Glow discharge mass spectrometry (GDMS) is a mature, versatile technique for the direct determination of trace elements in a variety of materials. The technique is an extension of the earliest forms of mass spectrometry. Processes inherent to the glow discharge, namely cathodic sputtering coupled with Penning ionization, yield an ion population from which semi-quantitative results can be directly obtained. Quantification in GDMS is achieved both through standard elemental mass spectrometric procedures and more innovative approaches. The analytical performance of GDMS compares favorably with competing elemental mass spectrometric methods and newer experiments use this ionization method for both molecular and elemental analysis. As with any analytical technique, the future of GDMS lies in improvements with respect to instrumental implementation and extension to new areas of application. If the method is to remain competitive, commercial GDMS systems must incorporate advances in mass spectrometric technology to increase analytical performance while decreasing the size, complexity and cost of the technique. Continued efforts to develop improved quantitation procedures are needed to provide greater accuracy. The method should continue to mature as sustained efforts demonstrate its utility in the solution of new and more varied problems.

INTRODUCTION

Like most mass spectrometric methods, glow discharge mass spectrometry (GDMS) is a versatile tool with a range of applications spanning many disciplines. Whereas the analytical chemistry community views GDMS as a method for the direct determination of trace elements in solid state materials,¹ the materials science community often thinks of glow discharge mass spectrometry as a diagnostic tool for the characterization and control of reactive and non-reactive deposition plasmas.² In fact, members of the materials science community were the first to recognize the potential for GDMS as an analytical method capable of providing information regarding the composition of solid samples.³,⁴ This tutorial focuses on the realization of GDMS as an analytical chemistry tool. The reader interested in plasma monitoring GDMS should refer to reviews such as those listed in Ref. 2.

The first report of GDMS as a true analytical chemistry technique appeared in 1974,⁵ and in the subsequent years it has matured as an analytical technique. The steady increase in publications that occurred over the past 25 years, shown in Fig. 1, reflects the growing interest in GDMS. Since 1975 the volume of publications in this field has nearly doubled every 5 years.

Figure 1. GDMS publication vs. 5-year time periods, 1970–94. Publications in GDMS have doubled every 5 years from 1975 to the present. The relatively small number of total publications is reflective of the specialized nature of GDMS.
Although the total number of publications seems small, this observation is more indicative of the technique’s specialized nature than it is reflective of its impact. GDMS has carved out an important niche where the availability of electronic and optical materials of the greatest possible purity is important. It is GDMS that often provides certification of these materials at the required purity levels. In recent times, research has focused on extending the applicability of GDMS to include environmental monitoring of soils and ambient atmospheres, the characterization of organic and biological compounds, the identification of impurities in petroleum and the examination of polymers.

Through this tutorial we seek to present the reader with an overview of analytical GDMS. In keeping with the educational focus of this feature, the overview begins with a brief description of the historical relationship between plasma spectroscopy and mass spectrometry. The roots of GDMS are found in the early history of mass spectrometry. An introduction to the glow discharge and its inherent atomization and ionization processes provides the background necessary to appreciate the analytical capabilities of this ion source. Requirements for a generic GDMS system frame the various instrumental approaches to the implementation of GDMS. Methods of quantification and degrees to which it is achieved are summarized with a worked hypothetical GDMS analysis. The relation of GDMS to other elemental mass spectrometric methods is examined to define better its realm of application. Although this tutorial concludes with some representative applications of GDMS, the interested reader should refer to recent technical reviews and the current literature for detailed information regarding applications.

HISTORICAL PERSPECTIVE

‘It will be seen that of the 80 non-reactive elements now known to exist, 53 have been analyzed and their constitutions, isotopic or otherwise, determined in four and a half years’ work. Failing the discovery of new and more general methods of producing mass rays, it is not to be expected that progress with the remaining ones will be so rapid, but it seems reasonable to hope that in a comparatively moderate time every stable atomic species existent in any considerable quantity on earth will have been identified and weighed.’

F. W. Aston, in Isotopes, 1924

This passage is merely a remainder that the mass spectrometric determination of the elements and their isotopes is not a recent development. The modern shift of trace element analysis from optical spectrometry to mass spectrometry is a replay of history. Mass ‘spectroscopy’ originated as a tool for investigations into the formation and characterization of the positive, or anode, rays produced in ‘ordinary’ gas tube—investigations for which optical spectroscopic techniques would not suffice. Because the origins of modern GDMS date to the adolescence of mass spectrometry, a short recap of this history is in order.

In 1886, there appeared a report describing luminous streamers arising from rays that had passed through perforations in a cathode and travelling in the opposite direction to the cathode rays. Because the rays giving rise to these streamers were found to possess positive charge, Thomson termed them positive rays. Today we know, in large part because of work that began in Thomson’s laboratory, that these positive rays were loosely focused ion beams. Using the parabola method, Thomson embarked upon investigations into the nature of positive rays. Dempster followed up these investigations employing an instrument equipped with focusing slits to resolve the components of positive rays more clearly. This instrument of Dempster’s was the first that could be called a mass spectrograph. Thomson’s assistant, Aston, soon reported on the development of a mass spectrograph that achieved improved resolution through velocity and direction focusing. This instrument and its descendants were employed in Aston’s investigations of positive rays that led to the characterization of isotopes. Aston, employing electrical discharge ionization, and Dempster, employing thermal ionization, pioneered techniques that evolved into modern methods for trace element determinations such as plasma source and thermal ionization mass spectrometry.

