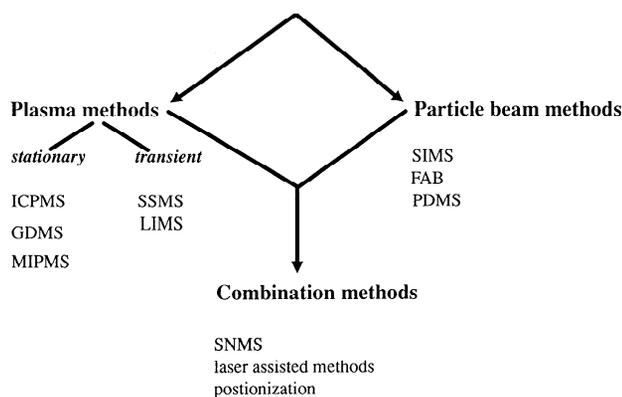


Fig. 1. Classification of the working principles in inorganic mass spectrometry

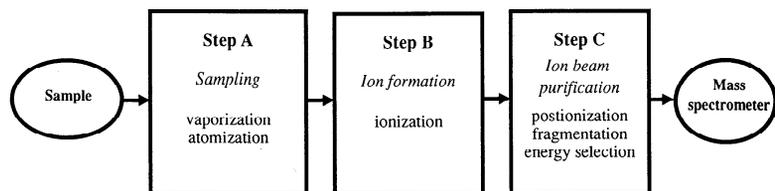


Fig. 2
The different steps of ion formation in ion sources

Plasma ion sources are constantly gaining importance in atomic mass spectrometry and a number of them are now available which serve differently more or less related analytical needs. The basic operation principle of all these sources is to deposit by a suitable process enough energy into the solid sample to ionize a representative and sometimes a physically controllable part of it and to achieve a plasma state for a longer or shorter period of time. A fraction of these ions is then extracted into the mass spectrometer and eventually measured. Differences among the available methods of plasma function are due to the distinct way energy is deposited in the sample and the amount of energy and/or its density. A number of methods utilize electrical energy as in the glow discharge (GD) or the spark ion source (SS), or rely on one form or another of electromagnetic radiation as in the pulsed laser induced (LI) or the microwave induced (MIP) or inductively coupled plasma (ICP) sources.

In particle beam ion sources the energy is deposited as kinetic energy in ion bombardment of the sample surface as in secondary ion mass spectrometry (SIMS), fast atom bombardment (FAB) and californium-252 plasma desorption mass spectrometry (PDMS).

Despite all care taken, mass spectra produced in any existing ion source do not consist exclusively of the ions of interest, i. e. the singly charged atomic ions, but also contain, with variable abundance, multiply charged ions, and, more disturbing for the analysis, polyatomic charged species. The latter are generated by interactions in the gas environment of the source or arise in the sample excitation process itself. Increasing the resolving power of the mass spectrometer is a costly, and in fact often inappropriate way to remove the influence of the resulting isobaric interferences. Attempts to decrease the abundance of the polyatomic ions by increasing the excitation energy also fail or lead to other problems e. g. to increased and more variable kinetic energies of the elemental ions.

New trends in ion source design are based on the understanding that vaporization and atomization of the sample (the sampling step) on one side and ionization of the resulting atom reservoir on the other side are two distinct processes which often require different sets of conditions. When each process can occur in succession each might be optimized for its intended purpose. At least part of the present success of GDMS is based on the fact that both sets of processes are effectively decoupled in a simple and stable ion source, thus giving rise to a source which is relatively free of matrix effects. Other recent techniques use the same decoupling principle. In sputtered neutrals (or secondary neutrals) mass spectrometry (SNMS) the sampling step is effected through ion bombardment or sputtering, and the secondary neutrals are separately ionized. In other ion sources the removal of the polyatomic species by fragmentation is done à posteriori to their formation, e. g. by collision in gas cells, Penning-ionization with metastable atoms, electron impact ionization in dense and energetic electron gas, or photon(laser)-particle interactions. Lasers are also

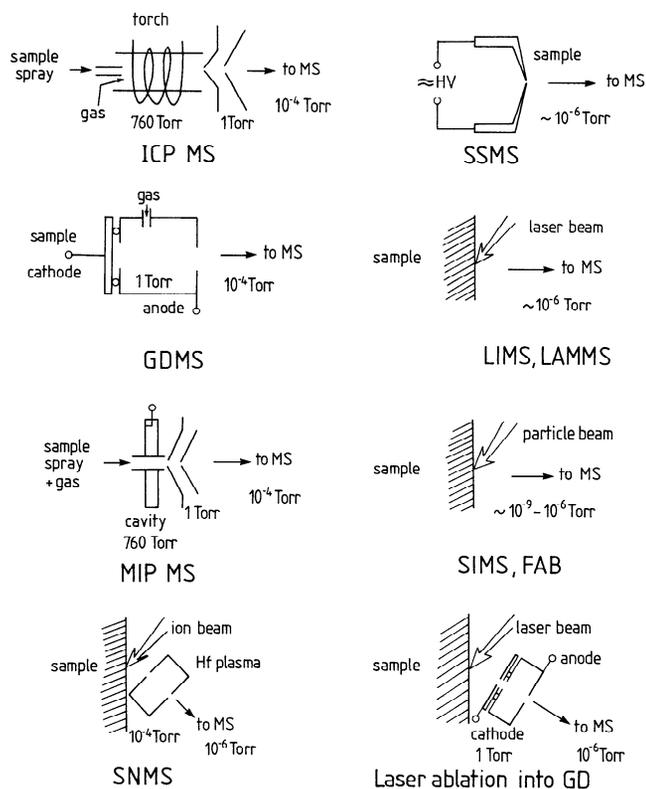


Fig. 3. Schematic representation of the different mass spectrometric ion sources discussed

