Germanium NMR, Applications

See **Heteronuclear NMR Applications (Ge, Sn, Pb).**

Glow Discharge Mass Spectrometry, Methods

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MASS SPECTROMETRY
Methods & Instrumentation

Introduction (synopsis)

This article describes the basic characteristics and methodology of glow discharge mass spectrometry (GDMS). First, the working principles of the glow discharge source will be explained, and its use for mass spectrometry will be clarified, followed by a short historical background of GDMS. Further, the various glow discharge source configurations and mass spectrometers used in GDMS will be outlined. GDMS can be operated in three different electrical operation modes, with either a direct current, radiofrequency powered or pulsed-glow discharge system. The glow discharge can also be 'boosted', by combining it either with a laser, a graphite furnace, a microwave discharge, magnetic fields or external gas jets, in order to improve the analytical results. The three electrical operation modes and the boosting methods will be briefly discussed. Moreover, the quantification methods in GDMS will be described, as well as possible solutions to overcome spectral interferences. Finally, although GDMS is particularly suitable for the analysis of conducting materials, considerable effort has been undertaken also to analyse nonconductors, and three commonly used methods to achieve this will be briefly discussed.

Principle of the glow discharge and its use for mass spectrometry

A glow discharge is a kind of plasma, i.e. a partially ionized gas, consisting of positive ions and electrons, and a large number of neutral atoms. It is formed when a cell, consisting of an anode and a cathode, is filled with a gas at low pressure (e.g. 1 torr; 1 torr = 133.3 Pa). In glow discharges used for mass spectrometry, argon is most frequently used as the filling gas. A potential difference (of the order of 1 kV) is applied between the two electrodes, and creates gas breakdown (i.e. the splitting of the gas into positive ions and electrons). The ions are accelerated towards the cathode and cause the emission of electrons upon bombardment at the cathode. The electrons arrive in the plasma, and give rise to excitation and ionization collisions with the argon gas atoms. The excitation collisions (and the subsequent decay, with emission of light) are responsible for the characteristic name of the 'glow' discharge. The ionization collisions create new ion–electron pairs. The ions are again accelerated towards the cathode, giving rise to new electrons. The electrons can again produce ionization collisions, creating new electron–ion pairs. Hence, the latter processes make the glow discharge a self-sustaining plasma.

The use of the glow discharge as an ion source for mass spectrometry is based on the phenomenon of sputtering. The material to be analysed serves as the cathode of the glow discharge. The argon ions from the plasma (and also fast argon atoms) that bombard the cathode can also release atoms of the cathode material, which is called sputtering. The sputtered atoms arrive in the plasma where they can be ionized. Thus formed ions of the material to be analysed can be detected with a mass spectrometer, giving rise to GDMS. **Figure 1** illustrates the basic principles of the glow discharge and its coupling to mass spectrometry.

Typical discharge conditions used for GDMS are about 1 kV discharge voltage, an argon gas pressure in the order of 1 torr, and a d.c. discharge current in the mA range. The detection limits of this technique are generally in the ppb range.

Short history of GDMS

The glow discharge has been known as an ion source for mass spectrometry for more than 60 years. Gas discharges were indeed already used in the 1920s and 1930s as ion sources in the first mass spectrographs of

Aston and Thompson. However, the early popularity was followed by a decline into relative obscurity during the next 30 years, due to the development of the simple electron impact ion source. There was indeed more interest at that time for the analysis of organic samples with relatively high vapour pressure; hence simple ionization in the gas phase by an electron beam was largely sufficient. When the interest also shifted to the analysis of inorganic materials with lower vapour pressure, there was again need for other sources, with sufficient energy for atomization and ionization. Since spark and arc discharges were already widely used as excitation sources for atomic emission spectrometry, it was obvious that these sources could also be applied for mass spectrometry. These sources exhibit a high sensitivity, large applicability and only a few spectral interferences, but they do not yield a stable ion population. This led to the reexamination of the glow discharge as a stable, low energy ion source. The first come-back of GDMS was due to Coburn and coworkers; but later, Harrison and co-workers in particular were pioneers in the development of modern GDMS.