The early work by Thomson revealed an important fact regarding the spectra of positive (or mass) rays—not only were these spectra characteristic of the discharge support gas, but also they were considerably less complex than the corresponding optical spectra. Because mass spectrometry exhibited both high sensitivity and spectral simplicity, its combination with a method of generating a large, representative population of sample ions made it a powerful tool for trace analyses. Although ion generation from gaseous samples was relatively straightforward using electron beams, the generation of representative sample ions from solid materials presented more of a challenge. This challenge was met by the glow discharge because it conveniently yielded ionized sample atoms not only from the discharge support gas but also from contiguous solid state materials.

Until the advent of GDMS, trace element analyses of solid-state materials were achieved by means of spark-source mass spectrometry (SSMS). SSMS employs an energetic spark for the thermal atomization and ionization of sample material. Mass spectrometric monitoring of the resulting ions yields detection limits in the parts per billion (ppb) range. However, the spark provides a relatively unstable ion beam characterized by a wide distribution of ion kinetic energies. Although signal integration and double-focusing mass spectrometric systems were employed to alleviate these undesirable attributes to SSMS, new methods were sought that would improve analytical performance and minimize instrumental complexity.

Secondary ion mass spectrometry (SIMS) appeared to be the most likely successor to SSMS, but, it too was not without limitations. The principal limitations, large variations in elemental sensitivity and severe matrix effects, arise through the direct production of analyte ions from the solid-state sample. In SIMS, the bombardment of the sample surface by a primary beam of
ions directly sputters neutral and ionized analyte atoms. Mass analysis of the secondary ions provides analytical data for the determination of elemental concentrations in the sample. The chemical nature of the matrix controls not only the rate at which sample atoms are released by the sputtering process, but also the extent to which these atoms are released as ions. Clearly, separation of atomization and ionization into discrete steps would be expected to improve analytical capabilities.

Many groups have investigated the use of auxiliary ionization of the neutral atom population generated by ion beam sputtering.\textsuperscript{20} This auxiliary ionization could increase the analytical signal, because the sputtered neutral population greatly exceeded the sputtered ion population, and reduce matrix effects because of the separation of ionization and atomization. The resulting technique was termed sputtered neutrals mass spectrometry, SNMS.\textsuperscript{21} Interestingly, one of the principal auxiliary ionization methods employed in SNMS was the use of an r.f.-powered glow discharge plasma.\textsuperscript{22} The use of the glow discharge allowed SNMS operation with or without the primary ion beam needed in SIMS. SNMS was found to exhibit reduced matrix effects and smaller variations in elemental sensitivity across the Periodic Table. Analytical GDMS is a close relative of both SIMS and SNMS. In all three methods the solid sample is atomized by sputtering. Similarly to SNMS, GDMS reduces variations in elemental sensitivity by decoupling the atomization and ionization processes. To some extent GDMS can be considered as a variation of SNMS in which the plasma generates the primary bombarding ions.

THE GLOW DISCHARGE

The development of a potential difference between two electrodes immersed in a low-pressure inert gas environment results in an electrical discharge.\textsuperscript{23} Under certain conditions of pressure, current and voltage, a brilliant discharge is established. Close observation of this discharge reveals the existence of various regions. A faint cathode glow region is directly adjacent to the negatively biased cathode. Moving away from the cathode, there exists a non-luminous cathode dark space. The dark space extends one mean free path from the cathode glow region and hence is a region essentially free from collisional excitation or recombination involving electrons. In this dark region, where 80% of the discharge potential is dissipated, the cathode fall, electrons and ions undergo maximum acceleration and reach their maximum kinetic energy. At distances greater than one mean free path from the cathode, collisional excitation and ionization processes abound. Radiative relaxation of electronically excited species in this region results in the characteristic negative glow of the discharge. This glow is familiar as the light emitted from a conventional neon lamp. Glow discharges modified to enhance the emission from the negative glow such as the hollow-cathode glow discharge\textsuperscript{24} and Grimm glow discharge\textsuperscript{25} lamps are familiar in atomic absorption and atomic emission spectrometry. A spectroscopic study of analytical glow discharges reveals that their optical spectra are rich in transitions arising from excited states of analyte ions. This observation alone suggests the potential utility of the glow discharge as an ion source for elemental mass spectrometry.

