Review

Radio-frequency glow discharge spectrometry:
A critical review

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Abstract

This paper presents a critical review of analytical radio frequency glow discharge spectrometry (rf-GDS). The historical foundations of rf-GDS are described, and current knowledge of the fundamental physics of analytical rf glow discharges is discussed. Additionally, instrumentation, methodologies, and applications of rf glow discharge optical emission spectrometry (rf-GDOES) and mass spectrometry (rf-GDMS) are reviewed. Although other rf-GDS techniques have appeared e.g. rf glow discharge atomic absorption spectrophotometry (rf-GDAAS), the emphasis is placed upon rf-GDOES and rf-GDMS, because they have received by far the most interest from analytical chemical metrologists. This review also provides explanations of some developments that are needed for further progress in the field of analytical rf-GDS.

Keywords: Bulk analysis; Depth profiling; Glow discharge; Mass spectrometry; Optical emission spectroscopy; Plasma; Radio frequency; Speciation

1. Introduction

Glow discharges are used in a wide variety of applications in modern science and technology [1]. One of the largest and most important fields of application is the microelectronics industry, where glow discharges are used for etching of surfaces to form topographical surface features, as well as for depositing thin films. Similarly, glow discharges are used extensively in the materials processing industries for deposition of various thin films, coatings, and surface layers, and may additionally be employed for surface cleaning, pretreatment, and modification processes. Still other applications include use as the lasing medium in various types of lasers, such as metal vapor ion lasers, and as common light sources, such as fluorescent and neon lamps. Finally, glow discharges are used as atomization/excitation/ionization sources for analytical spectrochemistry [2–4]. This application may not be as large as some of the other application fields described above. Nevertheless, it is important within the scope of modern analytical chemical metrology, and is likely to become more so in the future.

The development and application of glow discharge devices and associated spectroscopies for chemical analysis began as early as the 1930s and 1940s [5,6]. However, glow discharges did not become a major focus of research in many analytical chemistry laboratories until about the 1960s and 1970s. In general, research interest has increased since that time. The research work conducted to date has been directed toward glow discharge source development and the fundamental study of the physical characteristics of the analytical glow discharge, and toward the development and application of glow discharge spectroscopic techniques for various analytical applications.

In the usual analytical form, a glow discharge is a plasma sustained between two electrodes that are
immersed within a reduced pressure, inert gas environment. The sample usually serves as the more negatively charged electrode [i.e. the cathode in a direct current (d.c.) glow discharge system]. Common discharge support gas pressures are in the range 100–1500 Pa, and the discharge support gas is typically Ar, though other inert gases are sometimes used. The plasma is initiated when a high potential is applied between the two electrodes. The application of the high potential causes the discharge gas to break down electrically to form electrons and positively charged ions. The positive ions are attracted toward the sample surface by the electric fields within the plasma, and may reach substantial kinetic energies. When an ion strikes the sample surface with sufficient energy, the transfer of momentum into the atomic lattice structure of that surface may cause the release of surface material into the gas phase. This process is called ‘sputtering.’ In reality, some sputtering of the sample surface may also result from fast atom bombardment, rather than fast ion bombardment [7–9]. This is because the probability of symmetric charge exchange between an accelerating positively charged ion of the support gas and a neutral atom of the same type is not necessarily insignificant, owing to the very short mean free paths associated with commonly used support gas pressures.

Upon entering the gas phase environment of the glow discharge, the sputtered material may undergo a large number of collisional processes in the plasma. From an analytical point of view, the most important processes are electronic excitation by means of collisions with energetic plasma electrons (i.e. electron impact excitation) and ionization by means of collisions with either energetic electrons (i.e. electron impact ionization) or metastable species of the support gas (i.e. Penning ionization). Owing to these important collisional processes, sputtered sample material may exist in the glow discharge as atoms, ions, or various electronically excited state species. Molecular or atomic cluster species may also exist to varying degrees [10–16], depending upon factors such as sample type, but are usually far less abundant [17]. Glow discharge analytical spectroscopic techniques are based on the detection and quantification of sample species within the plasma. Glow discharge optical emission spectrometry (GDOES) is based upon the measurement of photons emitted by excited state species in the plasma, while glow discharge mass spectrometry (GDMS) employs a mass spectrometer to extract and quantify plasma ions. Glow discharge atomic absorption spectrophotometry (GDAAS) relies upon the detection and quantification of sample species by means of absorption of photons. To date, GDOES and GDMS have received by far the most attention from analytical spectrochemists, though a small amount of research has been directed toward GDAAS.

Analytical glow discharge spectroscopies have been applied to a wide variety of problems. The most successful area of application, whether GDMS, GDOES, or GDAAS, has traditionally been bulk analysis of solid materials, especially conductive solids. However, in recent years, depth profiling of layered surfaces has become a major area of application [3,18]. The importance of glow discharge depth profiling in science and technology is likely to grow in the future, as instrumentation and methods become more refined. Additionally, glow discharges have been employed for the analysis of powders [19], solutions [e.g. [20–22]], and gases [e.g. [23–25]], as well as for speciation studies [e.g. [26–28]].

One of the most exciting and interesting developments in glow discharge analytical spectroscopies in recent years has been the introduction of the radio-frequency (rf) powered glow discharge device [3,29–33]. Unlike the more traditional d.c. glow discharge, the rf glow discharge can be applied not only to samples that are electrically conductive, but also to those that are electrically non-conductive, whether bulk solids or layered materials. This added capability significantly broadens the applicability of analytical techniques that are based on the use of the glow discharge. Here we define an rf glow discharge source to be one in which the radio-frequency fields provide the primary, if not the only, power to sustain the plasma. This arrangement should be distinguished from the so-called ‘rf boosted’ glow discharge source, in which supplementary rf fields are employed in attempts to improve overall analyte signal strengths. In 1994, Leis and Steers comprehensively reviewed the topic of boosted glow discharges, including rf boosted sources [34].

The purpose of this review is to provide a critical evaluation of the current state of development of analytical rf glow discharge sources and analytical spectrometries. We should emphasize that this is a critical review, not a literature review, and so our intention is to highlight important developments in the field. We will begin by tracing the history of development of rf glow discharges leading into modern applications in analytical chemistry. Next, we will provide an overview of analytically important rf glow discharge physical processes in enough detail to give the unfamiliar reader a working knowledge base. Then, we will describe instrumentation, methodologies, and representative applications for the important rf glow discharge analytical techniques, which are rf-GDOES and rf-GDMS. (Rf-GDAAS will not be covered, because research interest has been minimal and no commercial instruments have ever existed.) Finally, we will provide some conclusions and explanations of needed future developments. While some previously published reviews have included discussion of some of these issues in more or less detail [1,30,33,35–37], to our knowledge this is the
first review to take such a wide-ranging approach devoted entirely to rf glow discharge analytical spectroscopies.

2. Foundations of development

A study of the history of the development of many analytical chemical techniques reveals that analytical chemists often borrow ideas, knowledge, or devices from seemingly unrelated fields, in order to adapt and refine them for applications in chemical analysis. Certainly, analytical chemists are not alone in this practice, as scientists and engineers in many other fields of study have also been known to borrow from unrelated fields, in order to advance their own endeavors. This sort of cross-fertilization is a healthy, desirable, and necessary characteristic of the progress of science and technology.

Much of the initial development and fundamental understanding of rf plasmas was actually undertaken by scientists and engineers involved with fields of study such as atomic, plasma, and solid-state physics long before analytical spectroscopists became interested in the possibility of employing rf glow discharge devices for chemical analysis. Rf plasmas have been studied since at least the 1920s. In fact, in a 1970 review paper on the topic of rf plasma sputtering, Jackson speculated that ‘it is probable that rf sputtering occurred in equipment used in the late 1920s by scientists investigating rf plasmas’ [38]. His speculation was based on the fact that rf sputtering is well known to take place in similar modern equipment. As we shall see, rf sputtering is probably the most important characteristic of rf glow discharge devices for applications in analytical chemistry. Whether or not rf sputtering was occurring in such equipment during the 1920s, the first recorded observation of sputtering in rf plasmas is probably that of Robertson and Clapp in 1933 [39]. Upon striking an rf discharge inside a quartz tube filled with air to a pressure of a few hundred Pascals by means of externally mounted electrodes, they observed that thin Ag layers deposited upon the inner walls of the tube were effectively removed in the vicinity of the electrodes. Moreover, they noted that the inner surface of the glass tube itself was also altered by the rf plasma, whether or not Ag layers were initially present. A few years later in 1938, Hay, working under Robertson’s direction, conducted a fairly detailed study of this phenomenon [40]. Radio-frequency discharges were maintained within tubes filled with air, N₂, O₂, or H₂, at pressures ranging from 10 Pa to 470 Pa, by means of externally mounted electrodes. Thin metallic films of Ag deposited onto the inner walls of the discharge tube were removed from some regions and redeposited onto other regions, creating geometric patterns that depended upon frequency, pressure, tube diameter, and the nature of the discharge gas. Hay correctly attributed the removal of material to sputtering by positively charged ions. An important observation from Hay’s work is that no sputtering occurred in a d.c. plasma or in a very low frequency (60 Hz) plasma. In 1948, Lodge and Stewart, who were also associated with Robertson’s laboratory, performed additional studies of high-frequency plasmas [41]. Specifically, they compared such plasmas with d.c. plasmas, and provided further evidence that the removal of various materials, including electrically non-conductive materials like glass and polystyrene, in high-frequency discharge tubes was due to sputtering by positively charged ions.

Other important fundamental work on rf plasmas was conducted during the 1950s and 1960s at Stanford University in the United States. Many experimentalists had previously observed that when a plasma is struck inside a discharge tube and radio-frequency potentials are then applied to electrodes mounted externally to the tube, the luminous portion of the plasma apparently constricts inwardly toward the tube axis, leaving a thick and relatively less luminous region adjacent to the inner walls of the tube [42]. At first, this phenomenon was attributed to plasma confinement induced by the radio-frequency fields. However, it was soon realized that this could not be the case, because the rf frequencies were always much lower than the plasma frequencies associated with the particular plasmas under investigation. The correct interpretation of the observations was suggested by Sturrock in 1958 [43], and then confirmed through research work performed by Butler [44] and Butler and Kino [45] in the early 1960s. By using a metal ring-electrode positioned inside the discharge tube to measure the electric potentials adjacent to the tube walls and a Langmuir probe to measure plasma ion and electron characteristics, it was concluded that the apparent constriction of the luminous portion of the plasma toward the tube axis was due to the development of a large negative d.c. wall potential that induced the formation of a positive ion sheath adjacent to the walls. The negative d.c. wall potential was explained as a natural consequence of the fact that plasma electrons are much more mobile than positively charged plasma species, while the net current flow to the electrically non-conductive walls, averaged over time, must be zero. These insights were very important, because they accounted for the previously noted positive ion sputtering of the walls of the plasma tubes.

