Fresenius J Anal Chem (1999) 364 : 367–375

REVIEW

A. Bogaerts · R. Gijbels

New developments and applications in GDMS

Received: 11 November 1998 / Revised: 29 January 1999 / Accepted: 6 February 1999

Abstract An overview is given about the new developments in GDMS, both with respect to the glow discharge source as to the coupling with various kinds of mass spectrometers. Moreover, as for every analytical technique, methodological and fundamental research is being carried out to improve the analytical results of GDMS, and some of the new developments in these fields will be discussed as well. Finally, the various analytical applications of GDMS will be presented.

1 Introduction

A glow discharge is a kind of plasma. It is formed in a cell, filled with a gas (e.g., argon) at low pressure (typically in the order of 100 Pa). A cathode and anode are inserted into the cell or they form the cell walls. Between these two electrodes, a potential difference of about 500–1500 V is applied, which causes “breakdown” of the gas, i.e., the gas atoms are being split up into positive ions and electrons. The positive ions are accelerated towards the cathode by the potential difference, and they cause the release of electrons from the cathode, which is called “secondary electron emission”. These electrons arrive in the glow discharge plasma where they can give rise to collisions. The most important collisions are ionization and excitation of the gas atoms. The excitation collisions, and the subsequent decays to lower levels with the emission of light, are responsible for the characteristic name of the “glow” discharge. The ionization collisions create new ion-electron pairs. The new ions are also accelerated towards the cathode where they can again cause secondary electron emission. The electrons can again give rise to ionization collisions, which makes that the glow discharge can be sustained. All these processes are illustrated schematically in Fig. 1.

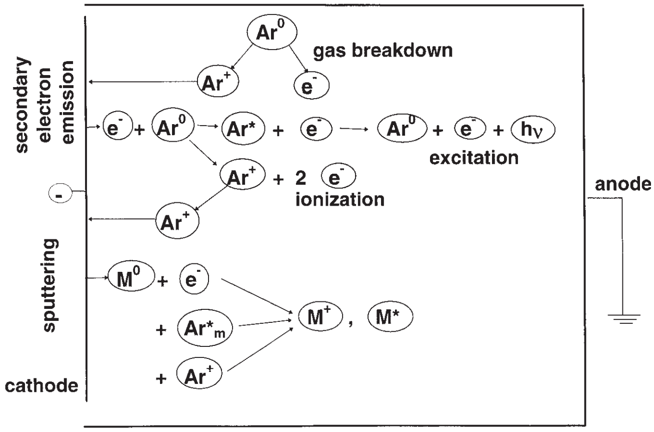

Fig. 1 Schematic picture of the main processes occurring in a glow discharge

The ions that bombard the cathode do not only release electrons but also atoms of the cathode material, which is called “sputtering”. This is the basis of the use of the glow discharge as spectroscopic source for analytical chemistry. Indeed, the material to be analyzed is used as the cathode of the glow discharge. Due to the sputtering effect, the atoms of the material to be analyzed arrive in the glow discharge plasma and are subject to ionization and excitation collisions as well, yielding the formation of ions and excited atoms. Hence, the plasma can be seen as an atom, ion and excited atom reservoir, with a composition characteristic for the material to be analyzed. The ions can be measured with a mass spectrometer, giving rise to glow discharge mass spectrometry (GDMS). The excited atoms emit characteristic photons which can be detected with an optical emission spectrometer, leading to GD-OES. Moreover, the atoms can also directly be probed with an external light source, making atomic absorption and atomic fluorescence spectrometry possible (GD-AAS and GD-AFS).

Invited talk at the 4th Symposium Massenspektrometrische Verfahren der Elementspurenanalyse (28 September – 1 October 1998, Mainz, Germany)

A. Bogaerts (✉) · R. Gijbels
Department of Chemistry, University of Antwerp,
Universiteitsplein 1, B-2610 Wilrijk-Antwerp, Belgium

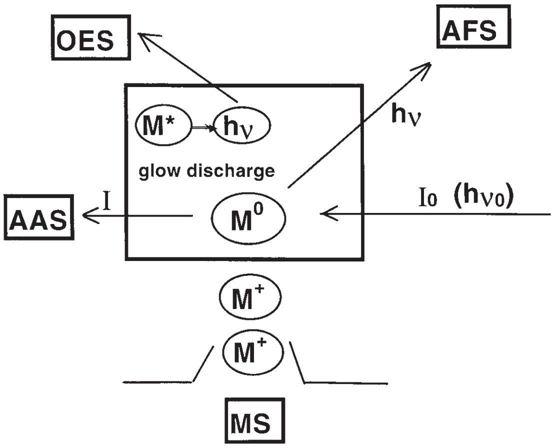

Fig. 2 The glow discharge, used as spectroscopic source for mass spectrometry, optical emission spectrometry, atomic absorption spectrometry and atomic fluorescence spectrometry

These techniques are summarized schematically in Fig. 2. In this review, however, we will focus only on GDMS.

---

2 New developments in GDMS

2.1 Source development

The glow discharge can be operated in a variety of source geometries (e.g., with a flat, a pin-type or a hollow cathode) and electrical operation modes. The ***direct current (dc) source*** is still the most widely used. It is often employed for routine analysis in the metal industry (see later), but new developments are being carried out as well. For example, Deng and coworkers have found that cluster ion interferences in GDMS can be suppressed by sampling from the cathode side of a hollow cathode source [1]. Indeed, the argon and cluster ions are generally characterized by low energy (i.e., a few eV) whereas the analytically important ions have high energy (i.e., more or less equal to the discharge voltage, e.g., 1000 eV). It should be realized that when the ions are sampled from the cathode side, they have traversed the cathode dark space (i.e., the region in front of the cathode, characterized by the total voltage drop) and they can, indeed, have acquired considerable amount of energy from the strong electric field in this region. The argon ions, however, loose the energy they gained from the electric field, also efficiently due to charge and momentum transfer collisions. By sampling only the high-energy part, the authors could get rid of most of the argon and cluster ion interferences. A related study was carried out by Oksenoid et al., who found that by modification of the source geometry, ion extraction scheme and discharge conditions in dc-GDMS, the intensity ratio of analytically important ions versus argon-related interferences could be increased by five orders of magnitude [2]. A possible explanation could be that the matrix and analyte ions can be separated from the discharge gas ions by selective energy filtering.