ANALYTE ATOMIZATION AND IONIZATION

In elemental mass spectrometry, it is necessary to establish an ion population that is representative of the sample under study. Mass spectrometric sampling of this population provides the analytical signal employed in quantification. When a solution is to be sampled the path from sample to ions is aspiration, atomization (nebulization) and ionization. Today, the inductively coupled argon plasma, the ICP,\textsuperscript{26} readily converts a solution sample in to gas-phase analyte ion. Solid sampling methods differ in that atomization must occur directly from the solid state. Thermal, photon and particle-induced desorption methods achieve such direct atomization of solid-state samples.\textsuperscript{17} Ionization occurs concurrently with the atomization process in many elemental mass spectrometric methods such as thermal ionization mass spectrometry (TIMS), laser ion-desorption mass spectrometry (LIMS) and SIMS. Although the simplicity of one-step atomization/ionization is appealing, the close coupling of these fundamental processes results in the severe matrix effects encountered for these methods. Such matrix effects arise because the conditions of analyte atom ionization are inextricably tied to the nature of the matrix that surrounds the atom at the time of ionization. Glow discharges achieve a decoupling of the atomization and ionization processes to yield a decreased dependence of the analytical signal on the analyte matrix.

A schematic diagram of an analytical glow discharge is shown in Fig. 2. The enlargement provides details of the atomization processes occurring at the surface of the sample cathode and of the ionization processes occurring in the negative glow region of the plasma. To appreciate fully the analytical capabilities of a glow discharge, it is necessary to understand these processes by which analytical signal carriers are generated.

The glow discharge ion source employs a modified particle-induced desorption approach to atomization. Inherent to the maintenance of the glow discharge is the cathodic sputtering process.\textsuperscript{27} The application of power to the glow discharge results in the partial ionization of the support gas through collisions with energetic primary electrons, viz. in electrical breakdown. Upon formation, the positively charged discharge gas ions begin to accelerate towards the negatively biased cathode. Impact of these primary ions on the cathode surface results in the deposition of their kinetic energy into the solid lattice. This increase in the energy of the lattice is sufficient to release near-surface atoms, clusters and secondary electrons. The sputter atomization process in the glow discharge is similar to the release of sample species in SIMS and fast atom bombardment mass spectrometry (FABMS).\textsuperscript{28}

In SIMS and FABMS, the analytical signal carriers are that small fraction of sample species that are sputtered as secondary ions. This is not the case for GDMS.
Figure 2. Schematic GDMS probe tip. Inset: atomization and ionization processes. Bombardment of the sample cathode by argon ions (Ar$^+$) formed in the negative glow results in the release of sample atoms, M$_0$, via sputtering. Any sputtered secondary ions redeposit on the sample surface owing to the electric field. M$_0$ escape into the negative glow region where collisions with electrons, e$^-$, and metastable argon atoms, Ar*, result in their ionization. The ionized sample atoms, M$^+$, are then available for mass spectrometric monitoring.

because the strong negative electric bias applied to the target cathode rapidly returns secondary ions to the sample surface. Only neutral species sputtered from the cathode can diffuse out into the plasma of the glow discharge. The release of neutral species in the cathodic sputtering process is dependent principally on the nature of the majority composition of the cathode, the flux of primary discharge gas ions, the kinetic energy of primary discharge gas ions and the discharge gas pressure. Any differential sputtering among major cathode components is offset by enrichment of the cathode surface in the less sputtered component. A rapid equilibration between surface enrichment and sputter preference results in the generation of an atom population in the plasma that is representative of the cathode composition.

A key analytical advantage, the freedom from excessive matrix effects, arises because ionization in glow discharge ion sources occurs independently of sample atomization. The population of neutral atoms sputtered from the sample cathode is subject to a variety of collisional processes in the negative glow region of the discharge plasma (Fig. 3). The principal mechanism responsible for the ionization of sputtered atoms, M, in r.f.-powered glow discharges involves collisions with metastable discharge gas atoms, Ar$^m$, Penning ionization [Fig. 3(b)]:

$$ M + Ar^m \rightarrow M^+ + Ar + e^- $$

Penning ionization affords an added advantage when the working gas is argon. The metastable excited states of argon, Ar$^m$, lie at 11.55 and 11.72 eV. This energy is conveniently sufficient to ionize the bulk of the elements in the Periodic Table without ionizing atmospheric impurities in the discharge gas. Investigations of ionization in steady state d.c.-powered glow discharges indi-

Figure 3. Principal collisional ion formation processes in GD plasmas. Electron ionization (a) and Penning ionization (b) are responsible for the generation of more than 90% of the sample ions, M$^+$. Resonant (d) and non-resonant (e) charge exchange account for a small fraction of the total ion population. Although associative ionization (c) and three-body association (f) contribute marginally to the total ionization in the plasma, they contribute most of the interfering metal argide ions, MAr$^+$.
cate that Penning ionization accounts for 40–80% of sputtered atom ionization. A study of the variation of sensitivity as a function of analyte element indicates that the cross-sections for ionization by the Penning process vary by only a factor of ten across the Periodic Table. This, in part, leads to the small range of relative sensitivities observed in GDMS compared with that observed in SIMS.