Meanwhile in 1955, Wehner suggested a practical arrangement for performing controlled sputtering of electrically insulating solids [46]. He suggested the application of high-frequency potentials to a metallic electrode that is placed in contact with the back side of the insulator to be sputtered, with both the backing electrode and insulator being immersed in a low-pressure plasma sustained independently by other electrodes, as illustrated in Fig. 1. Wehner reasoned that this approach
would provide effective compensation for any accumulation of charge on the surface of the insulator through the establishment of a controlled d.c. negative surface potential, thereby providing nearly continuous positive-ion sputtering of the insulating surface. Conceptually, the arrangement suggested by Wehner, as well as his explanation of its operation, were very similar to those described at Stanford University. Seven years later in 1962, Wehner and his colleagues demonstrated the potential usefulness of his design by sputtering quartz, diamond, and sapphire.

In 1966, Davidse and Maissel introduced a modification of Wehner’s device that employed the combination of the backing electrode and insulating solid as one of the plasma-sustaining electrodes. This somewhat simpler two-electrode system was developed and demonstrated for depositing thin dielectric films. While intended primarily for the sputtering of electrically insulating materials, the device could be used for sputtering electrically conductive solids, as well. Spurred on largely by the requirements of the microelectronics industry, development of this and other related rf glow discharge devices has continued to the present day. As we shall see, analytical spectrochemists have benefited greatly from these developments.

The first use of the rf glow discharge for analytical spectrochemistry appeared in the peer-reviewed scientific literature in 1971, when Coburn and Kay demonstrated the use of an rf powered glow discharge sputtering device, coupled with a quadrupole mass spectrometer, for the elemental analysis of thin surface layers as a function of depth beneath the surface. An example depth profile from the paper is presented in Fig. 2. While the work was certainly preliminary, it nonetheless implied the potential of the rf glow discharge in general, and rf-GDMS in particular, for this sort of application. The same research group published two additional papers on the subject in the mid-1970s, in which other example applications and more fundamental studies of the method were presented. At about the same time, Donohue and Harrison investigated the use of an rf glow discharge device, in which the sample took the form of a hollow cathode, for analytical mass spectrometry. They showed that the device could be used to generate mass spectra of both electrically conductive and non-conductive samples. This would be the last publication concerning analytical rf glow discharge spectrometry in the peer-reviewed scientific literature for 14 years.

In the mid-to-late 1980s, glow discharge spectrometrists in both the United States and Europe once again became interested in exploring the potential of the rf glow discharge for applications in analytical chemistry. At Renault in Paris, Chevrier and Passetemps applied radio-frequency potentials to samples mounted onto a glow discharge device of the Grimm geometry, which...
was originally designed for d.c. operation only [53,54]. Their experiments demonstrated the usefulness of this approach, and a patent on the new rf-powered glow discharge device was awarded in 1988 [55]. At the same time these events were taking place in Europe, Marcus’ research group at Clemson University in the United States was independently developing and studying the characteristics of a glow discharge device designed specifically for rf operation and intended for applications not only in GDOES, but also in GDMS and GDAAS (with some minor modifications). The device was similar in many respects to the Grimm design, but differed in some important details. The research work of Marcus and colleagues resulted in important papers in the late 1980s and early 1990s [56–64], and patents were awarded [65,66].

The decade of the 1990s witnessed significant growth of research interest in analytical rf glow discharge spectrometry, as illustrated in Fig. 3a. The numbers of publications since the 1990s seem to indicate a decline of interest over the past two or three years, though this by itself may be inconclusive. The research publication totals are broken down into categories in Fig. 3b. As shown, research interest in rf-GDMS peaked around the middle of the 1990s. This is probably the most important cause of the apparent peak in Fig. 3a. Returning to Fig.
3b, the data imply that research interest in rf-GDOES may now be leveling off. However, this by itself may also be inaccurate. The survey is inherently subjective and incomplete. Notably, publications in which rf-GDOES appears as an applied research component, rather than being the main focus of study, are likely to have been missed. As the numbers of commercial rf-GDOES instruments in the field continues to rise, and as methodologies become more advanced and useful for ‘real world’ applications, the numbers of such papers would be expected to increase. Certainly, additional time is necessary to evaluate reliably the trend of research interest in rf-GDOES.

3. An overview of radio frequency glow discharge processes

It is well known among analytical glow discharge spectrometrists that the analytical rf glow discharge is very similar to the more traditional d.c. glow discharge in many respects. The similarities are both wide-ranging and deep. For example, in terms of visual appearance, both the discharge devices and the glowing plasmas themselves are essentially indistinguishable at first glance, making it easy to mistake one for the other. Without careful examination, the only sure way to determine whether a given glow discharge device or plasma is of the d.c. or rf type is to take a look at the power supply and any associated equipment used to sustain it. The extreme similarities can be extended to the basic plasma physics, at least to a first approximation. For instance, in both types of discharge, sample material is introduced into the gas phase through sputtering. Additionally, in both discharge types, sputtered material is thought to be electronically excited primarily through electron impact excitation and ionized by means of either electron impact or Penning ionization [67]. Finally, d.c. and rf glow discharges are also similar in terms of their overall analytical performances. For example, the two types of discharge are for the most part prone to the same types and magnitudes of interferences and matrix effects. Further, many analytical figures of merit, such as precision, accuracy, sensitivity, and detection limits (DLs), are similar. Owing to the breadth and extent of similarities, the rf discharge has been described as a d.c. discharge with a superimposed high-frequency field [59].

Even though d.c. and rf glow discharge devices and plasmas are extremely similar in many ways, there are also some important differences related to the physics of high-frequency fields. Undoubtedly, the most important difference from an analytical point of view is that the rf glow discharge device can be used to sputter both electrically conductive and insulating solid samples, while the d.c. glow discharge device can be applied only to conductive materials. However, there are other more subtle differences, as well, such as the number densities and energy distributions of charged particles. These sorts of subtle effects can lead to differences in the efficiencies of important physical processes, such as excitation and ionization [8,9,30,68–71].

Only a few years ago, almost all knowledge of rf glow discharge physical processes was derived from experiments with rf glow discharge devices designed for use in fields other than analytical chemistry, primarily the microelectronics industry. This was an unfortunate situation for the analytical spectrochemist, because the conclusions drawn from experiments conducted in other fields may not always be wholly transferable to the analytical rf glow discharge device. This is due to the fact that rf glow discharge devices employed in other fields may differ significantly from those employed by analytical spectrochemists, most notably in the operating pressure of the support gas. Rf glow discharge devices used in the microelectronics industry, for example, are usually operated at pressures much less than 100 Pa, where Ar mean free paths may be greater than 0.1 mm. Analytical sources, on the other hand, may be operated with gas pressures in excess of 1500 Pa, where Ar mean free paths may be shorter than 10 μm. Additionally, the precise geometries of the electrodes may differ somewhat. Fortunately, experience has shown that the qualitative principles governing discharge operation generally remain unchanged by such variations in source design and operating conditions. However, quantitative numbers, such as electron densities, may be dramatically affected.

In recent years, a number of fundamental studies of analytical rf glow discharge devices have been reported in the scientific literature. These include both empirical studies [30,70,72–76,80] and computer modeling experiments [1,8,9,68,69,77–79]. Comparing these two general approaches, empirical studies have the advantage that physical parameters of interest are actually measured using real equipment in the laboratory. An example is the measurement of electron and ion characteristics by means of Langmuir probes. Because parameters are actually measured, empirical studies are sometimes assumed to be more accurate. However, it must be noted that the measurement process itself may in some cases disturb the system under study. Additionally, there may be uncontrollable or even unknown factors that influence the data, such as the fraction of rf power that is ultimately lost to stray impedances. Consequently, the results of empirical measurements must be carefully interpreted. The computer modeling approach has the advantage of flexibility, since almost anything can be done in the computer. For instance, a computer model may be used to estimate physical parameters that are difficult or impossible to measure empirically, such as the contribution of fast Ar atoms to sputtering. However, the data derived from a given computer modeling
experiment are only as good as the model itself, and the uncertainties associated with the input parameters and any simplifying assumptions must be carefully assessed. Owing to these kinds of influences, the results of computer modeling experiments must also be interpreted with care. To summarize, both the empirical and computer modeling approaches have advantages and disadvantages. It is prudent to view each approach as a valuable research tool, but appropriate caution in the interpretation of results is warranted.

In the following subsections, we seek to provide a basic understanding of the physics that govern the analytically important processes occurring in the rf glow discharge device. Such understanding is helpful for comprehending the basic analytical characteristics and capabilities of rf glow discharge analytical spectrometries.

3.1. Sputtering in the radio-frequency glow discharge

As noted earlier, the analytical rf glow discharge device can be used to sputter both electrically conductive and non-conductive solid samples. In order to explain this important capability, we make use of the diagram of a typical analytical rf device presented in Fig. 4, where an insulating sample has been assumed. The arrangement in the figure is conceptually the same as that of Wehner [46] and Davidse and Maissel [48]. It is useful to consider first what happens when a negative d.c. high voltage is suddenly applied to the backing electrode. When the voltage is applied, electric dipoles within the insulating material will align, causing the potential on the surface of the insulator opposite the backing electrode to drop instantaneously to approximately the applied potential. If the resulting surface potential is large enough, the support gas within the discharge cell will break down electrically, thereby igniting a plasma. Drawn by electric fields within the plasma, positively charged ions will bombard the insulator. This bombardment will cause the surface potential to rise toward zero, due to the ejection of electrons from the surface, as well as the neutralization of the bombarding ions at the surface. No net current can flow through the insulating solid. As a result, the electrons lost from the surface due to ion bombardment cannot be replenished. The surface potential will continue to rise until it becomes too small to sustain the discharge and the plasma is extinguished.

In order to sputter insulating materials effectively, it is essential to restore continuously the electrons lost from the surface due to ion bombardment, such that the necessary negative surface voltage can be maintained. Radio-frequency excitation applied to the backing electrode in the arrangement pictured in Fig. 4 enables the required restoration of electrons. This is because the application of rf excitation causes the surface to be bombarded alternately by positive ions and electrons. Electrons that are lost to positive ion bombardment in one half-cycle are restored by electron bombardment during the succeeding half-cycle. The rf excitation is usually sinusoidal and bipolar. Therefore, it would seem logical that the duty cycle for ionic bombardment, and, therefore for sputtering, is necessarily 50%. Fortuitously, the arrangement shown in Fig. 4 enables insulating samples to be sputtered almost, if not, continuously.

Consider the application of a bipolar, sinusoidal, rf potential to the backing electrode, as illustrated in Fig.
Fig. 6. Establishment of the d.c. self-bias potential in an analytical rf glow discharge device using the electric probe model of Butler and Kino. (a) Initial condition at onset of sinusoidal, bipolar, rf excitation (note excess electron current); (b) Steady-state condition (note zero net current and the d.c. shift in the time-averaged surface potential). [Adapted from Fig. 2 in Ref. [45]; reprinted with kind permission of the American Institute of Physics and the authors].