The dc source is quite simple in operation, but it has some disadvantages. The most important one is that it cannot directly be used for the analysis of non-conducting materials. Indeed, due to the continuous bombardment of positive ions, the cathode would be charged up and prevent the ions from further bombardment, so that sputtering would stop. However, by applying a radio-frequency (rf) voltage at one of the two electrodes (called the “rf-electrode”), the accumulated positive charge on the sample surface will be neutralized by the negative charge accumulation during part of the rf-cycle (i.e., when the rf-electrode is positive). In this way, no net charging occurs over the entire rf-cycle. A large number of publications are found in the literature with respect to ***radio-frequency (rf) source*** development, especially by Marcus and his group, who have coupled rf sources to a variety of mass spectrometers (e.g., [3, 4]). Moreover, Saprykin and coworkers have also developed an rf ion source for a double focussing mass spectrometer [5, 6].

Beside the rf-mode, also the ***pulsed glow discharge mode*** is attracting interest, especially under the impulse of Harrison’s group [7–10]. By applying a voltage (and current) during a short time-pulse (even microseconds!), higher peak intensities can be reached for the same averaged power. One of the advantages of a pulsed glow discharge is that time-separation is possible. The argon ions are formed immediately when the glow discharge is on, whereas the sputtered atoms and ions are only formed after some delay. When this pulsed glow discharge source is coupled to a time-resolved mass spectrometer (e.g., a time-of-flight instrument; see below), a mass spectrum taken shortly after discharge termination contains only argon-related peaks. However, when the spectrum is recorded after a delay of several 100 microseconds, it is dominated by the ions of the sputtered material, and argon-related interferences are minimized.

Beside these three electrical operation modes, a lot of research is also devoted to combining a magnetic field to a glow discharge source and to the development of ***magnetron discharges*** (e.g. [11–14]). By applying a magnetic field the electrons follow a longer path in the plasma and can give rise to more ionization. This gives higher ion intensities than in a glow discharge without magnetic field, which improves the analytical sensitivity.

2.2 Mass spectrometers

Glow discharges have been coupled to different mass spectrometers, e.g., ***sector-field instruments*** [15–17], ***quadrupoles*** [18, 19], ***ion traps*** [20–22], ***time-of-flight mass spectrometers*** [23, 24] and ***Fourier transform ion cyclotron resonance mass spectrometers*** [25–28]. However, only sector-field instruments and quadrupoles have led to commercial instruments at this moment. In sector field instruments a mass resolution of about 4000 is achieved, which can resolve most, but not all, of the spectral interferences. The latter are generally more problematic in quadrupoles. However, in ref. [19] a very high purity gas and a special vacuum system were used, so that interferences could be minimized and detection limits in the sub-ppm range could be reached, which is quite low for quadrupole GDMS.

Finally, it is worthwhile to mention that glow discharges have also been coupled in recent years to gas chromatographic columns with mass spectrometric detection, for speciation studies [29, 30].

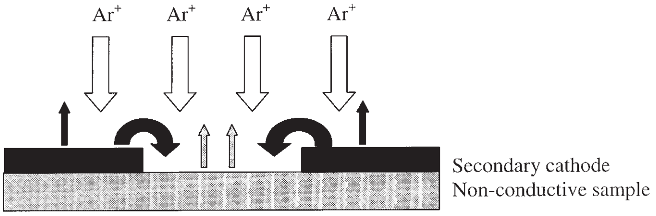

Fig. 3 Schematic picture of the principles of the secondary cathode technique for analyzing non-conducting materials by GDMS

2.3 Methodological developments

As for almost every analytical technique, quantification is of major importance for GDMS. It is attained by using relative sensitivity factors (RSF's), which have to be multiplied with the ion intensities to obtain the real concentrations. Hence, they express the "insensitivity" rather than the sensitivity of the elements:

$$\frac{c_X}{c_S} = RSF\left(\frac{X}{S}\right) x \frac{I_X}{I_S}$$

where C and I are the concentration in mass units and the ion current, of element X and internal standard S.

The RSF values of most elements in GDMS lie within one order of magnitude, which makes semi-quantitative analysis without standards possible. For quantitative analysis, differences in RSF's among the elements must be taken into account.

A large number of papers have been presented in the literature about measurements of RSF's for a variety of matrices (standard reference materials) and discharge conditions (e.g., [31–33]). Moreover, some models have been developed trying to predict RSF's (e.g., [31, 34, 35]). Most of these models are based on empirical relationships and make use of fitting parameters. However, based on our own modeling experience, we have developed a more explicit model without fitting parameters, and we have made plausible that it is asymmetric charge transfer which is mainly responsible for the variations in RSF's [35]. Indeed, transport of the sputtered atoms, as well as ionization of the atoms by electron impact ionization and Penning ionization are rather unselective processes, i.e., they occur for (almost) all elements (except for elements such as N, O, Cl, F, for which Penning ionization is impossible in argon), and the differences are only determined by the atomic mass, atomic radius and ionization potential of the elements. However, asymmetric charge transfer is a very selective process: it occurs only when there is good energy overlap between the argon ion level and the resulting element ion levels. Because we have systematically found that elements for which asymmetric charge transfer was theoretically impossible are characterized by higher RSF's (i.e., lower sensitivity) than the other elements, we have concluded that the latter process plays an important role in determining RSF's.