Glow discharge source configurations

As mentioned above, the glow discharge is formed in a cell consisting of two electrodes. These two electrodes can be mounted in five different geometries (see **Figure 2**).

The *coaxial cathode* (**Figure 2A**) is the most widely used source configuration in GDMS applications. Samples can be made in pin-form (with a few millimetres exposed to the discharge) or in disk-form (partly shielded so that only the top part is exposed to the discharge). The sample acts as cathode whereas the anode is formed by the cell body itself.

The *planar diode* (**Figure 2B**) is the simplest analytical source. It is used for analysing samples in disk-form. The cathode (sample) and anode are in parallel configuration and are placed inside a tube.

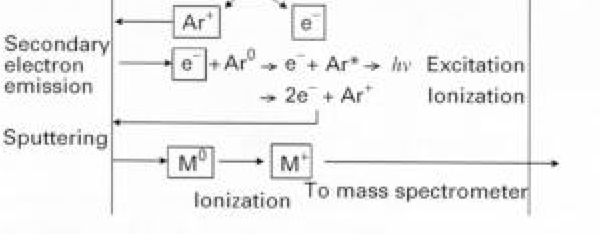


Figure 1 Schematic of the basic processes in a glow discharge.

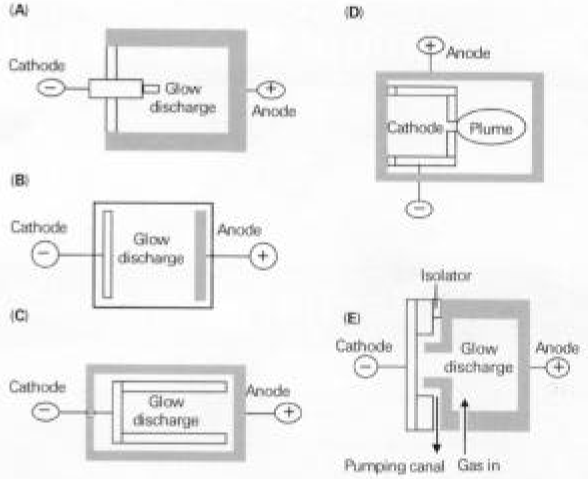


Figure 2 Different glow discharge source configurations: (A) coaxial cathode; (B) planar diode; (C) hollow cathode lamp; (D) hollow cathode plume; (E) Grimm source. Reprinted from Bogaerts A and Gijbels R (1998) Fundamental aspects and applications of glow discharge spectrometric techniques (Review). *Spectrochimica Acta Part B* **53**: 1–42, with permission from Elsevier Science.

In the *hollow cathode lamp* (**Figure 2C**) the cathode forms a cavity rather than a pin or disk. It can be considered as three planar cathodes placed so close to each other that their negative glow regions coalesce into a single negative glow. This results in increased sputtering and ionization/excitation, yielding much better analytical sensitivity. A disadvantage of this source is the extensive machining required to make hollow cathodes from metal samples. Because most of the sputtering occurs at the cathode base, studies have been performed using a disk sample as the base of the cathode.

In the *hollow cathode plume* (**Figure 2D**) the sample is mounted in the base of the hollow cathode, in which an orifice is also made. A highly energetic flamelike plume, where excitation and ionization processes occur, is ejected through this hole. Due to the high atom population, this geometry is also characterized by a high sensitivity. Nevertheless, it is rarely used for practical analyses.

In the *Grimm configuration* (**Figure 2E**) the cell body (anode) approaches the cathode very closely (at a distance smaller than the thickness of the cathode dark space), so that the discharge is constricted to a well-defined part of the sample surface. It is therefore called an 'obstructed discharge'. A similar concept is also used in the standard cells for analysing flat samples in commercial mass spectrometers (e.g. the VG9000 instrument, see below). Moreover, the Grimm source possesses an additional pumping canal close to the cathode, which reduces the pressure near the cathode, thereby minimizing redeposition. This geometry can, however, only be used for flat samples. Although this source is extensively used in glow discharge optical emission spectrometry (GD-OES; particularly for in-depth analysis), and forms the basic design for all commercial optical emission instruments, it is not so frequently used in GDMS.