Table 1. Working conditions of plasma ion sources

Source	Gas	Pressure (Torr)	Excitation (Torr)
Glow	Ar, Ne	0.01 – 10	DC/13.56 MHz; 5 – 50 W
ICP	Ar, He, Ar/N ₂	760	5 – 50 MHz; 1 – 10 kW
MIP	Ar, Hc, N ₂	760	150 – 2450 MHz; 50 – 500 W
Spark	none	10 ⁻⁶	10 – 100 ns; 10 ⁸ W/cm ²
Laser	none	10 ⁻⁶	~ 10 ns; 10 ⁸ – 10 ¹⁰ W/cm ²

used to ablate and atomize material, prior to the ionization in an ICP or GD source. Alternatively, laser ablation or more conventional sampling methods (e. g. thermal desorption, sputtering) can be combined with resonance ionization mass spectrometry (RIMS) [3, 4]. Figure 2 shows a general outline of the succession of processes in ion sources. In most conventional sources the steps A and B occur simultaneously.

The ion sources of relevance in this paper are schematically represented in Fig. 3, while the working conditions are summarized in Table 1. They gave rise to distinguishable analytical methods with specific merits and

drawbacks and give rise to particular applicational niches within the analytical world.

Most of the plasma ion sources now exploited in elemental mass spectrometry have previously been applied as radiation sources in optical atomic spectrometry, indeed, in general the mass spectrometric application often is a more sensitive and more generally exploitable alternative to optical emission spectrometry as an analytical tool. This is the direct result of the simplicity of the mass spectra compared to the optical spectra, the completeness of elemental coverage together with the superior sensitivity and detection limits attainable for ion detection, and finally the ability to obtain information about the isotope composition. Hence, mass spectrometry tends to direct the attention towards the exploitation for applications in the most demanding problem areas, unfortunately at the expense of adding instrumental complexity and cost.

Recently a growing interaction between the techniques which are available for organic mass spectrometry and inorganic mass spectrometry become apparent, e.g. in the application of Fourier transform, ion cyclotron resonance mass spectrometry (FTMS) [5] and plasma desorption mass spectrometry (PDMS) [6], whose potential in surface analysis was recently demonstrated with an information depth of a few monolayers.

Scope of available methods for inorganic mass spectrometry

The spark source mass spectrometer is the archetype instrument within the range of available methods. Two kinds of ion sources were originally used when the technique was introduced as a commercial instrument in the early '60s: the radiofrequency spark and the low voltage arc, but it is the first which eventually remained in the commercial instruments. In this source a pulsed radiofrequency voltage (typically 1 MHz, several tens of kV) is applied in short pulse trains across a gap between conducting electrodes. Spark parameters such as pulse length and repetition rate are adjusted according to the characteristics of the sample. The electrodes are present in a spark housing and an accelerating voltage potential extracts a fraction of the ions produced into the mass analyzer. The spectrometer is of the Mattauch-Herzog double focusing type which achieves angle and energy focusing on a plane in which an ion emulsion detector (photoplate) is used in the standard setup, allowing simultaneous detection of ions of different mass-to-charge ratio.

The advantage of this detection mode is that it integrates the entire mass spectrum with good detection power and excellent mass resolution. Hence, it is well suited to demands for panoramic analysis and it is adapted to the discontinuous, often erratic production of ions in the source. Drawbacks are the nonlinear response of the photoplate, its low dynamic range (which demands multiple exposure) and the lack of uniformity of response of the emulsion. An alternative way is electrical detection with Faraday cups or a multiplier with either scanning of the mass spectrum or switching to particular peaks. This detection mode never reached popularity as a result of the unstable characteristics of the source and, as the amount of material sampled is low, due to the exaggerated effects of any sample inhomogeneities. Electronic equivalents of the ion emulsion detectors, position sensitive electro-optical detectors, did not yet reach the size and spatial resolution to be considered as real direct reading alternatives [7].

Despite its drawbacks the method is at present the method of choice for the characterization of purity for a number of materials for microelectronics industry: high purity gallium, arsenic, selenium, tellurium, indium etc. [8]. However, as we will see in a later stage of this paper, the near absence of recent fundamental investigations and practical development work on the instrumentation at present limits its full exploitation. There is no drive now from the instrument makers to design a new generation of instruments which take into account presently available increased knowledge in concept, ion optics and ion detection.

Laser induced mass spectrometry (LIMS) in which the ion production follows the interaction of an energetic laser pulse, typically from a doubled, tripled or quadrupled frequency Nd YAG laser, followed two distinct lines of development. First, a number of spark source instruments were modified to allow a pulsed laser source as a replacement for, or an addition to the spark source. This approach never became adopted in a commercial instrument and the number of existing instruments is, hence, extremely limited. Second, specific instruments were developed for the microscopical analysis based on the interaction of a focused laser beam (through an optical microscope) with the sample. These instruments are based on the use of time of flight mass analysis utilizing the strictly momentary nature of ion production within the laser source. Several laser microprobe mass spectrometer (LAMMS) instruments have been developed, some of which are now commercially available and are used in a range of problems [9, 10]. They have found applications increasingly in molecular analysis, when used at low laser energy-sample interaction conditions, the so-called laser desorption mode [11].