An interesting study was performed by Smithwick and coworkers [34]. They found that when 1% H_2 was added to an argon glow discharge, the RSF's could be much better predicted with their simple empirical model. This would open perspectives for the future because when the RSF's could be accurately predicted, good quantitative analysis could be performed without standards. However, in the Ar-H_2 discharge a lot of spectral interferences due to hydrides are present, which complicates the analysis to a great extent, so that in practice this method is not being used.

As mentioned before, GDMS is particularly suitable for the analysis of conducting materials. However, some methodological research is also going on with respect to the analysis of non-conductors with GDMS, in order to widen the application field of this technique. Beside rf-GDMS, which is most frequently used to analyze non-conducting materials (see above), two strategies are often applied for the analysis of insulating materials with dc-GDMS, i.e., (i) mixing the non-conductor (as a powder) with a conducting binding powder and pressing it into a pellet, and (ii) using a metallic diaphragm on top of a massive non-conducting material as a "secondary cathode". The first technique is already used in routine analysis, although it has some major drawbacks, like the introduction of contaminants due to the binding powder, the need of a longer stabilization time before steady state is reached, the loss of spatial information of the nonconducting material (because it must be ground into powder form), etc.

The second technique, however, makes direct use of the solid non-conductor, so that no sample preparation is required and spatial information can hence be obtained (depth-profiling). Since this technique is rather new, it will be explained in a little more detail. The principle is as follows (see Fig. 3): a metallic diaphragm (called "secondary cathode") is placed on top of the insulating material, with the diameter of the opening less than the diameter of the glow discharge cell. Hence, this secondary cathode is also exposed to the discharge and is being sputtered by bombarding gas ions and atoms. However, a large fraction of the sputtered atoms is again redeposited on the cathode, and also on the non-conducting material. This results in the formation of a conducting surface on the insulating sample, so that the latter can be sputtered in a dc glow discharge and does not suffer from charging-up. The sputtering will therefore also remove atoms from the insulator. Although this technique was already more common for SIMS (secondary ion mass spectrometry), it was first introduced to GDMS a few years ago by Milton and Hutton [36]. Since then, a few groups have investigated the possibilities and limitations of this technique and applied it to a variety of non-conducting materials (e.g., [37–40]).

2.4 Fundamental developments

In order to improve the analytical performance of GDMS, a good insight in the glow discharge plasma is required. The latter can be obtained by mathematical modeling and by experimental measurements in the plasma. The purpose of the former approach is to simulate the behavior of the different plasma species (gas atoms and ions, sputtered atoms and ions, all of them in the ground state and also in excited levels, electrons, etc) and the various processes occurring in the plasma. We have developed a hybrid modeling network, consisting of Monte Carlo, fluid and collisional-radiative models, to describe the behavior of argon atoms, argon ions, argon atoms in various excited levels, sputtered atoms and ions, both in the ground state and in various excited levels, and electrons. Typical quantities that can be calculated, comprise the densities, fluxes and energy distributions of the various plasma species, information about collision processes in the plasma and about sputtering at the cathode, the potential and electric field distribution in the plasma, ion fluxes entering the mass spectrometer, ionization degrees, optical emission spectra, erosion rates and crater profiles, etc. More information about these models can be found, e.g., in ref. [41] and the references therein. Although this approach of explicit modeling is rather new for GDMS, it has been applied already for many years to glow discharges used for technological purposes (i.e., in the micro-electronics industry, as lamps, lasers, flat plasma display panels, etc). Recently, one of these models has also been adapted to a glow discharge ion source for mass spectrometry [42].

Finally, a better understanding of the glow discharge plasma can also be obtained by measuring the characteristic quantities (densities and energies of species, potential, distribution over excited levels, etc) directly in the plasma, i.e., by “plasma diagnostics”. A variety of techniques is being used, like Langmuir probe measurements, optical emission and mass spectrometry, laser-induced fluorescence and atomic absorption spectrometry, etc. A recent overview of these techniques, with their specific potentials and limitations, can be found in ref. [43].

3 Applications of GDMS

The most important applications of GDMS are found in the bulk analysis of metals, but semi-conductors, non-conductors, thin films, solutions and gaseous samples can in principle be analyzed as well. The detections limits of GDMS for metallic samples under optimum conditions (i.e., no severe interferences), are in the low to sub-ng/g level. Non-conducting samples have generally slightly higher detection limits. For solutions, the absolute detection limits can be quite low (i.e., lower than 1 pg; see below). The sensitivity of GDMS actually depends on many factors, like the nature of the sample (including its intrinsic sputter properties), discharge conditions, sample and source geometry, ion extraction and transmission efficiency, spectrometer background and resolution, and detection mode.

The internal reproducibility of GDMS (i.e., without changing the sample) is in the order of 5% RSD for metals, and the external reproducibility is generally about 10% RSD. The accuracy of GDMS for metals using the RSF-approach can be as good as 10% [44]. For non-conducting samples, these values lie again slightly higher. Table 1 presents an overview of the typical features and limitations of GDMS [45–48].