Metastable atoms can only be formed by radiative recombination of discharge gas ions with thermal electrons. The production of these species is favored in the negative glow region of the discharge. Therefore, most sample atom ionization occurs in the negative glow region. In steady-state glow discharge plasmas the remainder of ionization occurs via electron collisions of charge-exchange processes [Fig. 3(a), (d) and (e)]. Deconvolution of these processes is afforded by coupling pulsed power operation of the discharge with time-resolved GDMS. This approach takes full advantage of the Penning process by monitoring the

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**Figure 4.** Block diagram of typical GDMS system components. The glow discharge atomization/ionization source, the ion optical system and mass analyzer are all housed in a differentially pumped vacuum chamber. Operating parameters and data acquisition are controlled via software that also provides data processing, storage and display.

**Figure 5.** The most common GD ion source geometries. The coaxial cathode or pin sample source was the first commercial GDMS ion source. Its design is simple and straightforward but amenable only to samples that can be formed into pin-shaped cathodes. The planar sample source is akin to the Grimm source employed in optical emission spectrometry and has been developed for the examination of flat samples or samples not amenable to the formation of pins.
plasma under conditions when the only available ionization agents are the metastable argon atoms.

INSTRUMENTATION

The block diagram shown in Fig. 4 outlines the essential components of a typical GDMS system, with a PC acting as the central controller for all aspects of the instrument. Although individual systems may vary slightly with regard to the ion source, mass analyzer and ion detection system type, they all follow this general outline. Because the glow discharge ion source operates at pressures of approximately 1 Torr (1 Torr = 133.3 Pa), the vacuum system of a glow discharge mass spectrometer must employ differential pumping to maintain a mass analyzer operating pressure less than $10^{-5}$ Torr. Most systems are equipped with a high flow rate pump on the region between the ion source and mass analyzer, where the operating pressure is typically on the order of $10^{-5}$ Torr. A slightly smaller pump then suffices to maintain the mass analyzer in the $10^{-7}$ Torr range.

Glow discharges employed for the mass spectrometric determination of trace elements in solid-state materials can be operated with d.c. or r.f. power. R.f.-powered glow discharges allow the direct analysis of non-conducting solid samples, whereas such materials must be compacted with a conducting host matrix prior to analysis employed a d.c.-powered glow discharge. Although commercially available GDMS systems exclusively employ the simpler d.c.-powered glow discharge at present it is expected that r.f.-GDMS systems will be made available to meet demands for the analysis of non-conducting materials.

Two glow discharge ion source geometries, shown in Fig. 5, find wide application in elemental mass spectrometry: (i) the coaxial cathode or pin sample geometry and (ii) the planar sample or Grimm-type geometry. Commercial systems allow for the rapid interconversion of these two geometries, acknowledging that this provides the greatest versatility with respect to sample type. For both geometries samples can be introduced into the glow discharge ion source chamber by means of a direct insertion probe similar to those employed in traditional organic mass spectrometry. Such an approach allows faster sample turnaround because the discharge chamber vacuum is not broken between analyses.

The coaxial cathode geometry is most suitable to samples that are readily converted into pins of 1–2 mm in diameter and 7–10 mm in length. This includes powder samples compacted in a die-press assembly similar to that used to form electrodes for spark source mass spectrometry. The sample in this type of source is mounted at the tip of a direct insertion probe. An insulating cover confines the discharge to the sample cathode. These pin-type sources are the most commonly employed GDMS ion sources.

The principal limitation encountered with these sources arises from the fact that sputtering erodes the sample. Pin erosion and consequent decreases in surface area increase current density and discharge operating voltage for glow discharges operated at constant current. As the operating voltage increases the primary particle kinetic energy and discharge power increase, with the result that sputter rates increase. Constant voltage operation requires constant current densities and produces the opposite problem. As the cathode surface area decreases, the current must be decreased to maintain the constant current density. This decrease in current results in a decrease in ionization within the plasma and a decrease in analytical signal. Because operation in constant current or constant voltage modes results in these changes, it has been suggested that constant power operation would afford the most stable GDMS signals for pin cathodes.

The planar sample cathode geometry is preferred for refractory samples or when depth profiling analysis is desired. This flat geometry is also preferred when r.f.-power is employed in the direct analysis of non-conducting samples. The sample is mounted on the end of the direct insertion probe in a fashion that exposes a flat surface. This surface seals against an O-ring on the ion source. A circular area of the flat surface is then exposed as the cathode for the glow discharge. With the planar geometry the surface area of the sample remains constant, so the problem described for the pin sample is circumvented. By use of a low-mass support gas such as He or Ne, the planar geometry permits depth profiling of the sample. The depth resolution does not approach that of static SIMS but can be useful for many applications. It must also be considered that sample thickness influences analyses with r.f.-powered glow discharges because as the thickness of the dielectric sample increases the impedance of the r.f. circuit containing the sample cathode changes. As the sample thickness increases the analytical signal will decrease if all other variables remain constant.

Species effuse from the glow discharge source through an ion exit aperture (slit or orifice, depending on mass analyzer employed) into the ion optical region. The ion optics focus the effusing ions into a tight beam permitting their efficient transport into the mass analyzer region through a sampling aperture. Without such efficient transport the analytical signal suffers from a loss in intensity and a consequent decrease in analytical sensitivity.