In secondary ion mass spectrometry the ion production is the result of sputtering material from the sample surface through the interaction of an energetic primary ion beam. Two types of instruments can be distinguished. First there are the non-imaging ion probes used for depth profiling on laterally homogeneous samples. Often they are incorporated, together with other surface analytical systems (AES, XPS and electron microscopy), in setups for the study of the sample surface. Secondly, there are the imaging ion microscopes which are now rapidly evolving into instruments for the determination of the two- and three dimensional distribution of elemental impurities. There is a considerable interest in the further development of these methods which are needed for production control and development in materials science in general and microelectronics in particular, but they also find important applications in biology and geo- and cosmochemistry.

The glow discharge consists in its simplest form of a cathode and an anode present in a low pressure gas medium. Breakdown of the gas is obtained by the application of an electric field across the electrodes and ions are produced which are accelerated towards the electrodes and give rise to sputtering of material from the sample surface. The glow discharge hence produces the same kind of particles as those observed in ion beam sputtering but in the gas environment they are subject to a sequence of collisional processes leading to ionization by mainly two mechanisms: electron impact ionization and ionization as a result of transfer of energy from a metastable state of the discharge gas to the analyte atom (Penning ionization). These interactions in the gas medium effectively decouple the sputtering process from the process leading to the ion beam which becomes extracted

into the mass spectrometer, a characteristic which distinguishes the method from the others. Early in the history of inorganic mass spectrometry the development of the spark led attention away from the glow discharge, but the spark's eventual limitations recently brought interest back to the glow discharge source. At present there is much interest in the development of glow discharge mass spectrometry with commercial instrumentation [12–14] now becoming available. The commercial GDMS instruments are based on the use of two sector double focusing mass spectrometers but instruments also exist with simpler quadrupole type mass analyzers. A major problem that is encountered even with the double sector instruments [15] is that of isobaric interferences due to molecular species (residual gas species, dimers and argides of the analyte). Collision induced dissociation in a double quadrupole mass filter system is a demonstrated approach to eliminate these interferences [16].

Sputtered neutrals mass spectrometry (SNMS) is a method which is intermediate between SIMS and GDMS. In SNMS the neutral particles sputtered from the sample are post-ionized in a radio frequency plasma whereas the charged secondary ions are shielded by an electric field [17–19]. The decoupling of the sputtering and the ionization processes minimizes the matrix effects compared to SIMS [20]. In commercial instrumentation of this type the ions are analyzed in a low resolution quadrupole mass filter.

Inductively coupled plasma, microwave induced plasma and direct current plasma (DCP) mass spectrometry are not methods which allow direct analysis of solids as the sample needs to be introduced into the plasma as a nebulized solution, but both ICP and MIP methods are included in Fig. 3 for the sake of the now widely popular ICP-MS [21–23]. They can be applied for inorganic analysis of solid samples with the aid of a pulsed laser as a means for bringing controlled amounts of material within the source [24].

Ion sources

There are in general two working regimes for the ion sources for inorganic analysis which need to be clearly distinguished, those based on a stationary, in principle time independent regime such as the ICP, MIP and the GD and those in which ionization is produced in a transient or repetitious mode such as typically in the spark source or the pulsed laser source.

The properties of the ion source are intimately linked to the requirements of the particular application. According to the scope of this paper we will restrict our discussion to the ion sources which lead to practical utilization in inorganic mass spectrometry of solids as opposed to those which are exploited in organic analysis. There are indeed opposing needs for these two mass spectrometric applications which can be defined as follows. Inorganic mass spectrometry aims at destroying molecular structure in the production of ideally singly charged elemental ions. The organic ion sources, on the other hand, try to preserve something which elemental mass spectrometry attempt to avoid namely molecular (structural) information which will serve the need for identification of specific organic molecules. In recent years most progress in organic mass spectrometry appeared in the area of 'soft' ionization methods which minimize fragmentation and tend to yield spectra which provide simplicity, molecular weight and structural data.

There are several general comments that can be made in relation to the need of inorganic mass spectrometric analysis to efficiently ionize the material under study. They are concerned with the generation process of the ions from the vaporized material and deal with the ultimate goal of providing a functional relationship between the concentration of the sensed species in the sampled plasma and in the original sample. We will review the main problems in the following paragraphs.

Plasma processes in the ion source

The essential steps in the formation of the elemental ions to be measured with a mass spectrometer are the atomization, the ionization and finally the ion beam formation and extraction. Every ionization process includes the conversion of neutral particles which are obtained from the solid, into ions. Unavoidably one passes through a phase where neutrals and ions co-exist, i.e. a plasma.

To characterize a plasma we need a broad range of information:

- a) The variety and concentration of all species and the rate of their production and consumption.
- b) Distribution of momentum and energy and the fluxes of their sources and sinks.
- c) Cross sections of all possible processes involved.

Each of these quantities may show spatial as well as temporal variation.

The full real time characterization of a plasma is often a hopeless task but approximate methods for plasma diagnostics and modeling have been used to obtain a better understanding of the processes involved and to increase the reliability of the analytical results [25]. Both plasma diagnostics and modeling are easier to implement for stationary plasma sources, where temporal variations are absent. Electrical probes, optical spectroscopic methods as well as mass spectrometry are widely used in the characterization of ICPMS [26–28] and GDMS sources [29, 30], whereas mathematical modeling is developed for laser plasma ionization [31–33].

Indeed, in many situations it is sufficient to keep track of some species of particular interest. In analytical practice the bottom line approach is to follow the behaviour of electrons, analyte ions and atoms. If complete equilibrium or local thermal equilibrium (LTE) prevails, the characterization of the plasma boils down to the determination of electron densities, velocities and temperatures [34]. The mass action law and macroscopic charge neutrality then provide the related quantities for any other components [26]. To accomplish by calculation even this vastly reduced task, a wide diversity of material parameters are needed. Data on collision cross-sections, transition probabilities in the plasma phase, chemical behaviour of the solid surface and transport properties in both phases are important. A more realistic possibility is to set up semi-empirical relationships, with parameters which can be fitted from experimental data.