The problem of memory effects is generally not so severe in GDMS (<< 1 µg/g), unless there is a problem with the glow discharge cell or the sample geometry, so that the plasma is reaching areas in the cell which it is not supposed to reach (e.g., near the sample holder). For trace analysis, the glow discharge cell and the sample holder are generally changed when changing the matrix. For ultra-trace analysis the entire source (i.e., the lens stack and the source defining slit towards the mass spectrometer) has to be cleaned or exchanged, in order to avoid memory

Table 1 Typical features and limitations of GDMS

Features of GDMS	Limitations of GDMS
Simple ion source (i.e., cathode + anode)	Mainly applicable to solids
Economical operation (low power, low gas and sample consumption)	Spectral interferences from discharge gas + from polyatomic ions
Stable ion production	Expensive commercial mass spectrometers
High sensitivity (low till sub-ppb region)	Gas load requires differential pumping
Uniform response for most elements	Memory effects in the source chamber
Inert environment (which minimizes interferences)	
Minimal matrix effects (due to separated atomization + ionization)	
Direct analysis of metals without sample preparation	
Isotopic information can be obtained	
Spectra simpler than with OES	
Responsiveness to both metallic + nonmetallic elements	

effects. Moreover, for special matrices (e.g., silicon or aluminium) specially dedicated sources (glow discharge cells, sample holders and lens stacks with source defining slits) are being used[1].

In the following, the various applications of GDMS will be briefly overviewed.

3.1 High purity metals, alloys and steel

Since the material to be analyzed in GDMS is directly used as the cathode of the glow discharge plasma, GDMS is particularly suitable for the analysis of metals (metallic alloys, steel and also high-purity metals). The latter group is especially interesting, due to the low detection limits that can be reached with GDMS (i.e., sub-ppb level with a double-focusing instrument). The major advantage of GDMS is that the metal can be analyzed directly, without sample preparation (e.g., dissolving the solid material). Of course, as with every solid state analysis technique, quantification is an important issue. This is done by using relative sensitivity factors (see above), which differ less than a factor of 10 among all elements, with some exceptions, and in different matrices. Hence, even if the relative sensitivity factors are not exactly known (which is generally the case), semiquantitative analyses can still be performed. Although the scientific research about the use of GDMS for this main application is only limited (based on the rather low number of publications) it is, however, often the standard technique in routine analysis of metallic samples in the industry (e.g., [49–53]). Recently, a round robin analysis of a high purity 4N aluminium sample was carried out among 10 European laboratories using the VG9000 double focussing glow discharge mass spectrometer. The results showed that the reproducibility standard deviation among laboratories of the round robin exercise is, in some cases, lower than 10% RSD in trace (e.g., P) and 30% RSD in ultra-trace (e.g., Co) concentration ranges, respectively. The repeatability standard deviation within-laboratory showed that more than 50% of the concentration determinations are below 10% RSD, which demonstrates the high precision of the GDMS analyses even at very low concentrations. Also the obtained trueness for the GDMS results was satisfactory: the bias between the GDMS results and the accepted reference values was within 30–35% [54].

3.2 Semiconductors

Although semiconductors are nonmetallic in much of their chemical activity, they have certain forms that conduct electricity to a certain degree. Their resistance varies between ca. 10^{-6} ohms/cm (i.e., metal-like) and > 10^{10} ohms/cm (i.e., insulator-like), and at least in certain forms they can serve directly as cathode samples in GDMS. Since impurities in semiconducting materials can seriously alter the semiconductor properties even at extremely low concentration levels, the concentrations of these impurities must be known quite accurately. Hence, GDMS as an ultra-trace analysis technique is very suitable for the analysis of semiconductors. Typical applications include not only the detection of undesired contaminant elements but also the monitoring of appropriate dopants like B, Al, P and As.

Table 2 Detection limits for selected elements in a GaAs sample [55]

Element	Detection limit (µg/g)
Be	20
B	1
Na	30
Mg	5
Al	5
Si	10
P	40
S	200
Ca	60
Ti	0.7
Cr	4
Mn	1
Fe	3
Cu	10
Zn	20
Ge	300
Br	30
Se	400
Mo	10
Cd	20
In	200
Sn	20
Sb	20
Te	10
W	4
Hg	9
Au	20

Table 2 presents the detection limits for various elements obtained by GDMS for a GaAs sample by Evans and coworkers [55]. They appear to vary between 1 and a few hundred µg/g. However, it should be mentioned that the concentrations of the elements H, C, N, O and Cl could not be determined with their technique, and therefore, these elements had to be measured with SIMS. A different approach to allow the determination of these impurity gases, C, N and O, has been reported by Mykytiuk *et al.*, who used higher currents to yield more intense sputtering in GDMS [50].

In ref. [56] high-resolution rf GDMS was applied for the bulk analysis of GaAs and SiC samples. It was shown that singly charged positive ions of sample material have ca. 10 eV higher average energy than the ions of the discharge and residual gas. Therefore, effective energy separation of the analyte ions from the discharge and residual gas ions was achieved by adjusting the ion transfer optics,

---

[1] C. Venzago (private communication)

which improved the analytical sensitivity of the developed method. The detection limits obtained in these conditions were in the range from 0.1–100 µg/g [56].

3.3 Nonconductors

As mentioned before, non-conducting materials are not at all the ideal sample types for GDMS, due to the concept of using the material to be analyzed as cathode of the glow discharge, because of charging-up problems. However, this problem is overcome in radio-frequency GDMS, where the positive charge accumulated due to positive ion bombardment is neutralized by electron bombardment during one half-part of the rf-cycle. In ref. [57] rf-GDMS has been applied to the determination of trace elements in ceramic perovskite layers ($La_{0.65}Sr_{0.3}MnO_3$) using synthetic standards. The latter were prepared by doping high-purity powder of the basic material ($La_{0.65}Sr_{0.3}MnO_3$) with trace elements in concentrations from 20 to 500 µg/g and pressing this mixture to compact samples. It was found possible to determine trace elements in the whole µg/g range with a reproducibility of better than 15% [57].