Most GDMS systems sample ions from the anode region of the plasma. In those instances where cathodic sampling has been employed, large differences in ion kinetic energies have been observed to exist between discharge gas and cathode species ions, presumably because whereas the cathode atoms are ionized by the Penning process in the negative glow and accelerated across the full cathode dark space, discharge gas atoms are ionized by electron impact in the cathode dark space and are accelerated to a lesser extent depending on the location of their ionization in the dark space and hence have different kinetic energies. The use of a kinetic energy analyzer then affords the ability to distinguish electron ionized species from Penning ionized species. It has also been determined that there are differences in the kinetic energy of polyatomic metal argide ions, MAr+, depending on whether they are formed by associative ionization [Fig. 3(c)] or three-body collision [Fig. 3(f)] processes.
To date, all the common mass analyzers have been explored for use in GDMS (Table 1). The first commercially available GDMS systems employed double-focusing mass analysis systems originally employed with thermal ionization for isotope ratio measurements. This approach permitted the acquisition of high-resolution spectra with great sensitivity. However, modern GDMS began with quadrupole-based mass analyzer systems. Such systems were favored by those working on the development of GDMS and those performing fundamental research. These systems afford a more cost-effective alternative to spark source mass spectrometry. The demonstrated utility of quadrupole based GDMS has resulted in the commercial availability of such systems from various manufacturers. Some of these systems are designed to allow rapid switching between glow discharge sources for solids analysis and inductively coupled plasma for solutions analysis. Promising results have been obtained from ion trap mass spectrometric systems by investigators at Oak Ridge National Laboratory and from time-of-flight mass spectrometric systems at Indiana University and West Virginia University.

The use of Fourier transform (FT) MS coupled with a glow discharge ion source was found to permit difficult analyses requiring great mass resolving power. At present, the commercial GDMS systems available for trace element analysis employ only double-focusing or quadrupole mass analyzers. Trace analysis work requires that the full sensitivity of mass spectrometry be exploited. The demands of dynamic range (the range of concentrations that can be determined in a single measurement) and abundance sensitivity (the ability to determine a trace isotope (ppb) adjacent to a major isotope (%)) dictate detection and data analysis schemes that differ significantly from those employed in standard MS instrumentation, where the focus is more generally on identification rather than quantification. Elemental MS methods suited to these demands, such as peak area integration and peak hopping, have developed as the field has evolved from photoplate detection to electronic detection. The need for a large dynamic range led to the use of an automated dual detection system in one commercial GDMS system. A Faraday cup is employed to measure currents corresponding to major species (ion beam intensities down to $10^{-13}$ A). At a measured current less than $10^{-13}$ A, the data system automatically begins monitoring the ion beam with an electronic detection system based on a Daly detector, in which ions are converted into electrons that impinge upon a phosphorescent screen monitored with photomultiplier tube. The ion counting signal from the Daly detector is calibrated against the ion current on the Faraday detector so that all results are presented as ion beam currents. The dynamic range afforded by this approach is on the order of $10^3$, allowing both major components and trace (sub-ppb level) components to be measured in a single cycle. More reliable quantitative results are achieved by using peak areas rather than peak intensities as the analytical data from which concentration is calculated. With careful attention to all aspects of the measurement, detection limits in range of hundreds of ppt can be achieved.

### Quantification

In element mass spectrometry, a variety of approaches can be taken to achieve quantitative results. Most of these methods are identical with those employed with traditional optical spectrometric determination of elements; however, mass spectrometry also affords new approaches, such as isotope dilution, not open to the traditional optical methods of elemental determination. GDMS typically relies on two variations of internal standard calibration for qualitative and quantitative analyses.

#### Ion beam ratio method (semi-quantitative analysis)

The most common approach to quantification in GDMS is the ion beam ratio (IBR) method. The assumption is made that the ratio of ion current for any one isotope with respect to the total ion current, except the signal arising from the discharge support gas, is representative of the ratio of the number of atoms of that

<table>
<thead>
<tr>
<th>Mass analyzer system</th>
<th>Advantages</th>
<th>Limitations</th>
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<tr>
<td>Double-focusing sector</td>
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<td>Cost</td>
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<tr>
<td>Quadrupole</td>
<td>Speed</td>
<td>Speed</td>
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<td>Commercial availability</td>
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<td>Quadrupole ion trap</td>
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<td>Detection limits</td>
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<td>Size</td>
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<td>Signal saturation</td>
</tr>
<tr>
<td></td>
<td>Speed</td>
<td>Resolution</td>
</tr>
</tbody>
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Table 1. Mass analyzers for GDMS
Figure 6. Flow chart of typical GDMS analysis procedure. The initial sample, S, containing elements X, Y, and Z, must first be converted into a pin or flat cathode and loaded into the glow discharge ion source. Qualitative mass spectra are acquired to provide guidance as to the rough composition of the sample. Knowledge of the general sample composition allows the selection or determination of relative sensitivity factors (RSFs) to be employed in quantitative analysis. Examination of the qualitative spectrum allows the identification of the elements of interest for quantitative evaluation. Quantitative mass spectra are obtained under carefully controlled conditions. Quantitative results are obtained through the correction of analyte signals with the use of RSF values. Accuracies of 10-20% are obtained in quantitative GDMS.