5. As shown in the figure, in the initial cycles of rf excitation the potential on the surface of the insulator opposite the backing electrode shifts to more negative values. This results from the fact that the electrons in the plasma are much more mobile than the positively charged ions. As illustrated in Fig. 5b, after some period of time, a steady state condition is reached, in which the surface potential is negative for a very large majority of the rf cycle. The time-averaged surface potential that results is called the 'd.c. self-bias potential,' or simply 'd.c. bias' or 'offset.' It is the establishment of this d.c. bias that enables an insulating surface to be sputtered almost, if not, continuously in an analytical rf glow discharge device. One research group found that approximately 3400 rf cycles (0.25 ms at 13.56 MHz) were required for the establishment of the d.c. bias in their analytical rf glow discharge device [80].

The formation of the d.c. bias can also be understood by considering the surface of the insulating sample to act like an electric probe, such as would often be used in plasma diagnostics. This approach to understanding the establishment of the d.c. bias was originally described by Butler [44] and Butler and Kino [45]. Referring to the probe characteristic in Fig. 6a, the surface potential at which the surface draws no net current, known as the floating potential, is usually a few volts negative with respect to the plasma potential. At the floating potential, the flow of electrons to the insulating surface is impeded by the potential difference between the surface and the surrounding plasma just enough to ensure equivalent electron and positive ion fluxes to the surface. If the surface potential becomes more negative than the floating potential, there is a net flow of positive ions to the surface. Likewise, when the surface potential is positive with respect to the floating potential, there will be a net flow of electrons. Because of the shape of the probe characteristic, the electron current is much higher than the positive ion current for similar absolute deviations from the floating potential. This is a result of the very different mobilities of the particles.

As shown in Fig. 6a, the application of a bipolar sinusoidal excitation voltage to the surface results in the flow of positive ions to the surface during the negative half-cycle, and electrons during the positive half-cycle. But notice that there will be a substantial excess of electron flow, owing to the probe characteristic. The insulating surface cannot conduct this excess current, and so the surface potential will become negative just enough to ensure a time-averaged net current of zero, as shown in Fig. 6b.

At this point, we should emphasize that both approaches to understanding the formation of the d.c. bias potential and the sputtering of insulating surfaces are based upon several important assumptions. Specifically, it is assumed that the rf glow discharge device is designed to be geometrically highly asymmetric, meaning that the ratio of the effective electrode surface areas is large. Also, it is assumed that the sample to be sputtered serves as the smaller electrode. Finally, the rf power used to sustain the discharge is assumed to be capacitively coupled and applied to the sample. So long as these characteristics apply, the above discussion pertains equally to the sputtering of conductive materi-
als, in that a d.c. bias will be formed and the conductive sample can be effectively sputtered. However, the backing electrode is unnecessary when sputtering conductive samples.

It should also be noted that the rf excitation frequency is an important factor in enabling efficient sputtering and maximizing the d.c. bias potential. For analytical spectroscopy, it has been suggested that frequencies less than a few megahertz should not be used [47]. Analytical rf GDOES devices are usually operated with 13.56 MHz power, but other frequencies have also been employed [e.g. [81–84]].

Further insights into the physical process of sputtering in analytical rf glow discharge devices have been gained through computer modeling experiments. Bogaerts and Gijbels modeled the sputtering of a Cu sample in both d.c. and rf glow discharges under typical discharge conditions of 670 Pa Ar and approximately 38 W discharge power [8]. They estimated the sputtering rates due to bombardment of the sample surface by Ar+, Ar2+, and Cu+, where Ar2+ is a fast Ar atom produced through symmetric charge exchange within the plasma sheath that forms adjacent to the sample surface. As explained in the next subsection, this plasma sheath is very important. This is because it is characterized by a strong electric field that is responsible for the acceleration of charged particles toward or away from the sample. Interestingly, the results of the computer modeling experiments indicated that, for the system under study, most sputtering is produced by Ar2+ bombardment (69.5% for rf; 68.8% for d.c.). The contribution to sputtering made by Ar+ was found to be far less (18.3% for rf; 19% for d.c.), while that for Cu+ was found to be the same for both modes of operation (12.2%). Fast Ar atoms have the smallest kinetic energies of the bombarding particles under consideration, because they cannot gain energy from the electric field within the sheath. As a result, one might assume that the pairs of percentages for the two modes of operation quoted above are almost identical. This is one more indication that d.c. and rf glow discharges are extremely similar.

Another interesting result from computer modeling of analytical rf glow discharges is that the sample surface may in fact be sputtered continuously, even throughout the portion of the rf cycle during which the potential on the surface of the sample is most positive. There are at least two probable reasons for this. First, the positively charged ions that are being accelerated toward the sample surface for most of the rf cycle cannot react quickly to the changing electric fields within the plasma. As a result, bombardment of the surface by positively charged ions may continue during the most positive portion of the rf cycle [68]. Second, as described above, sputtering may occur through bombardment of the sample by fast atoms of the discharge support gas. Being neutral in charge, such atoms are unaffected by the changing fields.

Upon being sputtered from the sample surface in an analytical glow discharge device, there is a substantial probability that a given sputtered particle will be collisionally returned to the surface. The fraction of sputtered material that is redeposited in this way in a d.c. glow discharge has been estimated experimentally to be as high as 94% under some sets of discharge conditions [85]. However, this estimate is highly uncertain, because of the lack of knowledge about such important factors as the kinetic energy distributions and directionalities of the ions and fast atoms bombarding the surface. More recent computer modeling results have indicated somewhat smaller redosposition rates, on the order of 60–70%, for both d.c. and rf glow discharges [8]. At first glance, it would seem that such high redosposition rates would reduce the usefulness of glow discharge spectrometric depth profiling, which relies upon the layer-by-layer removal of surface material through sputtering. Nevertheless, as we will see in later sections of this review, experience dictates that any negative consequences of the redeposition of sputtered material are minimal. Finally, we should mention that sputtering rates measured in the laboratory are inherently net sputtering rates (i.e. absolute rates reduced by redosposition rates).

3.2. Radio-frequency plasma sheaths

In both d.c. and rf glow discharges, sheaths form around the surfaces in contact with the plasma. The sheaths are characterized by the presence of electric fields, positive space charge, and relatively low electron densities. Due to the low electron densities associated with the sheaths, relatively little electronic excitation occurs within them. For this reason, they emit little light compared to the glowing portion of the plasma (i.e. the negative glow), and so they appear relatively dark to the human eye. This is why the sheaths are often called ‘dark spaces.’ This common practice is more a matter of convenience in communication than technical accuracy, since a ‘dark space’ is simply the optical result of the presence of a sheath. Depending upon discharge conditions, typical sheath thicknesses are in the range 100 μm to 1 cm.

Consider a negative d.c. high potential applied to the cathode (sample) in a d.c. glow discharge device, as illustrated in Fig. 7a. A sheath forms adjacent to the sample surface, because the negative potential on the surface repels plasma electrons, creating a region of high net positive space charge. In a d.c. discharge, this
sheath is commonly called the ‘cathode dark space.’ Owing to Debye shielding, most of the potential applied to the sample surface is dropped within the cathode dark space, leaving the negative glow region of the plasma relatively field-free, as shown in Fig. 7b. The strong electric field within the cathode dark space accelerates positive ions toward the sample surface to sputtering energies. Computer modeling has shown that most of the sputtering ions originate near the interface between the cathode dark space and negative glow [7]. An ion that starts from rest at this interface and travels the full thickness of the sheath undisturbed will strike the surface with an energy determined by the difference between the plasma potential at the interface and the surface potential. However, ionic mean free paths associated with common analytical glow discharge gas pressures and temperatures are very short, on the order of 10 μm. Therefore, scattering and charge exchange collisions within the cathode dark space usually result in significantly lower ion energies, as the modeling experiments have also shown [7]. Fast atoms created through charge exchange within the sheath have still lower energies, because they continually lose energy through further collisions, but are unable to gain additional energy from the electric field. As discussed in the preceding subsection, sputtering by fast atom bombardment is nonetheless thought to be responsible for a large fraction of the total sputtering of the sample surface, because of the relatively large flux to the surface [8].

As stated before, the strong electric field within the cathode dark space repulses electrons away from the sample surface, accelerating them into the negative glow region of the plasma. This acceleration of electrons is a very important process for sustaining the plasma, because it serves as the principle source of energy flux into the negative glow in a d.c. discharge. Electrons accelerated through the cathode dark space may originate from the sample surface itself, having been sputtered as secondary electrons. Such electrons can gain very high kinetic energies from the field within the sheath. In addition to the secondary electrons, some electrons that are accelerated into the negative glow may originate from ionizing collisions within the cathode dark space. Such electrons enter the glow region with lower average kinetic energies than the secondary electrons, due to the fact that they originate closer to the interface between the cathode dark space and the negative glow, therefore experiencing a smaller potential difference.

Referring again to Fig. 7a, note that a sheath also forms at the anode surface in an analytical d.c. glow discharge device. Unlike the cathode dark space, this sheath is not caused by repulsion of electrons from the surface. Rather, it is the result of the fact that electrons diffuse out of the plasma more rapidly than positively charged ions, leaving a small net positive space charge (i.e. plasma potential) in the negative glow region. The resulting difference between the plasma potential in the glow and anode surface potential creates the weak electric field that characterizes this sheath. It is noteworthy that the magnitude of the plasma potential associated with the glow is limited by the phenomenon of ambipolar diffusion, which reduces the diffusion rates of electrons leaving the plasma to approximately the ion diffusion rates [86].

Now, consider the application of a sinusoidal, bipolar, rf potential to the sample in an analytical rf glow discharge device. So long as the device is geometrically highly asymmetric and capacitive coupling is employed, a negative d.c. bias potential is established on the sample surface for both conductive and insulating samples, as shown in Fig. 8. The spatial distributions of electric potentials within the discharge have been modeled for several different analytical rf devices and sets of discharge conditions [9,68,78]. The results of these computer modeling experiments indicate that the overall shapes of the potential distributions at π, 3π/2, and 2π during the rf cycle are very similar to those depicted in Fig. 7b for the d.c. glow discharge device. Obviously, however, the magnitudes of the potentials vary in time. In contrast, the results indicate a very different situation at π/2 in the rf cycle, when the potential on the surface of the sample is most positive. At this point in time, the plasma sheaths at both surfaces are thick and diffuse, and the electric fields within them are quite weak. This means that the plasma sheaths present in an analytical rf glow discharge are modulated at the rf excitation...
frequency, both in terms of thickness and electric field strength.