Beside rf-GDMS, also dc-GDMS is, however, able to analyze nonconductors, either when mixing them (as a powder) with a conducting binding powder or by applying a metallic diaphragm as secondary cathode (see above). Mixing with a conducting binding powder is a relatively straightforward technique, which has also been used already in arc and spark discharges. However, several parameters have to be taken into account to obtain a successful measurement, of which the most important are the type of host material and the relative concentrations of sample and host in the mixture:

- The host material is, of course, also sputtered in the discharge and thus results in a blank spectrum. Therefore, it is obvious that only high purity powder must be used and that interfering matrices should be avoided. Moreover, host materials with a good sputter yield are desirable to obtain a good overall sputtering of the compacted sample. Other characteristics of the host material include good mechanical strength upon pressing, low cost and availability in a variety of particle sizes. Several materials have been evaluated as host matrix, i.e., copper, silver, graphite, tantalum, indium and gallium. Gallium has the important advantage of being available in extremely high purity grade. Moreover, only little gallium (< 20% of the sample weight) is needed to make a conducting electrode, if the gallium is mixed as a liquid with the non-conducting powder. However, extremely thorough mixing is needed for this. More classically, the host material is used in powder form. Tantalum has then the advantage of being a getter material, tending to form strong oxide bonds and thereby removing oxygen from the discharge and minimizing oxide interferences. However, tantalum powder is generally not available in high purity grade. Generally, one can state that the choice of the host material has to be made for each specific analytical problem.
- Relative percentages of sample and host in the matrix: On one hand, the electrode must contain enough host material to be conducting, in order to yield good sputtering and to reduce the stabilization time. However, on the other hand, an excess of host material results in lower analyte signal intensities. In practice, 10–20% non-conducting material seems to give optimal results.

This host matrix method has extensively been used, both in GDMS and in GD-OES, and for various matrices. It has, for example, been applied to the analysis of rare earth oxides, soils, sediments, vegetation, geological and ceramic samples. In ref. [58] iron ore materials were mixed in a 1 + 7 ratio with either copper or silver powder. The internal repeatability was seldom worse than 6%, and the external repeatability was typically better than 10%. The accuracy was expected to be about 25% [58].

The secondary cathode technique is probably not so well-established as the host matrix method, but it has some advantages, like the absence of sample preparation and the possibility of obtaining spatial information (see before). Similarly to the host matrix method, the choice of secondary cathode material is of utmost importance, both because of its sputter yield (which should be low enough to prevent an excess of redeposited metal atoms on the non-conducting samples) and because of the impurities it contains. Only tantalum is found to be useful as secondary cathode for the analysis of truly non-conducting samples [59]. Further, the secondary cathode geometry is also an important factor to success. The secondary cathode aperture has to be restricted to 4–5 mm, in order to create a stable discharge, and its thickness should be limited to ca. 0.25 mm, in order to reach low detection limits (i.e., higher sample signal intensity and lower contribution of the secondary cathode in the mass spectrum). The reproducibility is generally in the order of 10% RSD. The major drawback of this technique for the direct analysis of non-conductors by GDMS, compared to rf-GDMS is the blank contribution due to sputtering of the secondary cathode material, which increases the detection limits. Another obvious disadvantage of this technique is that the discharge conditions cannot be chosen freely and that the required conditions can differ from matrix to matrix. However, a definite advantage compared to rf-GDMS seems to be that the signal intensities do not depend on the thickness of the sample, a problem that has been, up to now, inherent to the use of rf-GDMS. Moreover, the rf-GDMS equipment is much more complex and more expensive than the use of a simple diaphragm with dc-GDMS.

A variety of sample types have been analyzed in recent years with this secondary cathode technique, like glass, iron ores, marble and limestone, ceramic materials, longlived α-emitting radionuclides in sediment samples, atmospheric particulate matter (aerosols) and even polymers (e.g., [39, 60–62]). In the latter case, a fundamental difference was found between rf- and dc-GDMS. Indeed, in rf-GDMS the spectra have a clearly molecular character, which makes characterization of the polymer material possible [63], whereas in dc-GDMS with a secondary cathode, the spectrum was found to be rather elemental [62]. Hence, characterization of the polymer is then not possible, but on the other hand, quantitative elemental analysis is facilitated, due to the near absence of cluster peaks.

3.4 Thin layers, depth profiling

The concept of sputtering in a glow discharge implies that the sample is being eroded “layer by layer”. Therefore, it is possible to perform trace analysis of successive layers as a function of depth (“depth-profiling”). Although this is more typically done in GD-OES, some applications of GDMS can also be found in the literature [64–67]. Depth resolutions between 0.05 and 0.5 μm have been reported for GDMS, based on the commonly used “84–16-criterion”. This is the depth corresponding to the sputter time necessary to go from 84% of the initial matrix signal to 16% of it at a sharp interface. This is generally worse than for GD-OES, which is attributed to the non-flat crater profile, often obtained with GDMS, because the cells are not specifically designed for this depth-profiling application. Typical erosion rates in GDMS are about 1–10 μm/h, which is quite lower than for GD-OES, where higher currents are used (see below). A specific application has been performed with the VG9000 instrument, namely depth profiling of CuZn-coated steel wires and cables [44]. The end of the wire was shielded from the discharge by a tantalum cap. The whole surface of the pin sample was homogeneously sputtered, which is impossible with a beam sputter technique like SIMS.

Besides this feasibility study on a double focusing instrument, most of the depth profiling work has been performed with (faster) quadrupole mass filters, since transient signals have to be monitored. In ref. [65] a quadrupole analyzer coupled to a Grimm-type glow discharge has been used for the in-depth analysis of technical surface layers. The latter source type is standardly used for GD-OES depth-profiling, and is therefore particularly suited for this type of application (i.e., reasonably flat crater profiles). Because this source operates at the typical GD-OES conditions (higher pressure and current than for GDMS) the erosion rate will also be higher, i.e., up to 0.1 μm/s. Moreover, a depth resolution of about 10 nm could be achieved for a Cr-Ni multilayer system. One of the problems of depth-profiling for both GDMS and GD-OES, is the quantification, i.e., the conversion from “intensity vs. time” into “concentration vs. depth”. This problem appears, however, not to be so severe for GDMS as for GD-OES, as was illustrated in ref. [65], by the concept of elemental sensitivities.