isotope in the sample to the other constituent atoms of the sample. When trace analyses are performed on high-purity materials, the ion signal for the matrix is assumed to be large relative to individual trace species; therefore, the matrix ion current is a good approximation to the total ion current and the matrix can be assumed to have a concentration of 100%. The concentration, $C$, of an isotope X is obtained from the product of the ion beam ratio and the concentration of the matrix:

$$C_X = \left(\frac{I_X}{I_M}\right)C_M$$

This is a variation on internal standard calibration where M, the matrix element, serves as the internal standard. The power of this approach lies in the fact that any effect of plasma instability is normalized because the analytical quantity is the ratio of two sputtered species ionized by the same processes. The limitation to this approach, and the reason why it provides only semi-quantitative results (accuracies of a factor of 2-3 are typical), is that it cannot correct for the variation in analytical sensitivity that occurs between different elements.

Relative sensitivity factor method (quantitative analysis)

Quantitative results require that differences in elemental sensitivities be characterized using standards similar in composition to the material under study. This characterization generates relative sensitivity factors (RSFs) that can then be employed to correct the measured ion beam ratios. This is the most widely employed approach to quantification in GDMS and has historically been the approach used in other forms of mass spectrometry in which trace element analysis is of interest, such as SIMS and SSMS. Relative sensitivity factors can be defined for any element X in a matrix M as the sensitivity, S, of X with respect to the sensitivity of M, where $I$ is the ion current and $C$ is the concentration of the selected species:

$$RSF_X = \frac{S_X}{S_M} = \frac{(I_X/C_X)_{STD}/(I_M/C_M)_{STD}}{}$$

RSF values for the elements of interest are calculated from data acquired on standard samples, such as NIST Standard Reference Materials, which closely match the matrix of interest. Quantitative results are obtained for an unknown sample of matrix M containing element X by dividing the IBR results by the $RSF_X$:

$$C_X = [(I_X/I_M)C_M]/RSF_X$$

Because RSF values vary only slightly between matrices of the same general composition, it is not necessary to have exact matrix matching for the $RSF$ method to yield quantitative results with accuracies of 15–20%.

Hypothetical GDMS determination

To provide a flavor for the GDMS approach to elemental analysis, consider a hypothetical case. Investigator A brings the analyst a sample of high-purity material, S, containing trace levels of X, Y and Z. Fortuitously, S is conducting, and therefore straightforward d.c.-powered GDMS can be employed. Unfortunately, S is a powder. Employing compacted sample methods learned from SSMS, the power can be converted into a pin cathode,
mm in diameter and 7 mm in length. This cathode is then introduced by direct insertion probe into the source region of the glow discharge mass spectrometer. A potential is applied to this pin cathode, biasing it by \( \sim 1.1 \text{kV} \) with respect to the source chamber anode. The source chamber is pressurized with argon to 0.75 Torr and a discharge with a current of 2.7 mA is established. Analysis is performed following the steps outlined in the flow chart shown in Fig. 6.

After sputtering the sample for 15 min to remove any surface contamination and to permit discharge stabilization, mass spectrometric data are acquired for the next 30 min. In the resulting mass spectrum, the total ion current corresponding to the isotopes of the matrix metal, S, is \( 4.3 \times 10^{-10} \) A. The ion current for the isotope of X that has a natural abundance of 9.32% is \( 2.0 \times 10^{-16} \) A, the more abundant isotope of X suffers interference from \( \text{SAr}^+ \) and requires a resolution of 12 000 for analytical separation. Element Y is monoisotopic and free from spectral interference. An ion current of \( 7.3 \times 10^{-18} \) A is observed for Y. The major isotope of Z is present at only 60.9% but suffers no spectral interference. This isotope of Z exhibits an ion current of \( 1.7 \times 10^{-18} \) A, that is, just four times greater than the standard deviation of the background signal. Employing the ion beam ratio method, a semiquantitative answer can be given: X is present at \( \sim 5.0 \text{ ppm} \), Y is present at \( \sim 17 \text{ ppb} \) and Z is present at \( \sim 6 \text{ ppb} \).

Because the analyst is unfamiliar with the sensitivity of X, Y and Z in samples of matrix S, it is necessary to determine \( RSF \) values for these elements in S to convert the IBR results into quantitative results. A surrogate pin cathode is produced by doping pure S powder with X, Y and Z at known trace levels close to those of the unknown sample (recall that approximate levels of X, Y and Z in S were determined by the IBR method). Using this surrogate, cathode data are acquired from which \( RSF \) values are determined to be 1.1 for X, 0.77 for Y and 1.8 for Z. Based on the data available, a report is prepared in which the amounts of X, Y and Z in S are stated to be 4.5 ppm, 22 ppb and 4 ppb, respectively.
### Table 2. Summary of elemental MS methods

<table>
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<tr>
<th>Method</th>
<th>RSF* range</th>
<th>Detection limit</th>
<th>Sample requirement</th>
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<td>Depth profile</td>
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<tr>
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<td>Isotope ratio, quant.</td>
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</table>

* Relative sensitivity factor.
* Glow discharge mass spectrometry.
* Inductively coupled plasma mass spectrometry.
* Secondary ion mass spectrometry.
* Laser ionization mass spectrometry.
* Spark source mass spectrometry.
* Thermal ionization mass spectrometry.