Assuming a plasma in local thermodynamic equilibrium (LTE), the formation of an ion can be considered as the dissociation of a neutral particle: $M \rightleftharpoons M^+ + e^-$. The Saha-Eggert equation can be applied to this reaction and if one assumes that the concentration of atoms is proportional to atomic concentrations in the sample, c_M , and that the ion intensity I_M is proportional to the ion concentration in the

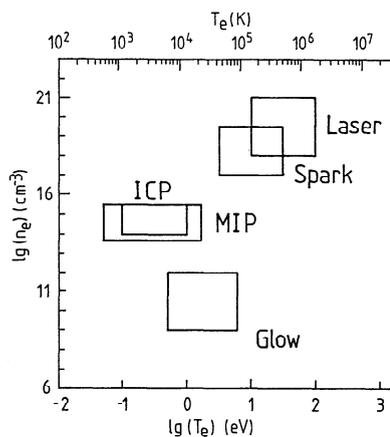


Fig. 4. Approximate temperature and number density range of electrons for the different plasma sources ('plasma map')

plasma, the following simplified equation can be obtained [34]:

$$\ln(I_M Q^\circ / c_M Q^+) = \text{constant} - (E_i / kT)$$

where Q° and Q^+ are the internal partition functions of neutrals and ions, T is the temperature and E_i is the first ionization energy. The constant depends on the electron density and weakly on the temperature in the plasma.

In the elemental analysis the plasma fulfills a twofold requirement. It must be capable of disintegrating the inter- and intramolecular bonds in the sample and at the same time it must be effective in the ionization of the different species. Requirements for design and efficient operation of any plasma ion source initiated efforts to understand and describe the underlying physical and chemical phenomena.

It is possible to include all plasmas of interest in the plasma map shown in Fig. 4. The range of estimated electron number densities, n_e and electron temperatures, T_e are shown for the different sources. The transient sources lead to considerably higher temperatures and densities which cannot be sustained for extended periods of time.

There are clearly shortcomings in both too low and too high electron temperatures. If the plasma is not hot enough, the disintegration of the sample material stays incomplete. A typical consequence of this in the appearance of molecular ions (for example oxide ions in ICPMS) causing disturbing interferences. On the other hand, extremely elevated temperatures lead to considerable amount of doubly and multiply charged ions making quantitation complicated. Furthermore, the high temperature plasmas in stationary sources may interact with the metal parts and the refractory material of the source constructing elements, producing spurious signals in the spectrum. The MIP and the ICP largely overlap within Fig. 4. The MIP source input power seems, however, to be unable of efficiently atomizing and ionizing the sample. Reduced pressure MIP operation provides higher electron temperatures, but the 'thermal' temperature is lowered, thereby making it less suitable for atomizing the sample [23].

Optimal plasma parameters for sample disintegration and for ionization are frequently in conflict, making the physical separation of these processes necessary. Introduction of secondary discharges in ICPMS and GDMS, as well as the advent of combination techniques including the application of a separate laser for ablation in LIMS, ICPMS

and GDMS, and studies in laser postionization of particles sputtered by ion beams are all ideas conceived in this context.

Ion extraction and analysis

The ion sources must produce ion currents with appropriate characteristics for mass analysis or by inverting the argumentation the mass spectrometer must be designed in such a way as to be able to cope with any of the analytical drawbacks of the source. The different sources available at present suffer from a number of drawbacks if one relates their characteristics with what one would really like them to be. From the mass spectrometrist's point of view the ideal source for panoramic elemental analysis of the entire periodic system of elements is based on an interaction which creates a plasma in which:

- the individual elemental singly charged ion densities are proportional with the concentration of impurities in the solid as closely as possible;
- there are few if any remnants of 'chemical memory' effects and matrix effects, which render quantitative analysis difficult if not impossible;
- the ion density of molecular or cluster species and that of multiply charged ions are low enough not to interfere with the measurement of the ions of interest, allowing the use of a simple mass spectrometer for mass separation and avoiding the operationally complex and expensive double focusing devices.

All these conditions can, in general, only be realized with – often unrealistically – high energy processes, in general terms those that lead to high electron densities and electron temperatures in the upper right corner of the plot in Fig. 4. Such a violent interaction between the excitation and the solid leads to wide – and often variable – ion energy distributions which in general are incompatible with the utilization of simple (and inexpensive) mass spectrometers.

Ions must be extracted from the plasma which is usually accomplished by the incorporation of electric fields. While some transient plasmas can be created directly inside the mass spectrometer due to its negligible load on the vacuum system, stationary plasmas need to be interfaced using orifice, sampler and/or skimmer cones together with two or more steps of differential pumping for a gradual transfer of pressure to the vacuum of the mass analyzer. Avoiding distortions of the original plasma composition in such interfaces is one of the main aims of interface design. In general it can be achieved only on the basis of diagnosing the plasma inside the interface [21, 25, 35, 36].

Three different regimes of ion extraction can be observed in the different ion sources, depending on the pressure in the plasma. If the plasma is very dilute, or if its expansion leads to particles with negligible interaction, the ions can be extracted directly using external electrostatic fields (Fig. 5a). In this case individual ion trajectories are traceable.

In atmospheric pressure plasmas, on the other hand, the ions are transported mainly by gas-dynamic flow, towards the vacuum of the mass spectrometer (Fig. 5c). Only after attaining pressure where the mean free path of the particles is large compared to the dimensions of the ion source, can the ions be guided by electric fields. Thus, in this case the plasma is probed by gas-dynamic flow rather than by an extraction field.