3.5 Solutions

Although the glow discharge is a typical solids analysis technique, some attempts have been made to analyze solutions as well. Some groups have tried to couple directly a solution introduction system to a glow discharge [68–70]. This required, however, specific instrumentation and moreover, these complicated devices could not compete with a widespread and successful technique as ICP-MS. Glow discharges have however, like graphite furnaces, successfully been used for the analysis of solution residues and thus for extremely small amounts of solution samples (1–100 μL). The solution is deposited on the surface of a high purity electrode, either a pin-shaped, a planar or a hollow cathode. The sputter-atomization and consequent ionization of the residue results in this case in a transient signal, typically lasting about 1 min. With this method, Jakubowski *et al.* reached absolute limits of detection lower than 1 pg using a quadrupole mass filter [71]. To change the transient signal into a uniform signal that lasts for more than 30 minutes, aliquots of a solution sample have also been mixed with a high-purity conducting powder (e.g., Ag). In this case, limits of detection are clearly higher; a preliminary study of the mixing technique, applied to 200 μL samples, revealed limits of detection of about 2.5 μg/g (i.e., 0.5 μg) [72–74].

A very specific and unusual application of the glow discharge for solution analysis has recently been presented by Sikharulidze *et al.* [75]. The glow discharge ion source consisted of a metal capillary with an inner diameter of 0.2–0.5 mm, which was inserted into a discharge chamber through an insulator. A direct voltage of up to 3 kV was applied between the capillary and the discharge chamber. A liquid fed from an outside reservoir to the end of the capillary was evaporated. A glow discharge was generated in the vapor from this liquid, and a miniature hollow cathode was formed at the end of the capillary. The obtained mass spectra of water were dramatically different from the mass spectra typical of an ICP. Indeed, due to the direct injection of the liquid into the ionization zone without the need for liquid nebulization and vapor separation, the analyte losses were dramatically decreased, and the absolute detection limits in the elemental analysis of liquids were lowered by two or three orders of magnitude compared with ICP sources [75].

3.6 Gases

Since a stable glow discharge can be obtained with molecular gases (N_2, O_2, air, water vapor,...) GDMS can also be used for gas analysis. McLuckey and coworkers recently designed a glow discharge, which used air as discharge gas, to analyze trace impurities in the sampled air [76]. This set-up was, for example, used for the detection of trace quantities of vapor explosives in the field, by glow discharge ion trap mass spectrometry [77]. Recently, Schelles *et al.* have measured atmospheric particulate matter with GDMS using the secondary cathode technique [60] (see above). The sample preparation was very simple: air was sucked by a pump through a single-orifice impactor stage, in which the atmospheric aerosols were impacted on a metal support, forming a central spot. This metal plate was then directly used as the cathode of the glow discharge. Evaluation of the sample loading and of the discharge parameters allowed the authors to optimize the signal intensity and to minimize its decrease, the latter being a consequence of its consumption by continuous sputtering in the discharge. The available aerosol analysis time could be prolonged to more than 3 h, a time span necessary to perform a multi-element analysis using a magnetic sector instrument and long integration time. A NIST reference aerosol was measured to evaluate the quantitative analysis potential. The internal reproducibility was better than 10% RSD, and the limits of detection were estimated to be in the low μg/g to sub μg/g region [60].

3.7 Organic samples

GDMS is predominantly used for the analysis of solid inorganic samples, because the material to be analyzed is mainly sputtered in atomic form, and most molecular information, which is of interest for organic analysis, is lost. However, some attempts have been made to analyze organic samples as well, either as liquid or gas chromatographic effluents or as ionization source for organic vapors (e.g., [76, 78–82]). In the latter case, samples can be introduced as a gas (e.g., for the determination of organic compounds in ambient air) or as a liquid deposited on a support cathode. The liquid will evaporate in the low pressure discharge and then be ionized. Barshick and coworkers applied GDMS to the analysis of trace metals in petroleum [81, 82]. Cathodes were prepared by pipetting 50–500 μL of petroleum leachates into 1 g of high purity silver powder. The resulting slurry was placed in a low temperature asher to reduce the viscous oil solution to a dried residue. The blend was mixed to obtain homogeneity and pressed to an electrode. The main advantage, in comparison with, for example, the ICP, is the rapid and time-saving sample preparation. On the other hand, the population of organic interferents in the GDMS mass spectrum precluded the determination of some elements.

3.8 Nuclear samples

Finally, it is worth mentioning that GDMS has been applied for the analysis of “nuclear” materials [83–85]. The VG9000 double-focussing instrument was adapted for this purpose, and all parts of the instrument that come into contact with the sample (i.e., ion source chamber, sample interlock and pumping system) were placed inside a glove-box. The results showed that there was no compromise in the analytical performance of the instrument when it was placed inside this glove-box. In ref. [85] it was demonstrated that radio-isotopes of cesium, strontium, plutonium, uranium and thorium in soils, sediments and vegetations could be determined with good precision and accuracy. Internal precisions were in the order of 3–7%; external precisions (over different days) ranged from 5 to 20%, and the accuracy was in the range of 9–30%, which is acceptable considering the very low concentration levels. Detection limits in the pg/g level could be obtained by optimizing the integration time and the mass resolution [85].