Mass spectrometers coupled to the glow discharge

To date, all common mass analysers have been explored for use in GDMS. The first commercial GDMS instruments used a double-focusing mass analyser, permitting the acquisition of high-resolution spectra with high sensitivity. **Figure 3** shows a schematic of the 'VG9000' GDMS instrument, with first a magnetic and then an electrostatic sector (VG Elemental, Thermo Group). This instrument was made commercially available in 1985. About 60 instruments of this type are currently being used worldwide. Beside this VG9000 instrument, two other double-focusing GDMS instruments are used nowadays: the Kratos 'Concept', from which only two instruments have been manufactured, and the 'Element' from Finnigan MAT, which is essentially an inductively coupled plasma mass spectrometer (ICP-MS) that also became recently available with a glow discharge source. **Figure 4** shows a typical GDMS mass spectrum obtained with the VG9000 glow discharge mass spectrometer.

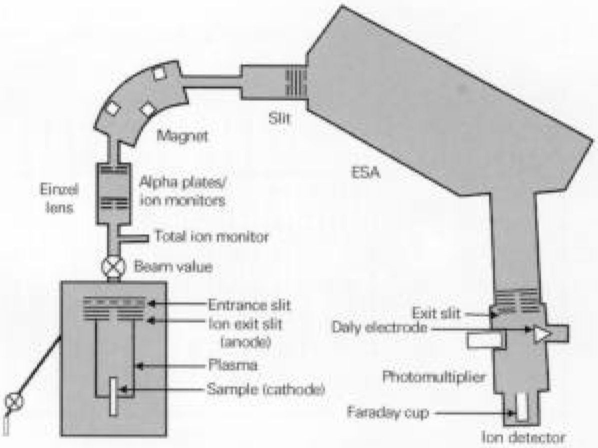
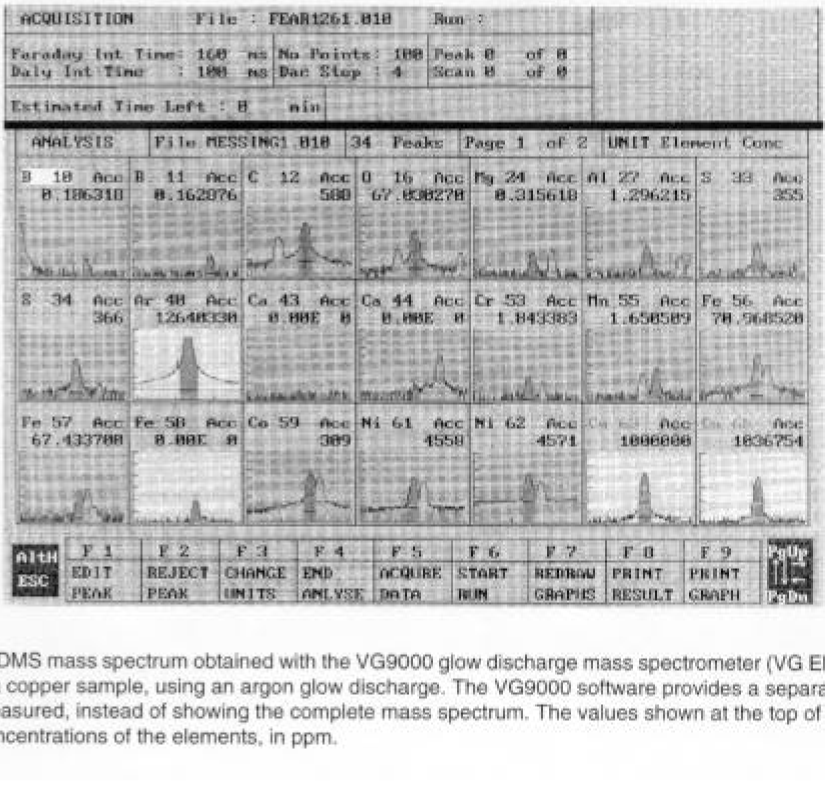


Figure 3 Schematic of the VG9000 glow discharge mass spectrometer (VG Elemental, Thermo Group).