Somewhere, in between the two extreme cases discussed above, there is a domain of mixed extraction, where the

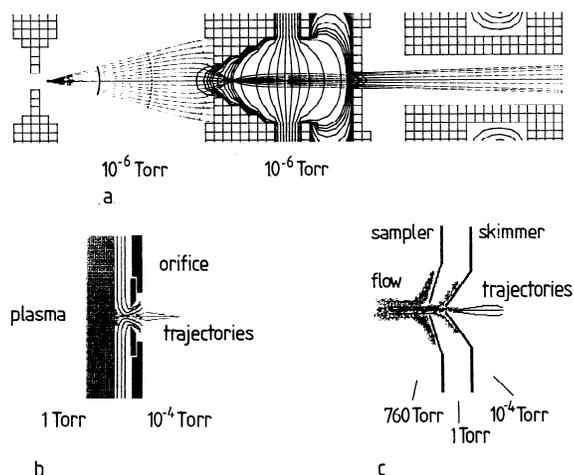


Fig. 5 a–c. Three different regimes of ion extraction depending on the plasma pressure. **a** Extraction in vacuum, where the ion trajectories are unperturbed by collisions; **b** Mixed extraction, where the importance of convective transport is comparable to the transport by the external field; **c** Convective extraction by flow

reduced pressure of the plasma makes field penetration possible (Fig. 5b). In this regime the convective ion transport of the flow towards the higher vacuum and the transport by external electric field coexist.

There are two peculiarities of the ion extraction systems in plasma ionization sources most apparent at those working in stationary regime. The first is the above mentioned relatively high pressure of the plasma maintaining medium. Therefore, the plasma region and the extraction optics have to be separated and differentially pumped. This feature is clearly observed in GDMS, ICPMS and MIPMS [37–39]. Even in the case of SSMS and LIMS [40, 41] transient expansion of the evaporated sample material during and after the excitation pulse has been demonstrated recently [25]. Thus, in these sources the ions are transported not only by external electrostatic fields, but also by the plasma flow. In some cases, it is necessary to compensate (as with the ion reflector commonly used in LIMS) or filter (e.g. with the electrostatic sector in SSMS and GDMS instruments) this excess kinetic energy, because it can deteriorate the performance of the instrument [42, 43].

The other special feature of plasma sources is the large density of charged particles. This has twofold effect on the extraction process. On one hand the external electric fields are only able to penetrate into the plasma to the extent of the Debye-length, determined by the number density and the temperature of the electrons. In practice this means that frequently not the whole volume but only the surface layer of the plasma is probed by the ion extraction optics. In the case of transient sources the Debye-length and the plasma probing depth varies in time providing a time dependent volume and location for ion extraction [31]. The other important consequence of high charge density is the so-called space charge effect, i.e. the mutual repulsion of the extracted ions inside the ion optics. It has been demonstrated recently that space charge effects can lead to matrix effects in ICPMS [44].

Furthermore, the rapidly changing electrical characteristics of the plasma can backfire on the power supplies of the source, leading to important transient disturbances. To illustrate the complexity of these interactions we outline the transient behaviour of the spark ion source.

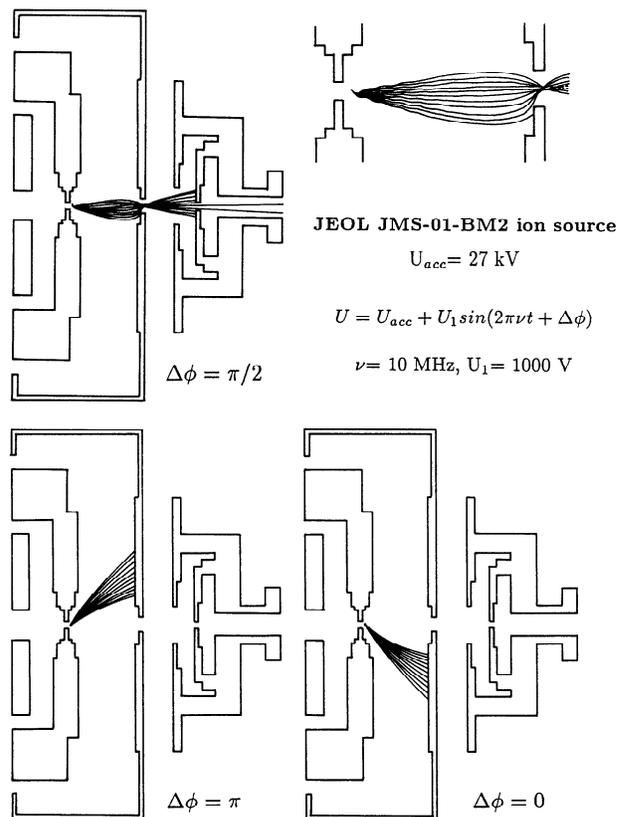


Fig. 6. Time dependent extraction in SSMS. (See explanation in the text)

It is well known that after attaining the breakdown voltage between the sparking electrodes an avalanche of atomization and ionization processes develops, and the dense, low impedance plasma ‘short circuits’ the power supply. Consequently, the high voltage drops and high frequency residual oscillation can be observed on the electrodes [2]. It is the effect of these oscillations on the ion trajectories, what we would like to demonstrate.

Ion trajectory calculations were carried out with the ray tracing program SIMION [45] for the JOEL JMS-01-BM2 ion source configuration [46]. The time dependent potential distribution inside the source, U , consisted of the superposition of a static distribution stemming from the electrode voltages, U_{acc} , and the dynamic variations due to the residual oscillations:

$$U = U_{acc} + U_1 \sin(2\pi\nu t + \Delta\phi)$$

where $U_1 = 1000$ V is the amplitude and $\nu = 10$ MHz is the frequency of the oscillations. $\Delta\phi$ denotes the phase angle between the voltage and the departure time of the individual bunch of ions.