4 Conclusion

Considering the number of publications, scientific contributions on conferences and commercial instruments, it must be concluded that GDMS is not so widely used, in comparison to, for example, ICP-MS. Although the latter technique is typically a solution-based technique (combined with nebulization), its application field is now being widened to the analysis of solids as well, by the combination with laser or spark ablation, electro-thermal vaporization, etc. Especially laser ablation-ICP-MS (LA-ICP-MS) is gaining increasing interest in recent years, using now mainly lasers in the UV and even far UV. Its applications are in geology, materials and environmental science, polymers, the semiconductor industry, etc., with potential for micro-analysis and even depth-profiling. There are, however, still some problems for quantitative analysis (due to a limited number of reference materials). Moreover, it seems not completely true that LA-ICP-MS for bulk analysis requires no sample preparation at all [86].

GDMS, on the other hand, permits more easily quantitative analysis, because the relative sensitivity factors are more or less uniform for most elements and do not differ drastically among various matrices. Moreover, for conducting samples, no sample preparation is needed. Hence, we can conclude that GDMS is still the superior technique, for specific applications, like the analysis of high-purity metals and alloys, especially when low detection limits have to be reached. For nonconductors, dc-GDMS requires some sample-preparation; the dilution with a conducting binding powder or the use of a secondary cathode is necessary, which increases the detection limits and also the possibility of spectral interferences. In rf-GDMS, nonconductors can be analyzed directly, but up to now, no commercial rf-GDMS instrument is available, which obviously limits its routine applications. If in the future, a suitable commercial rf-GDMS instrument would become available, the application range of GDMS could also be widened to routine analysis of non-conducting samples (e.g., for geological applications), besides the already well-established analysis of metals.

Acknowledgments A. Bogaerts is indebted to the Flemish Fund for Scientific Research (FWO) for financial support. The authors also acknowledge financial support from the Federal Services for Scientific, Technical and Cultural Affairs (DWTC/SSTC) of the Prime Minister’s Office through IUAP-IV (Conv. P4/10).

References

1. Deng R-C, Williams P (1994) Anal Chem 66 : 1890
2. Oksenoid KG, Liebich V, Pietzsch G (1996) Fresenius J Anal Chem 355 : 863–865
3. Duckworth DC, Marcus RK (1989) Anal Chem 61 : 1879–1886
4. Shick CR, Marcus RK (1996) Appl Spectrosc 50 : 454–466
5. Saprykin AI, Becker JS, Dietze H-J (1995) J Anal At Spectrom 10 : 897–901
6. Saprykin AI, Melchers FG, Becker JS, Dietze H-J (1995) Fresenius J Anal Chem 353 : 570–574
7. Hang W, Walden WO, Harrison WW (1996) Anal Chem 68 : 1148–1152