The rf modulation of the plasma sheath adjacent to the sample surface can have consequences in terms of the kinetic energies of positively charged ions that bombard the surface. Rf excitation frequencies that are commonly used in analytical discharge devices are usually far below the electron resonant frequency, but may be above the resonant frequencies for positive support gas ions, under commonly used discharge conditions. Consequently, a support gas ion within the sheath may oscillate back and forth in response to the oscillating excitation potential as it transits the sheath. Even if it does not change direction of motion, its kinetic energy may still be modulated. In either case, the energy with which it strikes the surface will depend in part on the phase at the moment of impact. This results in a broadening of the associated distribution of ion kinetic energies at the sample surface.

The kinetic energy distributions of positively charged ions bombarding surfaces in contact with rf glow discharges have been studied using mass spectrometry. Coburn and Kay [87] sampled ions through a small orifice in a planar electrode and measured the distributions for three species (see Fig. 9). Note that none of the species were likely to undergo charge exchange collisions in the plasma. As shown in the figure, narrower distributions were measured for heavier ions. This is because heavier ions cannot respond to the changing electric field as quickly as lighter ions. Therefore, the kinetic energies of the heavier ions are determined to a greater extent by the average sheath field due to the d.c.
self-bias potential, rather than by the oscillating field. In contrast, very light ions are dramatically affected by the oscillating field, and, therefore may have very broad energy distributions. Coburn and Kay sampled the ions through the grounded electrode in their system. The rf modulation in the energy distributions of the lighter ions is the result of rf modulation of the plasma potential. The energy distributions of ions bombarding the powered electrode in the system would probably have been similarly broadened. It is noteworthy that these results were obtained using equipment designed for use in the microelectronics industry.

Christopher et al. measured the kinetic energy distributions of positively charged ions sampled through an orifice in a grounded sampling cone in an analytical rf glow discharge system [76]. The distributions were measured by means of an electrostatic energy analyzer mounted directly behind the sampling cone. Unfortunately, the instrumentation did not allow discrimination of the various ionic species, and so the measured distributions corresponded to total ion currents only. The ion kinetic energy distributions obtained were generally bimodal, with a larger peak at very low energies and a smaller peak at high energies. While the shapes of the distributions imply the possibility of rf modulation broadening, the data are inconclusive. This is because of the possibility of overlapping distributions for different ionic species.

At this point in time, it is impossible to know for sure whether the kinetic energy distributions of ions bombarding sample surfaces in analytical rf glow discharge devices are significantly broadened by rf modulation. Certainly, the prevalence of scattering and charge exchange collisions within rf sheaths would tend to mask the effects of rf modulation for ions of the support gas, even at pressures as low as a few tens of Pascals. At any rate, even if ion kinetic energy distributions are significantly rf modulated, it is unlikely that serious analytical consequences would result. One possible consequence is that sputtering efficiencies could be affected.

3.3. Excitation and ionization in the radio-frequency glow discharge

As stated earlier, the excitation and ionization mechanisms that characterize the rf glow discharge are the same as those that characterize the d.c. discharge. Specifically, electronic excitation is primarily the result of electron impact collisions, while ionization is caused primarily by either electron impact or Penning collisions. In any particular glow discharge, both of these ionization mechanisms are operative. Whether or not one dominates over the other often appears to depend on the discharge conditions and location within the plasma [56,91]. Of course, the identities of the collision partners are important, as well. For example, Ar in the electronic ground state cannot readily be ionized by the Penning process in an Ar plasma. This is because the ionization potential of Ar is far greater than the excitation potentials of the Ar metastable states, and the large energy deficit cannot usually be provided by kinetic energy. For this reason, Penning ionization is important only in terms of the ionization of analyte atoms in the analytical glow discharge.

Although the excitation and ionization mechanisms are the same in rf and d.c. glow discharges, ionization in the rf discharge is apparently more efficient. One supporting observation is that the rf discharge can be operated at pressures well below 1 Pa, while the d.c. discharge normally cannot be maintained at pressures below approximately 100 Pa. Whether through electron impact or the Penning process, ionization efficiencies are ultimately determined by the plasma electrons. Larger electron number densities and energies produce faster electron impact ionization rates. However, they also result in larger densities of metastable atoms, which in turn produce faster Penning ionization rates. Consequently, the more efficient ionization associated with the rf discharge suggests higher electron densities and energies.

Charged particle populations in analytical glow discharge devices have been studied both experimentally and through computer modeling. The most complete experimental characterizations have been carried out using Langmuir probe techniques at Clemson University in the United States. Notably, the Clemson researchers have compared charged particle populations in analytical d.c. and rf glow discharges using the same discharge device, simply by switching the power supply [30]. This approach helps to mitigate confounding effects attributable to source design, making the comparisons more meaningful. Typical results from these studies are summarized in Table 1. As shown, the electron and ion densities associated with the rf discharge are found to be slightly lower than those associated with the d.c. discharge. In contrast, computer modeling of d.c. and rf glow discharges predicts slightly higher charged particle densities in the rf discharge [68]. The lower densities observed experimentally could be the result of unintentional power losses in the rf mode, such that the actual rf power dissipated in glow discharge processes might be reduced.

Referring again to Table 1, the most obvious difference between the d.c. and rf operational modes is that the electrons in the rf discharge are significantly more energetic. The much higher electron energies seem to be the source of the higher ionization efficiencies in the
rf discharge. Researchers in the microelectronics industry have proposed several theories to account for the existence of energetic electrons in rf glow discharges commonly used in that industry. These same theories may also be applicable to analytical rf glow discharge devices. Briefly, the glow region of the rf plasma is known to be characterized by the existence of rf electric fields. Although these fields are certainly much weaker than the fields associated with the plasma sheaths, they are nonetheless sufficiently strong to cause electron oscillation. As a result, electrons oscillating in response to these rf fields likely attain higher energies than electrons in the relatively field-free d.c. glow [92]. Moreover, an electron may collide elastically with an Ar atom or some other massive particle, such that its direction of motion is reversed at nearly the time the oscillating rf field changes direction. If this occurs, then the electron may be accelerated to an energy that is much higher than its energy prior to collision [93]. Given the relatively small mean free paths associated with the relatively high pressures in analytical rf glow discharge devices (on the order of 2 μm to 20 μm), it seems that this sort of mechanism would be especially important. A similar phenomenon may occur at the interfaces between the plasma sheaths and the glow region [94]. In this case, the rf excitation causes the thicknesses and potentials of the rf sheaths to oscillate. When an electron enters a given plasma sheath from the glow region, it experiences the event as a collision with a massive particle. If this collision occurs at an appropriate time with respect to the phase of rf excitation, then the electron may be accelerated significantly. This mechanism is sometimes called ‘surf-riding’ or ‘wave-riding.’

By far the most comprehensive computer models of analytical rf glow discharge devices have been developed by researchers at the University of Antwerp [8,9,68,69,77,78,95,96], though other groups have also published in this area [97,98]. Results of the University of Antwerp computer models provide further evidence that rf plasma electrons are more energetic than electrons in the d.c. discharge. Two distinct groups of electrons with kinetic energies sufficient to induce ionization are delineated. The first group consists of fast electrons, released as secondary electrons from an electrode surface or produced in ionization events, which have not yet been collisionally thermalized. Ionization caused by collisions with such fast electrons is referred to as ‘γ-ionization.’ The second group consists of thermalized electrons that have been accelerated to ionizing energies through the sorts of interactions with rf fields described in the preceding paragraph. Ionization caused by these electrons is referred to as ‘α-ionization.’ Integrated over time and space, the computer models suggest that α-ionization may dominate in the analytical rf glow discharge device. For example, under one set of conditions, α-ionization has been found to contribute as much as 72% of all Ar ionization. In contrast, γ-ionization was found to contribute only 23% of Ar ionization, with the remaining 5% being accounted for by collisions with fast Ar atoms (4%) and fast Ar ions (1%). Ionizing collisions with fast Ar atoms and ions primarily occur within the plasma sheaths. Given that the electrons responsible for γ-ionization have much higher energies than those responsible for α-ionization, it might seem surprising that α-ionization would dominate. The explanation is found in the fact that the densities of the electrons responsible for α-ionization were found to be two to three orders of magnitude higher, integrated over time and space.

In contrast to the rf discharge, α-ionization is by definition unimportant in the analytical d.c. glow discharge device, owing to the complete absence of rf electric fields. Therefore, overall ionization in the plasma should be dominated by γ-ionization. Additional computer modeling experiments from the same research group have shown that under one set of conditions 89% of Ar ionization in an analytical d.c. discharge can be attributed to γ-ionization, while only 9% and 2% can be attributed to collisions with fast Ar atoms and fast Ar ions, respectively [68]. Again, the collisions with fast Ar atoms and ions occur predominantly within the plasma sheaths. The discharge power and gas pressure used to model the d.c. plasma were very similar to those used to model the rf plasma. Under such similar discharge conditions, the absolute rates of Ar ionization attributable to the γ-ionization process were found to be approximately the same in both the d.c. and rf discharge.

Table 1
Comparison of charged particle characteristics in the same glow discharge device operated in rf and d.c. modes, determined using Langmuir probe techniques. [Table 2 in Ref. [30], reprinted with kind permission of the author and the publisher.]

<table>
<thead>
<tr>
<th>Parameter</th>
<th>rf</th>
<th>d.c.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electron density (cm⁻³)</td>
<td>2×10¹⁰ to 6×10¹⁰</td>
<td>6×10¹⁰ to 18×10¹⁰</td>
</tr>
<tr>
<td>Average electron energy (eV)</td>
<td>4 to 7</td>
<td>0.7 to 1.0</td>
</tr>
<tr>
<td>Excitation temperature (K)</td>
<td>5000 to 8000</td>
<td>2500 to 4000</td>
</tr>
<tr>
<td>Electron temperature (eV)</td>
<td>1.5 to 2.5</td>
<td>0.2 to 0.6</td>
</tr>
<tr>
<td>Ion number density (cm⁻³)</td>
<td>3×10¹⁰ to 12×10¹⁰</td>
<td>4×10¹⁰ to 20×10¹⁰</td>
</tr>
<tr>
<td>Plasma potential (eV)</td>
<td>9 to 16</td>
<td>2 to 4</td>
</tr>
</tbody>
</table>
es. Given that the rf plasma is also characterized by the dominant α-ionization mechanism, this leads to the conclusion that the overall ionization efficiencies in the analytical rf discharge are higher than those in the analytical d.c. glow discharge.

Electron energy distribution functions (EEDFs) have been measured by the Clemson University research group for both d.c. and rf analytical glow discharges using Langmuir probe methods [70,73,99–103]. These EEDFs again point out the differences between the electron kinetic energies in the two types of discharges. Depending upon many experimental factors, such as plasma sampling location, source geometry, and discharge conditions, the EEDFs characterizing the electron populations in an rf discharge can exhibit very varied shapes, as illustrated in Fig. 10. As is evident in the figure, the EEDFs may sometimes exhibit bimodal behavior. Such EEDFs demonstrate the existence of multiple populations of electrons in the rf plasma. In contrast, the EEDFs for the analytical d.c. glow discharge are typically found to be unimodal and much more Maxwellian [99–101]. Nevertheless, even those EEDFs are not precisely Maxwellian, owing to the lack of local thermodynamic equilibrium at analytical glow discharge operating pressures.