#### An alternative approach to quantification

Recently, an alternative approach to quantification has been developed for use with ion trap mass spectrometric systems that are limited in their dynamic range. Dynamic range limitations arise from space charge effects that occur when too many ions are stored in the trap. The limitation, however, is true only if the ion injection time is constant and the ion current is employed as the analytical factor for quantification. This limitation can be ameliorated by fixing the ion current value and varying the injection time, then the injection time becomes the analytical factor of importance. Selective ion injection procedures allow the trap to be filled with the ion of interest and the time it takes to fill the trap to a predetermined level is related directly to the concentration of the ion. The top part of Fig. 7 shows the change in trapping potential as a function of time. The flat regions preceding each scan ramp in the regions numbered 2, 3 and 4 correspond to the effective injection time for ions of interest. Note in the bottom mass spectrum of Fig. 7 that each element is accumulated to the same nominal abundance. It is the injection time required to achieve this accumulation that is employed as the analytical parameter. The injection time in region 3, for Sn, is the longest because Sn is the least abundant element. Although this approach to quantification is unique to ion storage mass spectrometric systems, it effectively solves the problem of limited dynamic range associated with such systems.

![Figure 8. Comparison of molybdenum analyses by GDMS, SIMS and SSMS. The concentrations of 25 of elements in molybdenum samples are plotted as a function of the analyte element for the three methods. The labels on the x-axis alternate to fit all 25 elements on the chart. Typically all three methods yield similar results.](image)
Unfortunately, problems with the efficiency of injection of GD-generated ions into the ion trap has resulted in poor detection limits of only 10 ppm by this method.

COMPARISONS OF METHODS IN ELEMENTAL MASS SPECTROMETRY

In Table 2, various methods of elemental mass spectrometry are summarized in terms of the range of relative sensitivity factor values, the reported detection limits, sample requirements and types of information afforded by each technique. No one elemental mass spectrometric method is a panacea for all trace element determinations. Each technique possesses unique advantages and limitations making it suitable to particular determinations.

In 1987, a comparison between SSMS, SIMS and GDMS for the analysis of sintered tungsten and molybdenum samples was published.\(^47\) The results of this comparison did not indicate a clear choice solely on the basis of analytical capability. The chart in Fig. 8 shows the concentrations of trace elements in molybdenum determined by the three methods. The results for all methods typically fall within a factor of three from one another. Other factors that must be considered when comparing these techniques are the ability to perform ion microscopy with SIMS and so obtain regio-specific information from a sample. All methods claim an ability for depth profiling, yet the ability in SIMS to control the flux of primary ions makes this technique better suited to high-resolution depth profile analyses. The strength of GDMS lies in an ability to provide rapid survey scans and quantitative analysis of bulk materials.

The interest in GDMS by atomic spectrometrists followed the development of inductively coupled plasma mass spectrometry (ICPMS) into a successful method for trace analyses of solution samples. In a recent report the two methods were compared for the determination of trace elements in aluminum samples.\(^48\) The spectra...
shown in Fig. 9 illustrate the advantage of GDMS operation in an inert, reduced pressure environment compared with ICPMS with aqueous samples in an ambient environment. GDMS precludes the spectral clutter originating from the aqueous and atmospheric contributions to the ICPMS spectrum. In the region of the fourth-row transition metals, the spectra show interferences arising from oxide ions in ICPMS [Fig. 10(a)] but not in GDMS [Fig. 10(b)]. The authors pointed out that the detection limits obtained with both methods are comparable. For GDMS the detection limits were found to be of the order of 1–10 ng g⁻¹ (ppb). With ICPMS, solutions containing 1 mg ml⁻¹ of sample yielded detection limits of 1–10 pg ml⁻¹, which then converts to the same 1–10 ng g⁻¹ range reported for GDMS. As the authors pointed out, the need to dissolve the sample for ICPMS not only increases the analysis time but also introduces the possibility of contamination. Although cathode fabrication can lead to surface contamination, this is removed in the pre-sputtering or ‘burn-in’ of the cathode prior to analysis. A key point in this particular case was that the aluminum alloy containing higher concentrations of Si was not analyzed by ICPMS because of difficulty associated with dissolving this material.