8. Pollmann D, Ingeneri K, Harrison WW (1996) J Anal At Spectrom 11 : 849–853
9. Hang W, Baker C, Smith BW, Winefordner JD, Harrison WW (1997) J Anal At Spectrom 12 : 143–149
10. Harrison WW, Hang W, Yan X, Ingeneri K, Schilling C (1997) J Anal At Spectrom 12 : 891–896
11. Molle C, Springael S, Wautelet M, Dauchot J-P, Hecq M (1995) Appl Spectrosc 49 : 872–879
12. Heintz MJ, Meyers DP, Mahoney PP, Li G, Hieftje GM (1995) Appl Spectrosc 49 : 945–954
13. Shi Z, Brewer S, Sacks R (1995) Appl Spectrosc 49 : 1232–1238
14. Saprykin AI, Becker JS, Dietze H-J (1996) Fresenius J Anal Chem 355 : 831–835
15. Cantle JE, Hall EF, Shaw CJ, Turner PJ (1983) Int J Mass Spectrom Ion Proc 46 : 11
16. Jakubowski N, Feldmann I, Stuewer D (1997) J Anal At Spectrom 12 : 151–157
17. Chartier F, Tabarant M (1997) J Anal At Spectrom 12 : 1187–1193
18. Hutton RC, Raith A (1992) J Anal At Spectrom 7 : 623–627
19. Valiga RE, Duckworth DC, Smith DH (1996) Rapid Comm Mass Spectrom 10 : 305–310
20. Duckworth DC, Barshick CM, Smith DH, McLuckey SA (1994) Anal Chem 66 : 92–98
21. Gordon SM, Callahan PJ, Kenny DV, Pleil JD (1996) Rapid Comm Mass Spectrom 10 : 1038–1046
22. McLuckey SA, Goeringer DE, Asano KG, Vaidyanathan G, Stephenson JL Jr (1996) Rapid Comm Mass Spectrom 10 : 287–298
23. Myers DP, Heintz MJ, Mahoney PP, Li G, Hieftje GM (1994) Appl Spectrosc 48 : 1337–1346
24. Harrison WW, Hang W (1996) J Anal At Spectrom 11 : 835
25. Barshick CM, Eyler JR (1992) J Am Soc Mass Spectrom 3 : 122–127
26. Watson CH, Wronka J, Laukien FH, Barshick CM, Eyler JR (1993) Spectrochim. Acta B 48 : 1445–1448
27. Watson CH, Wronka J, Laukien FH, Barshick CM, Eyler JR (1993) Anal Chem 65 : 2801–2804
28. Watson CH, Barshick CM, Wronka J, Laukien FH, Eyler JR (1996) Anal Chem 68 : 573–575
29. Olson LK, Belkin MA, Caruso JA (1996) J Anal At Spectrom 11 : 491–496
30. Belkin MA, Olson LK, Caruso JA (1997) J Anal At Spectrom 12 : 1255–1261
31. Vieth W, Huneke JC (1991) Spectrochim Acta B 46 : 137–153
32. Venzago C, Weigert M (1994) Fresenius' J Anal Chem 350 : 303–309
33. Saito M (1997) Anal Chim Acta 355 : 129–134
34. Smithwick RW III, Lynch DW, Franklin JC (1993) J Am Soc Mass Spectrom 4 : 278–285
35. Bogaerts A, Gijbels R (1996) J Anal At Spectrom 11 : 841–847
36. Milton DMP, Hutton RC (1993) Spectrochim Acta B 48 : 39–52
37. Schelles W, De Gendt S, Muller V, Van Grieken RE (1995) Appl Spectrosc 49 : 939–944
38. Schelles W, De Gendt S, Maes K, Van Grieken R (1996) Fresenius J Anal Chem 355 : 858–860
39. Betti M, Giannerelli S, Hiernaut T, Rasmussen G, Koch L (1996) Fresenius J Anal Chem 355 : 642–646
40. Wayne DM, Schulze RK, Maggiore C, Cooke DW, Havrilla G (1999) Appl Spectrosc (submitted)
41. Bogaerts A, Gijbels R (1997) Anal Chem 69 : 719A–727A
42. Fiala A, Pitchford LC, Boeuf JP, Baude S (1997) Spectrochim Acta B 52 : 531–536
43. Bogaerts A, Gijbels R (1998) Spectrochim Acta B 53 : 1–42
44. van Straaten M (1993) Ph. D. Thesis, University of Antwerp
45. Marcus RK (1993) Glow Discharge Spectroscopies, Plenum, New York
46. Harrison WW, Hess KR, Marcus RK (1986) Anal Chem 58 : 341A–356A
47. Harrison WW (1988) J Anal At Spectrom 3 : 867–872
48. King FL, Harrison WW (1990) Mass Spectrom Reviews 9 : 285–317
49. Jakubowski N, Stuewer D, Vieth W (1987) Anal Chem 59 : 1825
50. Vassamilet LF (1989) J Anal At Spectrom 4 : 451
51. Mykytiuk AP, Semeniuk P, Berman S (1990) Spectrochim Acta Reviews 13 : 1
52. Itoh S, Hirose F, Hasegawa R (1992) Spectrochim Acta B 47 : 1241–1245
53. Wayne DM, Yoshida TM, Vance DE (1996) J Anal At Spectrom 11 : 861–869
54. Venzago C, Ohanessian-Pierrard L, Kasik M, Collisi U, Baude S (1998) J Anal At Spectrom 13 : 189–193
55. Application Note, GDMS-AN-002–01, Charles Evans & Associates, Redwood City, California, 1988
56. Jaeger R, Saprykin AI, Becker JS, Dietze H-J, Broekaert JAC (1997) Mikrochim Acta 125 : 41–44
57. Jaeger R, Becker JS, Dietze H-J, Broekaert JAC (1997) Fresenius J Anal Chem 358 : 214–217
58. De Gendt S, Schelles W, Van Grieken R (1995) J Anal At Spectrom 10 : 681–688
59. Schelles W (1996) Ph. D. Thesis, University of Antwerp
60. Schelles W, Maes KJR, De Gendt S, Van Grieken RE (1996) Anal Chem 68 : 1136–1142
61. Schelles W, Van Grieken R (1997) J Anal At Spectrom 12 : 49–52
62. Schelles W, Van Grieken R (1997) Anal Chem 69 : 2931–2934
63. Shick CR Jr, DePalma PA Jr, Marcus RK (1996) Anal Chem 68 : 2113–2121
64. Hecq M, Hecq A, Fontignies M (1983) Anal Chim Acta 155 : 191–198
65. Jakubowski N, Stuewer D (1992) J Anal At Spectrom 7 : 951–958
66. Raith A, Hutton RC, Huneke JC (1993) J Anal At Spectrom 8 : 867–873
67. Behn U, Gerbig FA, Albrecht H (1994) Fresenius J Anal Chem 349 : 209–210
68. Foss GO, Svec HJ, Conzemius RJ (1983) Anal Chim Acta 147 : 151
69. Brackett JM, Vickers TJ (1983) Spectrochim Acta 38B : 979
70. Strange CM, Marcus RK (1991) Spectrochim Acta 46B : 517
71. Jakubowski N, Stuewer D, Toelg G (1991) Spectrochim Acta B 46 : 155–163
72. Barshick CM, Duckworth DC, Smith DH (1993) J Am Soc Mass Spectrom 4 : 47–53
73. Hess KR, Barshick CM, Duckworth DC, Smith DH (1994) Appl Spectrosc 48 : 1307
74. Headrick KL, Chakrabarti CL, Bicheng Z, Marchand B (1994) Spectrochim Acta 49B : 975
75. Sikharulidze GG, Lezhnev AE (1998) J Anal Chem (USSR) 53 : 375–380
76. McLuckey SA, Glish GL, Asano KG, Grant BC (1988) Anal Chem 60 : 2220–2227
77. McLuckey SA, Goeringer DE, Asano KG, Vaidyanathan G, Stephenson JL Jr (1996) Rapid Comm Mass Spectrom 10 : 287–298
78. Zhao J, Zhu J, Lubman DM (1992) Anal Chem 64 : 1426
79. Mason R, Milton D (1989) Int J Mass Spectrom Ion Proc 91 : 209–225
80. Carazzato D, Bertrand MJ (1994) J Am Soc Mass Spectrom 5 : 305–315
81. Barshick CM, Smith DH, Hackney JH, Bole BA, Wade JW (1994) Anal Chem 66 : 730
82. Barshick CM, Smith DH, Wade JW, Bayne CK (1994) J Anal At Spectrom 9 : 83–87
83. Betti M, Rasmussen G, Hiernaut T, Koch L, Milton DMP, Hutton RC (1994) J Anal At Spectrom 9 : 385–391
84. Betti M (1996) J Anal At Spectrom 11 : 855–860
85. Betti M, Rasmussen G, Koch L (1996) Fresenius J Anal Chem 355 : 808–812
86. Guenther D (1999) Invited talk presented at 1999 European Winter Conference on Plasma Spectrochemistry, Pau, France, 10–15 January 1999