In terms of analytical glow discharge spectrometry, the larger electron kinetic energies associated with the rf plasma as compared to the d.c. plasma would be expected to produce more efficient ionization of sputtered analyte atoms, whether via electron impact or Penning collisions. Moreover, more efficient electronic excitation of analyte species would also be anticipated.
Such increases in analyte ionization and excitation efficiencies would be expected to result in improved analytical sensitivities and detection limits for GDMS and GDOES, respectively. Nevertheless, the sensitivities and DLs provided by d.c. and rf analytical glow discharge devices, whether used for GDMS or GDOES, tend to be similar.

Before proceeding to the next section, it is useful to call attention to an apparent disagreement between the results of computer modeling experiments and those obtained through Langmuir probes. The disagreement in question is concerned with the absolute electron number densities in the analytical rf glow discharge. As shown in Table 1, electron densities measured through the use of Langmuir probes typically fall in the $10^{10} \text{ cm}^{-3}$ range, though some papers from the same research group have reported densities as small as $10^9 \text{ cm}^{-3}$ and as high as $10^{11} \text{ cm}^{-3}$, depending on such factors as the source geometry, discharge conditions, location within the plasma, and sample matrix [70,73,101,104]. At least one other research group has reported similar electron densities in an analytical rf glow discharge device [75].

Computer modeling of rf glow discharge plasmas, on the other hand, have most often resulted in values that are two to four orders of magnitude higher [9,68,77]. This discrepancy is not easily explained. Certainly, many factors can affect the electron density, as mentioned above. Additionally, rf power losses to stray impedances would tend to bias electron densities observed experimentally toward lower values, but would not affect the results of computer modeling. Nonetheless, it is difficult to understand such large disagreements, and further research and reflection are warranted.

4. Techniques and applications

Now that we have discussed the foundations of analytical radio-frequency glow discharge spectrometries and the fundamentals of radio-frequency glow discharge physical processes, we describe in some detail the most commonly employed analytical rf glow discharge methods. In the following subsections, we specifically address the most analytically important aspects regarding instrumentation, methods, capabilities, and representative applications of rf-GDOES and rf-GDMS.

4.1. Radio-frequency glow discharge optical emission spectrometry

From its beginnings in 1967, with the announcement of Werner Grimm’s new source, GDOES has principally been used for the direct elemental analysis of solids, coatings, and surfaces. Initially, with d.c. only, it was restricted to the analysis of conductive materials, mainly metals and metallic coatings. Then, with the introduction of rf in the late 1980s, it was extended to the direct analysis of both conductive and non-conductive materials. The first commercial rf instrument was the JY 50S, released in 1992 by Jobin-Yvon (France), a combined d.c./rf instrument with two polychromators and a monochromator. The first commercial rf only instrument was the JY 5000 RF (also Jobin-Yvon), released in 1995. Since then Leco (USA) and Spectruma Analytik (Germany) have released several combined d.c./rf instruments, and Rigaku (Japan) has introduced an rf only instrument. There are now more than 100 rf-powered GDOES instruments around the world. They are used principally in universities and institutes for investigating new coatings and in industrial laboratories for analyzing raw materials, monitoring production processes, and characterizing commercial products.

The competition among the companies manufacturing GDOES instruments has led to many important developments in instrumentation and rf control, as well as to an increasing diversity of designs and performance levels. Available optical spectrometers now vary in focal length from 150 to 1000 mm, vary in design from simultaneous photomultiplier-based polychromators and scanning monochromators to simultaneous solid state spectrometers (i.e. incorporating solid state detectors, such as charge-transfer devices), and vary in optical resolution from over 100 pm to below 10 pm. Many of these innovations have occurred through direct links between the manufacturers and researchers in universities and institutes around the world. The first ISO (International Organization for Standardization) standard for GDOES, including both rf and d.c. operational modes, ‘Surface chemical analysis – Glow discharge optical emission spectrometry (GD-OES): Introduction to use,’ was published in 2000 [105]. The second ISO standard, ‘Surface chemical analysis – Determination of thickness and chemical composition of zinc and/or aluminium based metallic coatings by glow discharge optical emission spectrometry,’ by rf- or d.c.-GDOES, is nearing completion.

4.1.1. Instrumentation

RF-GDOES instruments usually comprise a GD source, rf power supply and associated components, one or more optical spectrometers, vacuum and gas-handling systems, electronics, a computer, software for control and analysis, and a printer. Lavoine et al. have recently described a new optical interface [106]. In this review, however, we will concentrate mainly on the rf-GD source design and control.

4.1.1.1. Source design. All commercial rf-GD sources for OES have much in common in their overall concep-
tion, and many differences in their finer details. They have all inherited much from the original Grimm source and are, therefore, often referred to as Grimm-type sources. The principle of the source is shown in Fig. 11, modified to allow rf operation [107,108].

Many readers will be familiar with the Grimm source but possibly not understand how it functions in detail. It is in this detail why Grimm and Ritzl, at RSV, Germany, took years to develop the source into a commercial reality. In his early papers, Grimm described his source as a hollow cathode/hollow anode source. In the original Grimm design, the cathode was a conductive annular plate with a hole in its center for the hollow anode tube. The anode was either 7 mm or 8 mm in inside diameter. Both cathode and anode were made from a hard Cu–Co–Be alloy no longer available. The anode reached to within approximately 0.1 mm to 0.2 mm from the outer surface of the cathode. The sample was mounted externally in contact with the cathode and sealed to it by pressure onto an O-ring in the cathode. In this way the sample could be changed rapidly to allow large numbers of samples to be analyzed quickly. A d.c. voltage was applied to the cathode and by electrical contact to the sample. Argon was introduced into the source past an observation window, to keep the window clean, and then directed partly down the center of the anode tube, to form the plasma, and partly through an outlet in the middle of the source, to keep the source clean, and then to a vacuum pump. The argon travelling down the center of the hollow anode exited through the small gap between the anode and sample surface and travelled back up the outside of the anode tube to a second vacuum pump. The gap between the outside of the anode tube and the cathode was kept to approximately 0.2 mm to avoid creating a plasma there.

Such a source is not suitable for rf operation because of the strong rf coupling between the conductive cathode and anode. The breakthrough came when Chevrier and Passetemps replaced the conductive cathode plate with a ceramic disk and applied the rf voltage directly to the sample [55], which then became the driven electrode, still often called the ‘cathode’ for historical reasons. Independently, Marcus and co-workers developed a very different rf source that also electrically isolated the sample from the source body and applied the rf voltage to the back of the sample, see Fig. 12 [59]. Variations on this source are often referred to as the ‘Marcus source,’ though Marcus has argued that the essential invention was the back-of-sample application of the rf that distinguished these sources from the Grimm-type sources [109].

Some of the changes introduced by different commercial manufacturers, with varying success over the years, are:

i. different anode inside diameters from 2 mm to 8 mm, mainly aimed at improving depth resolution and managing smaller and smaller samples;

ii. shortened anode tubes, mainly to increase light throughput;

iii. copper, stainless steel, or ceramic anodes;

iv. stainless steel body, to improve vacuum tightness;
v. one combined vacuum pump instead of two, mainly to reduce cost;
vi. oil-free vacuum pump(s), to reduce carbon pollution;
vii. large parallel plates for sample mounting, to improve precision with large samples;
viii. a copper cathode with an insulating sleeve between the cathode and anode;
ix. rf voltage applied to the front face of the sample;
x. argon bath around the sample, to reduce air ingress;
xii. special sample holders for small samples; and
xii. laser alignment of sample position.

4.1.1.2. Boosted sources. Over the intervening years, many laboratories have tried to boost the output of the GD source. Possible boosted sources have included secondary discharge from a filament, various magnetic field designs, gas jets, and microwaves [110]. Despite this, no commercial source for GDOES currently uses any of the possible means available for boosting. This lack of commercial application is probably because the small benefits of boosting, such as 2–3 times improvements in intensity for some lines, have not been shown to outweigh the additional costs and complexity.

To illustrate the difficulties for manufacturers, consider the work of Su et al., who coupled a microwave induced plasma (MIP) device to a microsecond-pulsed GD source [111]. The microwaves were coupled to the GD plasma by replacing part of the tubular anode with a quartz tube. They found the source operated best at pressures below 150 Pa, below the normal operating range of commercial sources of between 400 Pa and 1000 Pa. They found much improved intensities, signal-to-background ratios (SBRs), and relative standard devi-
ations (R.S.Ds), for four lines from Cu and Zn in brass, for the combined system compared to a pulsed system alone. To date, such synchronised pulsed systems (i.e. where the source and detector are synchronised) only work with monochromators. In their paper, there is no information on crater shapes. This is certainly not the authors’ fault, since it was not the purpose of the study. However, it is essential information for a manufacturer. Also, to optimize the source, an operator must select pressure, pulsing frequency and duty cycle, pulse power or voltage, and microwave power. This is not a simple task.

Recently, Cho et al. designed an improved gas-jet boosted GD source and applied it to the analysis of steel [112,113]. Rather than the earlier discrete entrance holes that adversely affected crater shapes and hence depth resolution, they employed a cone-jet design to give uniform flow across the sample surface. With the jet boosting, sputtering rates were doubled compared to the conventional GD design, mainly through a reduction in redeposition, and detection limits were thereby improved. They also introduced magnets inside the anode body. Being so far from the sample surface they had little effect on sputtering rates, which were slightly reduced, but a big effect on emission yields (emission yield is a measure of the relationship between emission intensity and sputtering rate) and intensities (e.g. for a copper sample, Cu I 324.7 nm and Cu I 327.4 nm both increased by a factor of 3, while Cu II 224.7 nm increased by 10 times). Without the magnets the excitation temperatures were 3100 K to 3300 K, and with the magnets 3800 K to 3900 K. Though these temperatures show a significant increase with the magnets, they are lower than the 5000 K generally assumed to be present in GDOES, and lower than some arc/spark excitation temperatures [114].

Low intensities in GDOES were previously thought to be due to low plasma densities rather than low excitation. Recently, Wagatsuma measured excitation temperatures for a variety of Cr atomic lines [115]. He found excitation temperatures varied from over 4000 K to over 5000 K at 13.56 MHz, depending on the upper excitation energy of the excited state, with the lower energy states giving higher excitation temperatures. This discrepancy increased with increasing rf frequency. Excitation temperatures appeared to be relatively insensitive to changes in pressure but changed significantly with injected current. This topic clearly needs more study.