The wide expansion of modern GDMS began, however, with the quadrupole-based mass analysers, which are mainly being employed for fundamental and development research of GDMS. Nevertheless, this research resulted also in the commercial availability of quadrupole GDMS systems, e.g. the 'VG Gloquad' (VG Elemental, Thermo Group).

Moreover, glow discharges have also been coupled to ion trap mass spectrometers, double and triple



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ANALYSIS   File MESSING1.010   34 Peaks   Page 1  of 2   UNIT Element Conc

B  10   Acc  B  11   Acc  C  12   Acc  O  16   Acc  Mg 24   Acc  Al 27   Acc  S  33   Acc
  0.186310     0.162076          500   67.030270    0.315610     1.296215          355

S  34   Acc  Ar 40   Acc  Ca 43   Acc  Ca 44   Acc  Cr 53   Acc  Mn 55   Acc  Fe 56   Acc
       366    12640330     0.00E  0     0.00E  0     1.043383     1.650509   70.560520

Fe 57   Acc  Fe 58   Acc  Co 59   Acc  Ni 61   Acc  Ni 62   Acc  Cu 63   Acc  Cu 65   Acc
 67.433700     0.00E  0          309         4550         4571      1000000      1036754
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Figure 4 Typical GDMS mass spectrum obtained with the VG9000 glow discharge mass spectrometer (VG Elemental, Thermo), for specific elements in a copper sample, using an argon glow discharge. The VG9000 software provides a separate window for each of the isotopes to be measured, instead of showing the complete mass spectrum. The values shown at the top of each window give the isotopic-corrected concentrations of the elements, in ppm.

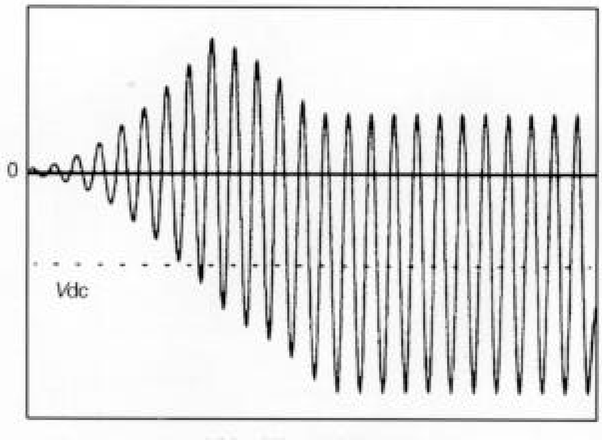

Figure 5 Formation of a d.c. bias voltage in an RF-powered glow discharge with a nonconducting sample.

quadrupole instruments, time-of-flight mass spectrometers, and Fourier-transform mass spectrometers, but these investigations can rather be considered as research topics. Indeed, the commercial GDMS systems available at present employ only double-focusing and quadrupole-based mass spectrometers.

Glow discharge electrical operation modes

The simplest and cheapest operation mode is the *direct current* (*d.c.*) mode. Voltages are typically 500–1500 V, yielding electrical currents in the order of mA. This type of discharge mode is the oldest and the most widely used in glow discharge applications. However, it has the serious drawback of not being able to analyse nonconducting samples directly. Indeed, since in a glow discharge the sample to be analysed acts as the cathode, which is sputter bombarded by positive ions, it must be conducting. If not, the surface will be charged, preventing the positive ions from bombarding further. Due to this drawback of the d.c. mode, attention has been drawn during the 1990s to the *radiofrequency* (*RF*) operation mode.