Thermal ionization mass spectrometry (TIMS) is an elemental mass spectrometric method that bridges the gap between solid sampling and solution sampling methods.⁴⁹ In TIMS the sample is applied as a solution, slurry or resin bead to a wire filament. The passage of electrical current through the filament results in resistive heating sufficient to volatilize the sample and ionize a fraction of those volatile species in accordance with the Saha–Langmuir equation.⁵⁰ In some thermal ionization sources, a secondary filament serves to ionize species volatilized by the primary filament. TIMS is well known for its ability to yield isotope ratio data of extreme precision and accuracy.⁵¹ It can be coupled with isotope dilution calibration to afford a very accurate method for the determination of trace elements using small

Figure 10. High-gain, fourth-row transition metal mass range spectra from an aluminum sample.⁴⁸ The ICP mass spectrum (a) shows interferences from oxides species that are absent in the GD mass spectrum (b). Detection limits by both methods were found to be in the 1–10 ppb range. Reprinted with permission from Applied Spectroscopy, 1994, 9, 823. © 1994 by the Society of Applied Spectroscopy.
Table 3. GDMS determination of trace elements in forest soil

<table>
<thead>
<tr>
<th>Element</th>
<th>GDMS*</th>
<th>LA-ICPMS*</th>
<th>ICP-AES*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg (%)</td>
<td>0.341</td>
<td>0.440</td>
<td>0.390</td>
</tr>
<tr>
<td>Al (%)</td>
<td>7.03</td>
<td>5.32</td>
<td>4.89</td>
</tr>
<tr>
<td>Si (%)</td>
<td>33.9</td>
<td>35.8</td>
<td>15.4</td>
</tr>
<tr>
<td>Ca (%)</td>
<td>0.298</td>
<td>0.310</td>
<td>0.330</td>
</tr>
<tr>
<td>Ti (%)</td>
<td>0.779</td>
<td>n.a.</td>
<td>n.a.</td>
</tr>
<tr>
<td>Fe (%)</td>
<td>3.50</td>
<td>3.10</td>
<td>2.70</td>
</tr>
<tr>
<td>Sr (ppm)</td>
<td>119</td>
<td>57</td>
<td>n.a.</td>
</tr>
<tr>
<td>Ba (ppm)</td>
<td>175</td>
<td>322</td>
<td>290</td>
</tr>
<tr>
<td>U (ppm)</td>
<td>3</td>
<td>8</td>
<td>n.a.</td>
</tr>
</tbody>
</table>

*a* Glow discharge mass spectrometry.

*b* Laser ablation inductively coupled plasma mass spectrometry.

*c* Inductively coupled plasma atomic emission spectroscopy.

Analytical GDMS has expanded well beyond its initial utility for the trace determination of elements in conducting solid samples. A few examples of various GDMS applications are worth noting. These examples were selected to illustrate the variety of application areas covered and are not meant to exemplify typical GDMS applications. As mentioned in the Introduction, recent technical reviews and the current literature provide the best details of GDMS applications.

For atmospheric monitoring, a glow discharge was coupled with an ion trap mass spectrometry system. The glow discharge operated at a reduced pressure of 0.2–0.8 Torr and sampled the ambient atmosphere at a rate of 5 ml s⁻¹. Successful detection of TNT at the ppb level was reported for the atmospheric sampling glow discharge ion trap mass spectrometric system. This application of GDMS is unique because it combines the pioneering technology of ion injection for ion trap mass spectrometry with the ability of a glow discharge to generate analytically useful negative ions of 2,4-dinitrotoluene.

Glow discharges have been explored for use in organic and biological mass spectrometry, particularly for applications involving the interfacing of liquid chromatography with mass spectrometry. A cited advantage of this plasma ionization is its compatibility with oxygen-containing solvents that lead to the oxidation and failure of filaments employed in conventional ion...
sources. The early work demonstrated that a glow discharge source yielded spectra that were similar to those obtained by chemical ionization for a variety of amino acids. In the most recent work, an atmospheric pressure helium glow discharge yielded picogram detection limits for tyramine present in a nebulized liquid sample. This plasma ionization approach is found to be very 'soft', producing high abundances of the protonated molecular ion with minimal fragmentation.

The application of GDMS to the elemental analysis of non-conducting materials is an area of current interest particularly with regard to the examination of environmental samples. Recent work has been conducted with d.c.-powered GDMS for the analysis of soil samples. Employing a variety of standard soils and clays compacted in a copper host matrix, linear calibration graphs were constructed and RSF values determined. These results from the standard materials were employed to obtain quantitative results for field-collected soils and clays. The GDMS results compared favourably with determinations made by laser ablation ICPMS and ICP optical emission spectrometry (Table 3). In this application the detection limits were found to be in the single ppm range for samples diluted to 1 : 5 in a conducting host matrix.

Another approach to GDMS of non-conducting samples uses r.f.-powered glow discharges to permit direct sampling of the material. Figure 11 shows a recently reported mass spectrum obtained for a standard firebrick material examined by r.f.-powered GDMS. The various expansions in scale clearly show the minor components in the firebrick sample. Semi-quantitative ion beam ratio results yield concentrations that are within a factor of two of the certified values. This level of accuracy is consistent with the range of relative sensitivity factors expected for such material. The detection limits for r.f.-GDMS of non-conducting samples are reported to be in the single ppm range.

REFERENCES