4.1.1.3. Rf Power. Most commercial rf-GDOES instruments use impedance matching for transmitting the rf power from the generator to the source. This will be considered in more detail later. An alternative to the impedance-matched system is the free-running rf generator developed by Hoffmann and co-workers [83]. In a free-running system the source forms part of the oscillator circuit, and all other components are fixed. The circuit varies the frequency to keep the whole system stable. The average frequency is kept low, approximately 4.4 MHz, to maximise the source reactance, which varies inversely with both frequency and source capacitance. The free-running design simplifies the operation because there is no need for a variable matching box. It should also have a very fast stabilizing time. Hoffmann et al. compared the start-up time of their free-running system with d.c. operation. With a steel target their results for the turn-on time for the Fe signal were approximately 20 ms in both rf and d.c. They commented that such fast start-up times were needed for surface analysis and would not be possible with a matched rf system. This has proven not to be the case, as evidenced by the many surface studies published using matched rf systems, especially those of Shimizu and co-workers described later. King and Payling showed the 20 ms start-up time was related to the need to remove approximately 2 nm of the sample surface to reach equilibrium sputtering, rather than to the response time of the electrical circuit [116].

Wagatsuma has combined an rf supply with a d.c. supply to provide an rf/d.c.-powered system [117]. At this stage, it is not clear what the advantages of such a system are, compared, for example, with simply increasing rf power.

4.1.1.4. Rf Frequency. Rf-GDOES sources are commonly operated between approximately 4 MHz and 13.56 MHz. Varying the frequency of the applied rf voltage is similar in many ways to varying the plasma gas pressure. At constant power and pressure, as the frequency is increased, the applied voltage and d.c. bias voltage necessary to maintain the plasma decrease and the current increases [81,118]. Generally, sputtering rates tend to decrease, while intensities tend to vary in a more complex fashion, possibly related to excitation energies, with resonance and low-lying levels enhanced by increasing frequency and higher levels diminished. In the plasma there may be many mechanisms responsible. For example, ionization may be more efficient at higher frequencies, while plasma gas ions will travel a shorter distance across the plasma sheath in each cycle.

Matsuta and co-workers compared GD operation in an impedance-matched system at 6.78 MHz, 13.56 MHz and 40.68 MHz [119,120]. They found that increasing frequency led to lower d.c. bias voltages and intensities. They interpreted the lower d.c. bias voltage as due to the lower mobility of the electrons with increasing frequency. The decrease in intensities appears mainly to be due to a decrease in sputtering rate with frequency. At 40.68 MHz, as the pressure is increased, the sputtering rate decreases virtually to zero, allowing the possibility of using these conditions as an excitation source.
if some other means, such as laser ablation, can be used for sampling.

4.1.1.5. Bias current control. In 1999, Wagatsuma introduced a novel and unexpected innovation that much perplexed the audience at a recent international symposium, where the idea was discussed: bias-current control [121–126]. Experimentally, the technique is simple to describe: a variable resistor (2 kΩ to 76 kΩ, i.e. comparable to the source resistance) with a series ammeter is connected between the two electrodes of an rf-powered GD source. The d.c. bias developed by the rf plasma causes a current to flow through the resistor that can be measured with the ammeter. Varying the resistance varies the measured current.

The benefit of this system may lie in the non-linear response of the plasma source. It appears that when the external resistor is connected across the source, the magnitude of the d.c. bias voltage drops. This means that, for a given pressure and power, there is a lower voltage and higher current in the plasma, both of which are advantageous for increased emission yield. The concept, however, will work only for conductive samples and will degrade the crater shape, making craters more convex (greater depth at the center) and deteriorating depth resolution.

4.1.1.6. Modulation. Wagatsuma has also been experimenting with modulated sources with considerable success [127–130]. He has tried, variously, modulating the applied rf voltage, the bias-current, or the d.c. voltage in a combined rf/d.c. source. When any one of these is combined with a synchronised detector, in this case a monochromator linked to a lock-in amplifier, the result is a large reduction in noise and much improved detection limits; though, it should be noted in passing that his detection limits without modulation were not as good as some published values with other instruments also without modulation. When the applied rf voltage is varied at 2 Hz between an amplitude of 155 V and 228 V, Wagatsuma found the sputtering rate decreased by a factor of 10, compared to a constant amplitude of 225 V, but the signal-to-noise ratio (SNR) increased by more than 50 times. Wagatsuma commented that the reduced sputtering rate is beneficial for depth profiling, echoing the thoughts of many who think that slower is better. But spectrometers are measuring photons and simply going slower means that there are fewer photons to measure per unit time and nothing is gained. The benefit here is the greatly improved SNR that allows shorter averaging times during the acquisition.

4.1.1.7. Pulsed GD. Harrison and co-workers began studying microsecond pulsed GD in 1975 [17]. It is an interesting point whether microsecond pulses constitute radio frequency operation. Microsecond pulses are certainly switching at radio frequency, but they could also be considered d.c. operation that is switched on and off. An rf system can also be switched on and off, as Winchester and Marcus showed in 1992 [63], so we will refer to the former as pulsed d.c. and the latter as pulsed rf, the essential difference being that in pulsed d.c. the amplitude of the applied voltage is constant during each pulse, while in pulsed rf, the amplitude varies at radio frequency during each pulse. For example, at 13.56 MHz, there would be 13.56 cycles in 1 μs.

In pulsed rf operation, Winchester and Marcus found enhanced emission at the beginning of the pulse for some Cu emission lines (i.e. a ‘pre-peak’), enhanced emission at the end of the pulse for some other Cu emission lines (i.e. a ‘post-peak’), and no enhanced emission for still some other Cu lines [63]. This line-specific response to pulsing means that the optimum lines for pulsing may be different from those commonly used for continuous operation. For example, the Cu I line at 324.7 nm is enhanced in the pre-peak, while the Cu II line at 213.8 nm is not. They noted that the sizes of the pre- and post-peaks varied with the plasma conditions, while their widths did not change with pulse width. They then discussed possible mechanisms for these enhancements. For example, easier sputtering of material redeposited from the previous pulse or temporal variations in the electron energy distribution function were discussed as possible explanations for the pre-peak. Of the two peaks, the pre-peak appears to be the more interesting analytically. As with high-frequency pulsing, only the pre-peak is observed at approximately 2000 Hz.

As part of his Engineering thesis, Vegiotti studied pulsed rf using a 30 W, 13.56 MHz, rf power supply switching at 400 Hz with a 50% duty cycle, corresponding to a pulse length of 1.25 ms [131]. When he observed the shape of the intensity pulses from sputtered atoms, he also found many lines showed enhanced emission (i.e. a pre-peak) in the first 100 μs to 150 μs, followed by a plateau. The pre-peak was often about twice the intensity of the plateau (see Fig. 13). Only some atomic resonance lines showed this effect, and he wondered if it was related to a lack of self-absorption at the beginning of each peak due to the absence of absorbers, since atoms from earlier pulses would have already exited the plasma. However, when he plotted calibration curves using either the pre-peak intensity or the plateau intensity, he found that they were both nonlinear, suggesting that they were both affected by self-absorption. If we consider the plasma is approximately 3 mm long and that average particle speeds are approximately 500 m s⁻¹ [132], then the plasma would be filled in approximately 6 μs, much faster than the observed length of the pre-peak. This suggests that the pre-peak is due to another mechanism, such as more...
effortless excitation in the plasma during the early part of each pulse.

Lewis et al. concluded, from studies of optical emission spectra using a copper sample, that millisecond-pulsed rf and millisecond-pulsed d.c. were virtually identical [133]. With pulsed d.c., Pollmann found instantaneous intensities were enhanced by a factor of 100 over constant d.c. or rf [71]. The excitation temperatures appeared unchanged at 3600 K to 3900 K, but the gas temperature (as indicated by rotational temperatures) remained much lower at approximately 400 K, compared with approximately 600 K for constant d.c. or rf, because of the short time the pulses were switched on. Longer pulses approached 550 K after only approximately 0.5 ms on-time. Presumably, this is related to the much lower average powers used in the microsecond-pulsed d.c. compared with the millisecond-pulsed and continuous d.c. or rf.

Bengtson, Yang, and Harrison employed a microsecond regime, pulsed d.c. with fast time-resolved electronics [134]. They found pulsing at between 5 μs and 50 μs with high instantaneous power (1500 W instantaneous, 6 W average) improved SBRs for copper samples by about a factor of 2 compared to continuous operation, and time-resolved detection integrating over 10 μs to 25 μs increased this improvement to about a factor of 5 to 10. They also found the contribution from the molecular background signal from N₂ leaking into the chamber was reduced by about a factor of 3.

Yan et al. studied the effects of pulse width and repetition frequency in pulsed d.c., with a disc GD rather than a hollow anode source [135]. They found the optimum pulse width (at 50 Hz) for optical emission from sputtered atoms was approximately 10 μs. If the repetition frequency was too low, they were concerned about pollution on the sample surface from residual gases, and if too fast, intensities decreased. They found they could use high instantaneous voltage and power, with their resulting higher intensities, and still maintain ‘conventional’ glow discharge characteristics.

Payling et al. compared calibration curves for elements in steel between pulsed rf and continuous rf (50 W applied power). For pulsing they used a 5000 Hz repetition (switching) frequency and a 32% duty cycle (corresponding to a pulse width of 63 μs and a time-averaged applied power of 15.8 W). They found the signal per watt was up to 3 times higher for some elements when pulsed, while the calibration curves were similar, suggesting that quantitative algorithms developed for continuous GD conditions should work for pulsed rf [136]. They also found they could depth profile a heat-sensitive coated-glass sample with pulsed rf (6.3 W average power). This was not possible with continuous rf, because the sample would shatter at the higher continuous applied power.

4.1.1.8. Characterising the rf source. The current measured externally to an rf GD source is the sum of a large displacement current, due to the source capacitance, and a much smaller total discharge current [137]. The total discharge current is the sum of particle currents (electrons and ions) and a plasma displacement current (due to the changing field during each rf cycle). The relative sizes of these displacement currents were initially a source of some controversy between the two main research groups modelling analytical rf glow discharges, until at least some of the differences in their models were resolved. For the first discrepancy, now resolved, the research group at CPAT (Centre de Physique Atomique de Toulouse, Toulouse, France) included a large cell capacitance in their model and predicted a large external displacement current, which was then observed.
[137]. For their model they simulated the Jobin-Yvon rf source with a 4-mm diameter cylindrical anode. The group at the University of Antwerp was focussed on the rf plasma and did not include the extraneous cell capacitance in their model. They compared their results with measurements where the effect of the large cell capacitance had been removed. For their model they simulated the IFW (Institut für Festkörper und Werkstofforschung, Dresden, Germany) rf source with a 2.5-mm diameter cylindrical anode [95,96]. In the second discrepancy, still under debate, from experience with other types of glow discharges, the group at CPAT also expected a significant plasma displacement current, which they observed at 13.56 MHz, though it was smaller than they had initially suspected. Since the size of this displacement current should increase with frequency, their results are not inconsistent with results from IFW Dresden at 3.37 MHz, which showed only a very small plasma displacement current [138]. But the calculations from the University of Antwerp group suggest a very small displacement current even at 13.56 MHz [95,96]. Perhaps the reason for the apparent differences between the models lies in the difference in sheath areas arising from the different anode diameters used, since for the same electric field the displacement current is proportional to the sheath area.