The *radiofrequency* mode is indeed able to analyse nonconductors directly, since the positive charge accumulated during one half-cycle will be neutralized by negative charge accumulation during the next half-cycle, so that no charging occurs. Operation with RF-power of a glow discharge using a nonconducting sample yields a negative d.c. bias voltage on the sample surface (see **Figure** 5). Indeed, during the half-cycles in which the nonconducting electrode is positive, surface charging will occur much faster than in the half-cycles in which the electrode is negative, due to the much higher mobility of the electrons compared to the positive ions. The self-bias phenomenon permits the establishing of a time-averaged cathode and anode in the glow discharge, so that sputter-bombardment of positive ions on the cathode is still possible. Since the electrons try to follow the RF electric field, they oscillate between the two electrodes and spend more time in the plasma before they are lost, which results in a higher ionization efficiency. This leads to the second advantage of RF discharges, i.e. they can be operated at much lower pressures for the same current than d.c. discharges, which is interesting for reducing redeposition and spectral interferences. The capability of RF-powered GDMS for direct analysis of nonconductors was demonstrated already in the 1970s by Coburn and Kay and by Harrison and co-workers. However, it took until the late 1980s before RF-GDMS was revisited by Marcus and collaborators. Since then, extensive work has been done in this field. RF-discharges used for GDMS have been combined with quadrupole mass spectrometers, a Fourier-transform mass spectrometer, an ion trap mass spectrometer, a time-of-flight system and two sector-based mass spectrometers, but up to now there is no commercial RF-GDMS instrument available.

The third mode of operation of a glow discharge is the *pulsed mode*, which can be employed in combination with a conventional d.c. or with an RF glow discharge. Voltage and current are applied only during short periods of time (generally the millisecond range). Hence, compared to a normal d.c. discharge, higher peak voltages and peak currents can be obtained for the same average power. Therefore, more highly energetic gaseous ions can be produced, yielding more sputtering, a higher concentration of analyte atoms in the plasma and hence better analytical sensitivity. In addition to the better sensitivity, the pulsed mode has a second advantage for mass spectrometry, i.e. the analytically important ions and the interfering ions are formed during a different time in the pulse. By coupling this ‘time-resolved’ production of ions to a time-resolved detection (time-of-flight mass spectrometer), spectral interferences in the mass spectrum can be reduced. Moreover, the construction of a pulsed dual discharge system allows for simultaneous analyses with two electrodes, rendering possible the *in situ* calibration of an unknown sample against a reference standard. Recently, Harrison and co-workers introduced the microsecond-pulsed glow discharge. Due to the still higher peak currents and voltages that can be obtained during the short pulses, this source exhibits an even better analytical sensitivity. As shown in **Figure** 6, the microsecond-pulsed copper signals are one order of magnitude higher than those in the d.c. glow discharge, and they can still be further enhanced, when the pulse power is increased.

Boosting of the simple GDMS systems

Beside these three electrical operation modes, which make use of the glow discharge in its simple form as a spectroscopic source, the glow discharge can also be employed in a hybrid construction, in combination with lasers, graphite furnaces, microwave discharges or magnetic fields. The common purpose of these constructions is to increase the sputtering (atomization) and/or ionization (or excitation), and hence to improve the analytical sensitivity of the glow discharge.

Laser-based methods

The development of cost-effective laser systems has generated a variety of laser techniques that can be coupled to a glow discharge. The atomization and the ionization/excitation steps occur independently of each other in the glow discharge, and a laser can be employed to enhance either of these two steps.