Quite surprisingly, it is the phase angle which had the most dramatic effects on the performance of the ion source (Fig. 6). At about $\pi/2$ phase angles the trajectories are heading towards the exit slit, whereas at $\Delta\phi = 0$ and at $\Delta\phi = \pi$ the ions are severely deflected. Because ions are departing continuously the phase angle changes between the transmitting and non-transmitting values causing heavy time dependence in ion extraction. This phenomenon was observed in time of flight experiments as well [47]. Moreover, the dynamic characteristics of the source are mass depen-

dent. In Fig. 6 the trajectories are shown for $m/z = 56$ u. For other masses the transmitting phase angles are different [48].

To close this example we mention that the mathematical, physical and computational tools are available to describe other plasma sources too, and they will be most probably utilized in the near future.

Bearing in mind the above mentioned specific features of plasma ion sources it is not surprising that ion extraction is one of the sensitive points of most instrumental designs. In the case of particle beam methods the number density of charged particles is much lower, therefore this aspect of ion extraction demands less attention.

Inorganic mass spectrometry for quantitative analysis

Precision and accuracy

In general, it is not the magnitude of the variation in sensitivity and the matrix dependence which are of importance for quantitative analysis but the possibilities to transfer the ion intensity data to real concentrations without the need to dispose of standard samples which compares closely to the unknown in composition and structure. In this SIMS fails except for simple sample compositions such as the base materials in microelectronics, where reasonable accuracy of a few tens of percent may be reached in practice on the basis of the measurements of standards [49]. The other methods are more successful in this respect.

A general phenomenological way for describing the deviations between the recorded mass spectrum and the solid sample composition consists in the use of relative sensitivity factors (RSF) defined as:

$$\frac{I_x}{I_y} = \frac{C_x}{C_y} \times \text{RSF}(x/y)_z$$

in which I_x , I_y and C_x , C_y are measured ion intensities and concentrations and the suffixes are for unknown element, x , and internal standard, y , in a matrix, z .

The particular value of an RSF characterizes the dependence of the sensitivity of an element x in a given matrix z . It includes all the discrimination effects present under given experimental conditions in the ion source, the mass spectrometer and detection system. In practice, these factors can be determined by analyzing standard samples or else it is sometimes possible to estimate or determine them from *a priori* physical and chemical considerations.

Within the range of methods discussed in this paper some respond closely to the ideal analytical situation in which relative sensitivity factors approach to unity for every element in any matrix; they approach the situation of an absolute quantitative analytical method in which the only *a priori* assumption to be made is the concentration of one single constituent, often a matrix species whose concentration is known from bulk analysis or from stoichiometric considerations. Others are prone to differences in sensitivity sometimes of many orders of magnitude with a large dependence on the other elements present in the matrix. Table 2 gives a summary of the ion sources considered in this respect. It is apparent that the glow discharge [12], the high intensity laser pulse [50–52], the SNMS [17] and the spark source [7, 8] come near to a uniform sensitivity with unimportant matrix effects compared to many other analytical methods especially SIMS.

Table 2. Figures of merit of some mass spectrometric methods

Method	Abs. sens.	With stand. (%)	Meth. of stand.	Detect. lim.
SSMS	2–3	20–30	RSF	~1 ng/g [8]
SIMS	10^7	5–50 ^a	MISR, LTE	10^{-3} – 10^{-10} µg/g
LIMS	semiquant.	100–300	LTE, standards	20–200 µg/g [51]
SNMS	20%–30%	10	standards	~1 µg/g [17]
GDMS	2–3	5–10	standards	~1 ng/g [12, 72]

^a For pure silicon

Relative sensitivity factors as they appear eventually in the mass are the result of different processes which take place in sequence: atomization, ionization, plasma expansion, ion beam formation, mass discrimination in the spectrometer and finally detection. Quantitative analysis relies on the proper understanding of at least the most important of the discrimination processes taking place, so that it becomes possible to take them into account for quantitation.

The theoretical understanding of relative sensitivity coefficients include efforts to establish correlations between basic material parameters of the matrix and the analyte and the sensitivity coefficients themselves. Such correlations have been demonstrated with the enthalpy of sublimation, the atomization energy, the ionization potential, the covalent radius, the vapor pressure and the atomic mass [7, 53–55]. Another approach is to follow time dependent ion distributions in the expanding plasma and relate the ion production for different elements to their relative sensitivity coefficients [56, 57].

According to some authors [58] it appears that a large body of data on RSF's published in the literature on spark- and laser source mass spectrometry over a period of 20 years can be explained by discrimination in three stages:

- atomization of the sample material dependent on the volatility of the impurities,
- ionization of atoms represented by the Saha equation and characterized by an ionization temperature, T_i ,
- recombination probabilities in the cooling, expanding and dispersing plasma.

Discrimination in the formation of the ion beam, mass analysis and ion detection are considered less important.

This approach for quantitative analysis based on a limited set of parameters reduces inaccuracies of trace element composition in complicated matrices such as granite to 30% [58]. The practical value of this and other approaches lies with the fact that they can be used to systematize large data sets and reduce substantially the systematic errors of analyses without standard reference materials.