From all this work, we now know the analytical rf GD plasma is highly resistive. Belenguer, Guillot, and Therese have estimated the first sheath resistance (at the sample, driven electrode), under typical analytical conditions, is approximately 13 kΩ, while the resistances of the second sheath (at the grounded electrode) and the plasma body are only approximately 350 Ω and 0.5 Ω to 5 Ω, respectively [137]. This means the overall resistance is dominated by the sheath resistance of the driven electrode. The sheath capacitance of the driven electrode is time varying and approximately 0.5 pF to 1 pF, while that of the grounded electrode is approximately 3.8 pF. Since these capacitances are in series, again they are dominated by the driven electrode. The estimated first sheath length is 0.18 mm, comparable to the anode-to-sample gap in the hollow anode source, and the second sheath length is only 0.07 mm. The estimated plasma length is 2.6 mm, the ion density in the first sheath is approximately $2 \times 10^{12} \text{ cm}^{-3}$, and the plasma density is $\sim 10^{14} \text{ cm}^{-3}$, consistent with the high calculated densities discussed earlier.

Payling et al. found their source capacitance was typically 30 pF, far in excess of the sheath capacitances, and since this capacitance is effectively in parallel with the sheath capacitances, the overall capacitance is dominated by the source (cell) capacitance [79]. This is seen in measured voltage and current waveforms without plasma gas, where the voltage and current signals are highly sinusoidal and 90° out of phase. When plasma gas is introduced, the current waveform is distorted by particle currents in the plasma. Payling et al. have, therefore proposed a simple equivalent circuit for the analytical rf GD (see Fig. 14), where $R_p$ is predominantly the first sheath resistance, $C_p$ is predominantly the first sheath capacitance, and $C_{\text{Stray}}$ the source capacitance [139]. By including the effects of the coaxial cable between the source and matching box, and by measuring the matching box component values in situ, they were able to derive a relationship between the matching box settings (i.e. the positions of the two variable capacitors) and the plasma resistance. Their values for $R_p$ of 5000 Ω to 6200 Ω, however, are lower than expected, so much work is still required.

Wilken et al. have included voltage and current probes in their rf source to monitor its current–voltage characteristics [138]. Their source includes several novel features, but the most impressive is the placement of the probes in close proximity to the grounded electrode (anode), ensuring good mechanical stability and shielding from the effects of changing sample sizes and any losses due to the cooling system. They studied harmonic content in both the voltage and current waveforms. They were also able to determine the d.c. bias voltage directly from the voltage at the moment the current crosses its zero value in the rf cycle, within a relative uncertainty of 5%, independent of whether the sample is conductive or non-conductive. With a low-cost electronic plasma power analyser they could monitor the effective plasma voltage and power in real time during a depth profile.

4.1.2. Source control

4.1.2.1. Rf vs. d.c. In an early comparison of rf and d.c. operation, Payling, Jones, and Gower found the analyt-
ical characteristics of rf-GDOES and d.c.-GDOES were essentially the same: similar elemental sensitivities (slopes of calibration curves) and similar background levels (background equivalent concentrations, BECs), and hence by inference similar detection limits [140]. For this comparison, the same pressure was used for both rf and d.c., the d.c. current was set at 70 mA (for a 7 mm anode) and the rf power adjusted (to 50 W) to give the same erosion rate as d.c. on a steel sample. This ensured the same numbers of atoms were entering the plasma in rf and d.c., and that the comparison between rf and d.c. was, therefore, of their emission characteristics. More recently, Wagatsuma studied argon the plasma in rf and d.c., and that the comparison give the same erosion rate as d.c. on a steel sample.

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especially likely when the excess energy, $\Delta E$, is small, perhaps 0.01 eV or 0.02 eV. For Cu II 224.70 nm and V II 265.565 nm emission, such transfer collisions with Ar lead to enhancements of at least 100 in intensity over values expected from an equilibrium plasma [152,153]. Similar enhancements might be expected for other lines and other plasma gases.

The subject of gas mixtures was reviewed recently by Wagatsuma, who probably has more experience in this area than any others currently working in GDOES [153]. Besides Ar/He and Ar/Ne, he also considered Ar/O$_2$, Ar/N$_2$, Ne/He, and N$_2$/He mixtures. The higher ionization potential of He (24.48 eV) compared with Ar (15.76 eV), for example, means that He offers more efficient excitation of higher-lying excited states in analyte atoms. But the lower relative mass of He means efficient excitation of higher-lying excited states in analyte atoms. But the lower relative mass of He means it is generally much less efficient at sputtering than Ar; hence the interest in gas mixtures to optimize both sputtering and sputtering. As we will see later, the low sputtering of a He plasma can be utilized for gas analysis.

Christopher et al. found, with conductive samples, that as He is added to an Ar plasma, the sputtering rate decreases, the electrical characteristics change (e.g. the d.c. bias voltage decreases), crater shapes change, and background signals increase [154]. The analyte intensities changed in a more complex way: at 1200 Pa of Ar, as He was added, the intensities increased significantly for Cu I 327.39 nm (3.82 eV), Co I 345.35 nm (4.02 eV) and Al I 396.15 nm (3.14 eV), increased slightly for Ni I 341.47 nm (3.66 eV), and decreased for Cr I 425.43 nm (2.91 eV), all atomic lines, where the energy of the excited state is shown in brackets [155]. Further work by Hartenstein, Christopher, and Marcus on both conductive and non-conductive samples suggests the main benefits of Ar/He mixtures may be improved crater shapes for some materials (e.g. metallic multilayers) and the enhanced emission of some ionic lines [e.g. Mg II 280 nm (4.42 eV)] [156]. Probably the most difficult element to analyze with GDOES is F. The most intense F line is at 685.60 nm with an upper excitation level of 14.50 eV, well above the metastable energies of Ar (11.5 eV to 11.7 eV). Here Wagatsuma, Hirokawa, and Yamashita recommended Ar/Ne, rather than Ar/He, where the Ne metastable energies are in the range 19.8 eV to 20.6 eV, compared with those of He in the range 16.6 eV to 16.7 eV [157].

4.1.2.4. Argon purity. Always a concern for the operator is the possibility of air entering the plasma past the O-ring seal. Contamination of the Ar plasma by air can have dramatic effects on the accuracy and reliability of GDOES analyses. It can increase signals for O, N, and C, affecting detection limits. It can introduce wide molecular bands that can overlap measured intensities for many elements, giving false readings [158]. It can alter the nature of the plasma, changing emission yields and sputtering rates. In an attempt to minimise this risk, Marcus introduced an Ar bath surrounding the sample, so that any leaks would be Ar rather than air [159].

Hubinois et al. have constructed a GD system inside a glove box to protect the operator and to allow the determinations of H, O, and N in U and Pu metals and oxides and nuclear waste glasses [160]. During the construction and early operation, they found the importance of maintaining Ar gas purity, anode cleanliness, and source window cleanliness. The glove-box was filled with Ar to minimise any air entering the plasma past the sample O-ring seal.

4.1.2.5. Effects of other gases. Small amounts (perhaps as little as 0.1% or less) of certain elements, notably H, N and O, in the Ar carrier gas can have significant effects on the GD plasma and measured intensities [161–163]. It does not appear to matter whether these elements are present as contaminants of the Ar carrier gas or enter the Ar plasma by being sputtered from the sample being analysed. Hodoroaba et al. have made extensive studies of the effects of H additions in d.c. and rf operation [164,165]. They showed that H, deliberately added to the Ar, can be used to improve the depth resolution for non-conductive coatings. Recently, Fernandez et al. studied the effects on stainless steel and glass samples of controlled amounts of these elements, from 0% to 10%, introduced as gases into the Ar carrier gas [166]. Intensities and emission yields changed in a complex way, but often the most dramatic change was in the range 0% to 1% (i.e. at levels commensurate with amounts sputtered from samples), rather than at the higher levels of deliberate Ar mixtures. Sputtering rates decreased, also most dramatically with additions of H$_2$, N$_2$, or O$_2$ in the range 0% to 1%. In contrast, the d.c. bias voltage was little changed in this range, but crater shapes became slightly more convex (deeper center) with more sloping sides [167]. Suitable mixtures of Ar/H$_2$ (e.g. 10% H$_2$) or Ar/O$_2$ (e.g. 1% O$_2$) had dramatic effects on depth profiles, mainly reducing sputtering rates and improving depth resolution of different layers on coated samples. The deliberate addition of such gases should also reduce the sensitivity of the plasma to sputtered amounts of these elements [165,168].

4.1.2.6. Sputter craters. One of the as-yet unfulfilled aims of GD source design is on-line measurement of crater depths. This would allow simultaneous estimates of sputtering rates and allow quantitative algorithms to avoid the normalization step where errors in one element can adversely affect both the calculated depths and the calculated compositions of all other elements. Hartenstein and Marcus took the first step towards this when they employed a laser confocal displacement sensor
(LCDS) to measure crater depths in situ in an rf GD source [169]. They found excellent agreement with external profilometer measurements, with an acceptable precision of 5%. Relying on the focusing of light, the device is restricted to depth resolutions of approximately 1 μm, adequate for thick coatings and for calibrations. The working distance of their device was only 28 mm, which meant the device was mounted on the source window, preventing intensity measurements. Clearly, a commercial version would require a much longer working distance and off-axis mounting.

Crater shape is critical to depth resolution and for measuring sputtering rates. Despite this, there is no agreement among glow discharge practitioners on how to describe crater shapes. When conditions are not too far from optimum, it is generally found that craters are either deeper at the edges or deeper at the center. Such shapes are called concave or convex, but depending on whether you look at the crater or at the hole, either one could be and has been described as concave or convex. This leads to confusion in the literature. To characterize the crater shape, Angeli et al. suggested the ratio of the depth at the crater edge to the depth at the crater center [170]. They described >1 as convex, and 1 ± 0.2 as nearly flat. But if we adopt the other convention, then when the ratio is >1 the crater is concave. Because of the difficulty of estimating a single value for the edge and center, more recently, Parker, Hartenstein, and Marcus suggested the ratio of the average of the central part of the crater to the depth of a flat crater having the same total volume (effectively, the average depth) [171]. When this ratio is >1, the crater shape is the opposite of that using the ratio of Angeli et al., yet another source of confusion. Until there is international agreement on these definitions, authors should be careful to define their terms adequately.