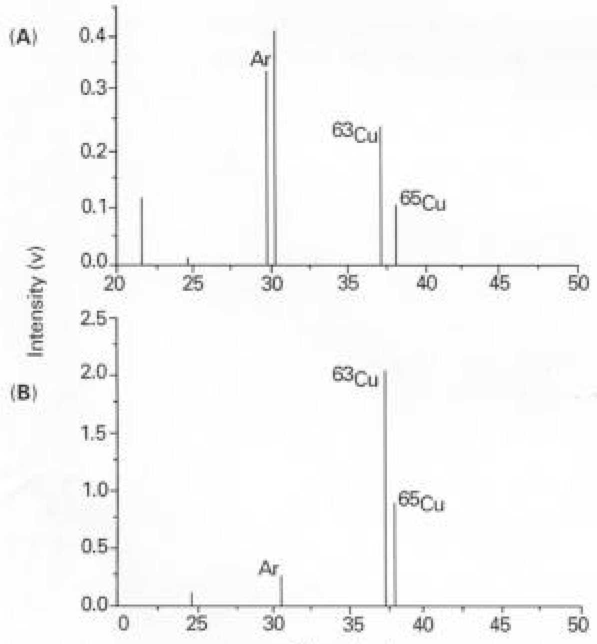

Figure 6 Mass spectra of a d.c. (A) and a microsecond-pulsed (B) glow discharge, at 1 torr gas pressure. Conditions for d.c.: 800 V, 3 mA; conditions for pulsed: 2 kV, 15 µs. Reprinted from Hang W, Baker C, Smith BW, Winefordner JD and Harrison WW (1997) Microsecond pulsed glow discharge time-of-flight mass spectrometry: analytical advantages. *Journal of Analytical Atomic Spectrometry* **12**: 143–149, with permission of the Royal Society of Chemistry.

First, the laser can be utilized to ablate material from the sample cathode, enhancing the atomization step. The laser can also ablate material from a secondary sample (not the cathode) into the glow discharge. In the latter case, the sample must not be conductive, expanding the analytical applications of glow discharges to the analysis of nonconductors without the need to apply RF powers (see above). Beside the enhanced atomization, the possibility of performing spatially resolved measurements is an additional advantage of this method.

Second, the laser can also be used to enhance the excitation/ionization processes in the discharge. The usefulness of this laser enhancement has been demonstrated in a variety of application areas, such as optogalvanic effect spectroscopy (i.e. the laser results in alternations in the ionization rate of the discharge, which are electrically detected by the resulting changes in voltage or current), laser enhanced ionization (i.e. directly measuring the electrons released when the ionization in the discharge is enhanced due to laser photons) and resonance ionization mass spectrometry (i.e. the laser is used for selectively ionization enhancement of sputtered species in the discharge, increasing both the sensitivity and selectivity in GDMS).

Furnace atomization nonthermal excitation spectrometry (FANES)

By analogy to the laser ablation glow discharge technique, FANES also makes use of an external atomization source (i.e. thermal vaporization from a graphite furnace) whereas the atoms created are excited and/or ionized in the glow discharge plasma. This source type is markedly different from a classical glow discharge source. Indeed, sample volatilization is accomplished thermally and the rate of volatilization can be three orders of magnitude higher than typical sputtering rates in a glow discharge. Moreover, this technique is mostly operated at much higher pressures than a conventional glow discharge, which results in a longer residence time for the analyte atoms in the plasma, and hence higher sensitivity.

Microwave boosted glow discharge

Coupling of auxiliary microwave power to a glow discharge, in order to enhance the ionization and excitation, can be performed in two different ways. An antenna can be inserted in the plasma to match the microwave power, or an additional microwave induced plasma can be applied. The latter technique has, in particular, been applied to GD-OES, where considerable enhancement of analytical optical emission lines has been attained. However, this technique is not commonly used for GDMS.

Magnetron discharges

Another method to improve the performance of a conventional glow discharge, is based on magnetic enhancement. One simple device among magnetically enhanced glow discharges is the magnetron glow discharge. In this device, permanent magnets are used to form a magnetic field of a few hundred gauss in the plasma. Electrons in the plasma are forced to move in closed-loop trajectories parallel to the cathode surface. Hence, the electron path length is increased and the ionization of the discharge gas is significantly enhanced. Therefore, the magnetron discharge can operate at much lower pressures than conventional discharges. Lower pressure operation provides higher ion and electron kinetic energies, leading to higher atomization and excitation/ionization efficiencies, and hence a better analytical sensitivity.

Gas-assisted sputtering glow discharges

Another way to increase the analytical sensitivity of a glow discharge is to use a gas-jet discharge. Due to the gas jet impinging on the sample surface, the sputter ablation is improved by both reduced redeposition and increased sample transport. This results in a higher sputtered atom population in the plasma and hence better analytical sensitivity. The gas-jet glow discharge was first developed for glow discharge atomic absorption spectrometry (GD-AAS), but a few applications in GDMS have also been reported.