It is at present too early to extrapolate the RSF concept to the situation of glow discharge mass spectrometry. GDMS has a uniform elemental sensitivity resulting from fairly uniform sputter yields and the non-discriminating character of the electron impact and Penning ionization processes [12]. Enough data are available for multicomponent samples to show, that the RSFs obtained with GDMS exhibit the same favorable characteristics as those of SSMS and LIMS. From one matrix to another the RSFs expressed as relative ion yields seem to be quite uniform (Fig. 7), hence they show a weak matrix dependence of about 30% [59, 60].

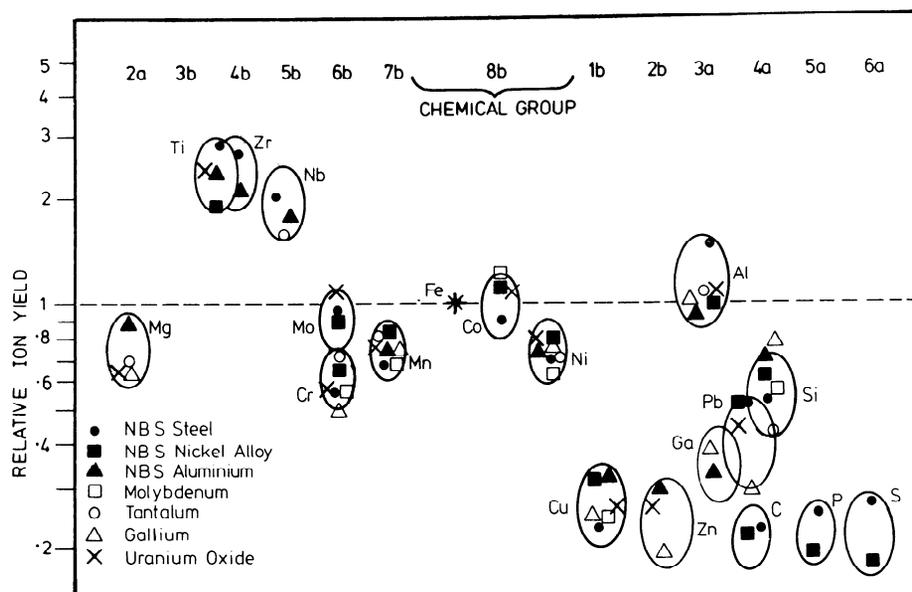


Fig. 7
Relative ion yields in GDMS for
different matrices [59]

Compared to the methods discussed thus far SIMS, on the other hand, poses formidable problems in quantitation. For example the sensitivity of boron is approximately 10,000 times larger in SiO_2 than in pure silicon when using Ar or O_2 primary ions of 12.5 keV [61]. In SIMS, the sensitivity factors also vary by orders of magnitude with instrumental conditions for sputtering and between elements because of important variations in ion to neutral ratios. This results in a strong dependence on the ionization potential, allowing corrections by simple methods based on the straightforward application of the LTE model [34].

Reports on the application of this model relate mostly to microscopical analysis where local heterogeneity and local matrix effects negatively influence some of the results obtained. The precision of the LTE model, therefore, may be better than it often appears. In SIMS the RSF approach is frequently adopted by relating the sensitivity factor, as determined with a standard sample, to a suitably chosen matrix ion species ratio (MISR). MISR and the RSF are then measured as a function of an experimental factor affecting measurements, e.g. the partial pressure of oxygen near the sample surface [62].

Detection limits

Here we only briefly quote some references, because there is ample of data in the literature. Detection limits are typically around a few ng/g for SSMS [8, 68] and GDMS [12], 20–200 ng/g for LIMS [51], in the $\mu\text{g/g}$ range for LAMMS, 10^{-3} – $10 \mu\text{g/g}$ for SIMS [2] (except if material consumption in ion microprobe work puts limitation) and around $1 \mu\text{g/g}$ for SNMS [17].

Localized analysis

The range of methods discussed, while all are multi-element, have widely differing characteristics as far as their localized analytical potential is concerned.

In its ion microscope version dynamic SIMS allows now localized and in-depth analysis with a lateral resolution of less than $1 \mu\text{m}$ and a depth resolution of 5–10 nm. Three

dimensional analysis is possible by combining the instrumentation with a computer based image processing system and position sensitive detectors. In the ion-microprobe equipped with a submicron liquid metal ion gun the lateral resolution has increased to 20 nm [63].

Laser microprobe mass spectrometry is bounded by the diffraction limit of the UV focusing optics, in practice to about 2–3 μm , whereas LIMS instruments provide craters with 30–50 μm diameter. The depth profiling ability of repeated laser shots is not yet fully elucidated.

The major weakness of the spark ionization source for optical and mass spectrometry, as we discussed earlier, is the erratic ion production. It has been known since the nineteenth century that spark discharges display spatial and temporal heterogeneity [64]. Not only is emission a complex function of time and space during a single spark, but patterns of emission evolve during a train of pulses [47, 48, 65]. This patterned and random time evolution of emission from spark to spark suggest that simultaneous detection is preferable to scanning or switching modes of ion detection. Even today photographic detection with its non-linearities, poor dynamic range and slow readout is still the method of choice for ion detection; its obvious drawbacks can be taken care of by the use of a computerized microdensitometer. Two dimensional electronic array detectors such as charge coupled device arrays (CCDs) and charge injection device arrays (CIDs) promise to provide a linear dynamic range of at least 3 orders of magnitude, low backgrounds and high sensitivities. If these devices will be available with the required dimension and resolution, with the addition of time gating techniques, they appear as ideal detectors for a next generation of ultrasensitive spark source mass spectrometers.