Quantification in GDMS

To obtain quantitative concentrations in GDMS, two main approaches can be used. The easiest approach is the ion beam ratio method. The assumption is made that the ratio of the ion current for any one isotope with respect to the total ion current (except the signal arising from the discharge gas ions) is representative of the concentration of that isotope in the sample. Since the matrix ion signal is generally large compared to the individual trace species, especially for a high purity metal or semiconductor, the matrix ion current is, to a good approximation, equal to the total ion current and the matrix atoms can be assumed to have a concentration of 100%. Since this method can not correct for the variation in analytical sensitivity among different elements (e.g. due to variations in sputtering and ionization of the elements), it provides only semiquantitative results, i.e. accuracies of a factor of 2–3.

Real quantitative results require the differences in elemental sensitivities to be characterized using standards similar to the material under study. This characterization generates relative sensitivity factors (RSFs) that can be employed to correct the measured ion beam ratios. Since RSFs vary only slightly between matrices of the same general composition, exact matrix matching is not required to yield quantitative results with accuracies of 15–20%. The RSF method of quantification is the most widely employed in GDMS. Generally, the RSFs of different elements in GDMS lie within one order of magnitude, which makes GDMS a technique with rather uniform sensitivity for most elements. Experimental RSFs have been reported in the literature for different kinds of matrices, and some empirical models based on fitting parameters have been developed to predict RSFs. Moreover, it was found that the theoretically calculated RSF values correlated better with the experiment when 1% H_2 was added to the argon discharge gas. This suggests that RSFs could be more accurately predicted theoretically in a gas mixture of Ar + 1% H_2, leading to satisfactory quantitative results without the need to analyse a standard. This might be very interesting, because solid reference materials with known concentrations at the (ultra-) trace level are not commonly commercially available. However, this method is not yet routinely used in practice.

Spectral interferences in GDMS

A common problem in GDMS, as in most mass spectrometric methods, is the occurrence of spectral interferences in the mass spectrum, e.g. by impurity gas ions, various types of cluster ions or multiply charged ions. This problem can partly be overcome by using a high-resolution mass spectrometer, such as a double-focusing instrument or a Fourier-transform mass spectrometer, or by using high purity gases and special purification systems to suppress these interferences. However, some interference problems cannot be overcome in this way. For example, ^{103}Rh (rhodium is monoisotopic) in a copper matrix (^{63}Cu has 69% abundance) is severely limited by the ^{40}Ar ^{63}Cu cluster. Even if one could separate both peaks with a high-resolution mass spectrometer (a resolution of $M/\Delta M = 7620$ is required), the tailing of the huge cluster peak would prevent one from reaching low limits of detection for rhodium. In this case, the problem can be solved using an alternative plasma gas, e.g. neon instead of argon. It is demonstrated that both discharge gases exhibit similar analytical performance if a correspondingly higher pressure is used for neon; and hence, specific interference problems can be overcome. To illustrate this, **Figure 7** presents a part of the mass spectrum (*m/z* 90–100) of a pure iron sample, both in argon and in neon. It appears that most peak intensities in this mass range are significantly decreased in the neon discharge. This clearly demonstrates that these peaks are interfering peaks due to $ArFe^+$ clusters, which can be avoided by using neon as the discharge gas.

Moreover, another method has recently been proposed in the literature, which tries to suppress the cluster interferences by sampling from a reversed hollow cathode ion source. Indeed, it was found that the analyte ions are characterized by a peak at high energy, whereas argon ions and cluster ions possess a peak at low energy. By sampling only high energy ions, the argon ion and cluster ion interferences can be suppressed. Finally, the clusters can also be used for quantification. Indeed, since argides, dimers and doubly charged analyte ions may be less disturbed by spectral interferences, they can therefore sometimes be better employed for quantification than singly charged analyte ions, as has also been recently demonstrated.

The analysis of nonconductors by GDMS

Since the sample in the glow discharge acts as the cathode bombarded by positive ions, the concept seems to restrict the applications of GDMS to the analysis of electrically conducting materials, because nonconductive materials will be charged. The analysis of conducting materials (e.g. high-purity metals or alloys) forms, indeed, the most important field of application of GDMS. Nevertheless, much effort has also been applied to analyse nonconducting materials with GDMS, to greatly widen the application field. As mentioned above, RF-discharges are often used to analyse nonconductors directly. Nevertheless, there is no commercial RF-GDMS instrument available up to now, which is a serious drawback for routine analysis.

In a d.c. discharge, nonconductors can, however, also be analysed when applying certain modifications. Two methods are reported in the literature. The first consists of mixing the nonconducting sample as a powder with a conductive binder (Cu, Ag, Ga) and pressing it into an electrode. This method is generally well established, as follows from the large number of papers in the literature. However, in addition to the increase in sample preparation time compared to direct analysis of conducting solids, the mixing with the conductive matrix can introduce contamination. Other problems arise from the trapping of water vapour and atmospheric gases in the sample during the compaction process. Also, the time to reach steady state conditions with a composite cathode can be prohibitively long.

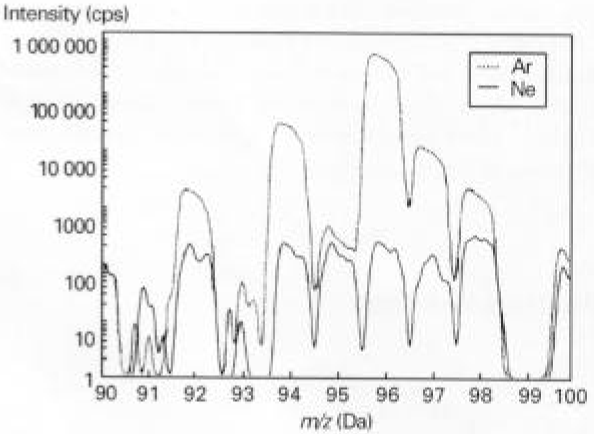

Figure 7 Mass spectra of a pure Fe sample in argon and in neon (*m/z* 90–100 range). The difference between argon and neon is caused by $ArFe^+$ interferences. Reprinted from Jakubowski N and Stüwer D (1989) Comparison of Ar and Ne as working gases in analytical glow discharge mass spectrometry. *Fresenius' Journal of Analytical Chemistry* **355**: 680–686, with permission of Springer-Verlag, Berlin.

The second approach in d.c.-GDMS is the use of a metallic secondary cathode diaphragm in front of the flat nonconducting sample surface. Due to the redeposition of a part of the sputtered metal atoms from the secondary cathode, a very thin conductive layer is formed on the nonconductive material. The sampling depth is large enough (~5 Å, or 0.5 nm) to allow atomization of the nonconducting sample as well. The principle of this method is explained schematically in **Figure 8**. This method is rather new, but has already been successfully applied to the analysis of glass, ceramics, marble, polymers and even atmospheric particulate matter (aerosols).

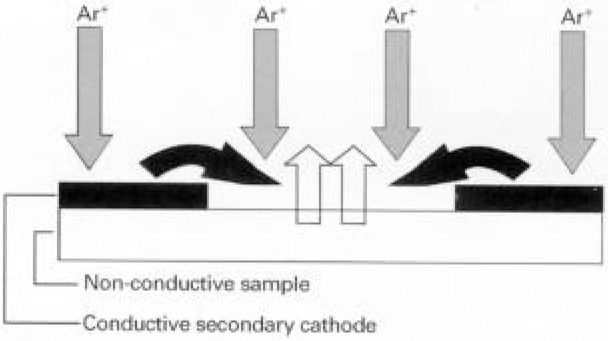

Figure 8 Schematic representation of the sputter-redeposited film formation on the nonconducting sample surface.

See also: **Atomic Absorption, Theory; Inorganic Chemistry, Applications of Mass Spectrometry; Laser Applications in Electronic Spectroscopy; Laser Microprobe Mass Spectrometers; Laser Spectroscopy Theory; Mass Spectrometry, Historical Perspective; Microwave Spectrometers.**

Further reading

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Gold NMR, Applications

See **Heteronuclear NMR Applications (La–Hg).**