In principle discharge wander results in effective random sampling which may be of advantage for obtaining quantitative results on an inhomogeneous sample. Positionally stable discharges are possible and microspark discharges have been reported that permit profiling of surfaces with 150 μm spatial resolution [66]. By the proper choice of spark parameters a wide range of erosion rates can be selected. This allows SSMS to be used for in-depth profiling in the micrometer to millimeter region (sputter rates vary from nm/s to $\mu\text{m/s}$, a

depth range not accessible by most of the sputter type methods [66]). Sampling efficiency (mass of sample eroded by unit energy dissipated in the spark) is very much matrix dependent.

In the cathodic sputtering process in GDMS material is removed at a rate of 10–100 nm/s and the sputter process produces craters with nearly flat bottoms. The high sputtering rate combined with a good time resolution makes it possible to profile surface layers ranging from a few nanometers to several tenths of a micrometer in depth [67].

Conclusions

In many areas of analytical instrumentation there is a synergic relation between new instrumentation and the experimental challenges of pure science and applications in science, technology and society. As applications become more difficult and demanding, users follow more closely the progress made with the latest new instruments. Also, as new techniques become widely adopted to analytically demanding problems, this tends to promote new refinements. A necessary catalyst in this interaction is a commercial sector that is able and willing to risk its future (and is capital) in providing the laboratories with well designed instruments.

The field of organic mass spectrometry for a long time has been an exemplary example of the interaction between these three factors: the analytical community developing analytical chemistry as a fundamental discipline, the community of analysis which sees the instrumentation as a tool for solving problems and the commercial world who wants to make a living (or a fortune) from selling its instruments. Today, we can observe a similar rapid evolution in inorganic mass spectrometry.

Development in microscopical SIMS is driven by the demands for the solution of specific and important problems. The evolution is especially pronounced in two distinct areas, the gain in lateral resolving power of high brightness sources and the increased potential of detection and image analysis.

In the '60s SSMS was a promising method with at one time several commercial suppliers which gradually disappeared because of a too restricted market, presumably as a result of the analytical drawbacks mentioned earlier in this paper. Today, the remaining instruments are intensively used and the fundamental knowledge acquired on the spark process together with a number of instrumental concepts in ion optics, gas phase ion chemistry and detection could trigger development work of a new instrumental design. A possible next generation SSMS instrument will have to compete with the glow discharge mass spectrometer which recently gained popularity for full elemental range analysis. Available GDMS instruments exploit quadrupole filters as a low cost instrument and high resolution magnetic sector mass spectrometers for sequential detection of the elements at low detection limit. Spark source and glow discharge sources could eventually be incorporated as options in one simultaneous recording high resolution mass spectrometer. The first is a work horse, restricted but extremely useful, while the other is a racing horse, with almost unlimited possibilities but perhaps not so easy to manage [69].

In all areas spectrometers of the future will take profit of the growth in computational power to perform a growing

number of tasks related to spectral acquisition and processing, techniques for spectral display and storage, methods for quantitative determinations and spectral interpretation, which will make the instruments more reliable and easier to use.

Resonance ionization mass spectrometry (RIMS) is a potentially powerful technique, which can be adapted to many of the ion sources described in this paper. Much of the work up to now is illustrative for its capabilities within the general field of inorganic mass spectrometry. The technique uses laser light to resonantly excite and subsequently ionize elements (or isotopes) after these are atomized by other means, with the aim of determining ultra trace concentrations or extremely unfavorable isotope ratios. Because of the extreme selectivity of the excitation process and further selectivity introduced by the mass analysis of the ions a few dozen atoms can be detected, in principle. The possibilities of RIMS were demonstrated in combination with thermal filament atomization, with laser ablation, with ion beam sputtering [in so-called sputter initiated resonance ionization (SIRIS) experiments] and with glow discharge. Recent reviews cover the most important instrumental considerations and literature to date [1].

Apart from the more conventional inorganic mass spectrometers discussed so far there is the special purpose instrumentation built at various laboratories for specific tasks. Accelerator mass spectrometry (AMS) [70] is not a prolific area but the fact that it is now possible to measure natural ^{14}C concentration (and those of other rare isotopes) by direct counting with cyclotrons and electrostatic (tandem) accelerators used as mass spectrometers (instead of monitoring the beta activity for carbon dating) is exemplary of a general statement: mass spectrometry can now replace radiochemistry as a more sensitive method to detect and measure rare isotopes. At isotope ratios of 10^{-12} and with the potential of resolving isobars, the requirements are extremely demanding. The possibilities for trace analysis are discussed but have not yet been investigated [71].

In several laboratories prototype instruments were built or are in the development stage to perform ultra sensitive elemental and isotope analysis. One example illustrating this evolution is the high resolution ion microprobe developed and constructed at the Australian National University in Canberra, which is characterized by ultra-high mass resolution and ion transmission. Another example is the highly sensitive mass spectrometer now being completed in Dubna (USSR) with the aim for searching for ultra-heavy elements beyond uranium. The design aim of this laser excitation instrument is detection limits of the order of 10^{-6} $\mu\text{g/g}$. It requires an ion beam path of the order of 15 m and the incorporation of collision chambers to decrease the background due to molecular interferences.

Concerning the general trends in inorganic mass spectrometry there are two further relevant observations: the introduction of new methods for plasma generation and the increasing importance of the combination methods.

In plasma generation the demands are pointing to the better control of plasma parameters combined with less contamination from the plasma maintaining medium and from the structural elements of the ion source itself. Among others, promising experiments have been reported with theta pinch and with exploding thin film ion sources [64].

As we have seen, the strength of the combination methods is related to the separation of atomization and ionization

processes. New combinations, such as laser ablation and glow discharge ionization, or ion beam sputtering and laser ionization are certain to come.

Acknowledgements. Thanks is due to the NFWO and DPWB, Brussels, Belgium, for their financial assistance.

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Received September 1, 1989