4.1.2.7. Sputtering rates. Parker, Hartenstein, and Marcus found that sputtering rates increased with pressure at constant applied power, levelling off at higher pressures [171]. From d.c. work, we expect that sputtering rates should not change significantly with pressure itself, but change because the ratio of current to voltage is changing as the pressure is varied at constant applied power. When pressure is increased, the current will increase and the voltage will decrease. Increasing current will tend to increase the sputtering rate, while decreasing voltage will tend to decrease the sputtering rate. Which one dominates depends on how close the voltage is to the threshold voltage for sputtering. The sputtering threshold voltage is lower in rf than in d.c. This means that increasing current is more likely to dominate in rf, and so sputtering rates will tend to increase. The situation is a little more complicated, because as pressure is increased the plasma resistance decreases. This means that the series load resistance seen by the matching box increases, and so the effective power increases [139], also tending to increase sputtering rates with increasing pressure.

Parker, Hartenstein, and Marcus found that sputtering rates for a non-conductive sample, Macor, decreased inversely to sample thickness [171]. Emission yields, however, remained nearly constant [172]. They found Ar I 404.442 nm intensities tended to show the same behaviour as the sputtering rates and suggested this Ar line could be used as an internal standard to correct for changes in sputtering rate. Alternatively, the constancy of emission yields suggests current, voltage, and power are all decreasing with increased sample thickness. The constancy of emission yields, therefore, means the algorithm for compositional depth profiling could be used, as this adjusts automatically, through composition normalization, for changes in sputtering rate.

4.1.3. Analytical characteristics

4.1.3.1. Emission yields. Perez et al. compared Ar I intensities between rf and d.c., finding that intensities were higher in rf for lines with excitation energies > 15.3 eV [173], suggesting that rf may be more efficient for high-level excitation of difficult-to-excite elements such as F and Cl. Indeed, Rodriguez, Pereiro, and Sanz-Medel found high sensitivity for Cl with rf [174]. Perez et al. also found that Ar II lines were not enhanced in rf over d.c., but Analyte atomic emission was characterized by higher emission yields in rf [173].

4.1.3.2. Self-absorption. The design of the GD source is ideal for promoting self-absorption. This is because the intense negative glow region located near the sample surface cools rapidly in the direction of the observation window. Indeed, self-absorption and self-reversal have been observed for strongly self-absorbing lines, even for analytes with elemental mass fractions in the solid sample as small as 3% [175]. Trace and minor element components are little affected. Sighting the spectrometer side-on to the negative glow would minimize this problem, but necessitate other complexities in source and optics design. For example, the size of the negative glow varies with the plasma conditions and sample type, and so the instrument design would have to accommodate this. Further, the position of the negative glow would shift across the entrance slit of the spectrometer as the crater depth grows during sputtering. The problem of self-absorption can be alleviated somewhat by reducing sputtering rates, but the best solution where possible is to choose non-resonance lines. This is not always possible or convenient, so appropriate non-linear calibration curves must be used when significant self-absorption is present [155,176].

4.1.3.3. Detection limits. In assessing the performance of rf, and in comparisons between rf and d.c. operation,
Some of this confusion has arisen because of differences in design between instruments in different laboratories, between different operating conditions used, and differences in sample selection. Some of the confusion has also arisen because there is no international standard for determining detection limits in GDOES, and different laboratories have calculated detection limits with different methodologies. Cho et al. have reported differences in detection limits have played a key but confusing role. Some of this confusion has arisen because there is no international standard for determining detection limits in GDOES, and different laboratories have calculated detection limits with different methodologies. Cho et al. have reported differences between different operating conditions used, and differences in design between instruments in different laboratories, some of which have arisen because there is no international standard for determining detection limits in GDOES, and different laboratories have calculated detection limits with different methodologies. Cho et al. have reported differences between laboratories using either the calibration curve SNR method or the SBR-RSDB method [112]. Boumans had warned about this problem [177]. The detection limit \( c_L \) in the SNR method is given by:

\[
c_L = \frac{k \, s_B}{x_A/c_0},
\]

where \( k \) is a constant, \( s_B \) is the standard deviation of the background signal, and \( x_A/c_0 \) is the sensitivity (i.e. the slope of the calibration curve of intensity vs. composition), where \( x_A \) is the net analyte signal (i.e. the signal above background) and \( c_0 \) is the mass fraction of the element in the sample. For uniformity, it is recommended that \( k = 3 \). The SBR-RSDB method is given by:

\[
c_L = \frac{k \times 0.01 \times \text{RSDB}\% \times c_0}{\text{SBR}},
\]

where \( \text{RSDB}\% \) is the relative standard deviation of the background (as %) and \( \text{SBR} \) is the signal-to-background ratio. It is easy to show that these two equations are the same mathematically. They should, therefore, lead to identical results. However, Cho et al. have noted that detection limits reported with the SNR method are often about a factor of 10 higher than those with the SBR-RSDB method [112]. It is interesting then to investigate why this difference in published values should exist.

There are three reasons apparent in the literature:

i. some authors have used a value for \( k \) other than 3;
ii. for signal, some have used the measured intensity at a particular wavelength, rather than the net intensity above background; and
iii. often too few points have been used to estimate \( s_B \) and RSDB\%, leading to over or under estimates that greatly affect the estimate of \( c_L \). The effect of using total intensity rather than net intensity is illustrated in Table 2. In this calculation, when total intensities are used with the SBR-RSDB method, detection limits vary with sample composition.

| \( c_0 \) (mg kg\(^{-1}\)) | \( c_L \) (mg kg\(^{-1}\)) |
|-----------------|-----------------|-----------------|-----------------|
| 100             | 3               | 3               | 2               |
| 30              | 3               | 3               | 1               |
| 10              | 3               | 3               | 0.5             |
| 3               | 3               | 3               | 0.2             |

Estimates of standard deviations based on the small number of measurements (\( \leq 10 \)) commonly employed in optical emission spectrometries (OES) are often unreliable. Empirically, it is found in OES that typical values for RSDB\% are approximately 2%. Values much higher or much lower than this may indicate inadequate statistics, or spectral interference in the background region chosen, or a problem with the instrument. For \( k = 3 \), the approximation that RSDB\% \( \approx 2\% \) leads to:

\[
c_L = 0.06 \times \text{BEC},
\]

where BEC is the background equivalent concentration given by the absolute value where the calibration curve crosses the composition axis. Typical values for BEC in the rf-GDOES analysis of steels and Zn/Al alloys are 20 mg kg\(^{-1}\) to 300 mg kg\(^{-1}\) [140], giving expected detection limits of 1 mg kg\(^{-1}\) to 18 mg kg\(^{-1}\). Being an intercept near the origin, there will often be a very large uncertainty in such BEC values, leading to very large uncertainties in estimates of detection limits, unless there are a sufficient number of points at low compositions in the calibration and the regression is properly weighted [155]. Estimates of detection limits should, therefore, be accompanied by estimates of uncertainty. For example, if we assume RSDB\% = 2% without uncertainty and use Eq. (1), the relative uncertainty in \( c_L \) will equal the relative uncertainty in BEC. Payling, Jones, and Gower found uncertainties in BEC were often 50% or more, at 95% confidence [140].

4.1.3.4. Optical interference. When thin transparent films are analysed with GDOES, an optical interference disturbs the measured intensities. An example is shown in Fig. 15, recorded with 50 W applied power and a pressure of 650 Pa [178]. The disturbance varies approximately sinusoidally in time as the film is sputtered. The
periodicity of the disturbance (beats) varies with the wavelength of the elemental line being measured, so that lines of shorter wavelength, such as P I 178.287 nm, as shown, vary more quickly than lines with longer wavelength, such as Si I 288.158 nm or Ar I 404.442 nm. Some lines, notably H I 121.567 nm and O I 130.217 nm, do not show the disturbance. The first to discover and then explain this phenomenon were Kimura and Mitsui, though they were late in publishing [179]. They were studying transparent borophosphosilicate glass (BPSG) films on Si wafers, similar to the one shown in Fig. 15. They decided the beats were caused by the difference in optical path length for reflections from the crater bottom and from the interface between the transparent film and substrate, the difference decreasing steadily during sputtering. No interference was seen at 122 nm and 130 nm because the BPSG film is not transparent at these short wavelengths. A correction algorithm is easily incorporated in software to remove the artefact [180]. The phenomenon has been explored in detail by Hoffmann and co-workers, who studied various oxide films, including SiO₂, TiO₂, and BaTiO₃ deposited on Si. They found that the phenomenon could be used either to determine layer thicknesses ≥ 100 nm with a precision better than 1% or to determine the refractive index of the film [84,181]. They were concerned that variations in surface reflectivity, of which transparent layers are just an extreme example, could affect quantitative GDOES methods of other materials by varying intensities in as yet unpredictable ways.

4.1.3.5. Analytical performance. Shimizu et al. have developed techniques for making nearly perfect oxide films. These films are anodic alumina on electropolished aluminum. They can be made to have different thicknesses, typically 360 nm, and flat to within 2 nm over microscopically large areas [182]. They can be doped with various delta-function layers, such as 2 nm thick Cr. These samples are ideal for GDOES analysis and for testing the limits of the GDOES technique. They found GDOES depth profiles of their 360 nm thick oxide films, at optimum conditions, had a sputtering rate of 28 nm s⁻¹ and were reproducible in thickness to within 1% and intensities to within 3% [183]. By monitoring the transition from aluminum oxide to aluminum metal for various oxide thicknesses and by moving the position of the Cr delta-function layer in the oxide films, they found they could achieve a depth resolution in the first 25 nm of ~1.3 nm. This value is close to the theoretical limit of 1 nm for low-energy Ar sputtering, due to atomic mixing [184,185]. Beyond 25 nm the depth resolution was determined by variations in sputtering rate across the crater (i.e. by crater shape). For a 4-mm diameter crater, they found the sputtering rate for the inner 3.2 mm diameter was uniform to within 1%, but beyond this the outer ring had a 6% higher sputtering rate. Though small in width (0.4 mm), this outer ring accounted for 36% of the crater area and was responsible for the degradation in depth resolution, increasing the depth resolution from 1.3 nm at 25 nm to 7 nm at 360 nm depth. Despite this, the rf-GDOES results were comparable to or better than those achievable with SIMS, without the charging problems of SIMS and with much higher sputtering rates [186].

By controlling the degree of surface roughness on the anodic oxide films, Shimizu et al. were able to demon-
Fig. 16. Development of crater shape over time, in a thick borophosphosilicate (BPSG) film on Si. (Fig. 5 in Ref. [179]; reproduced with kind permission of the author and the publisher.)

strate the deterioration in depth resolution caused by rough surfaces [187]. TEM (transmission electron microscopy) photographs of cross-sections of the surface before and after sputtering showed that the ridges sputtered more quickly than the valleys (because of enhanced rf fields at the ridges), slowly smoothing the surface during sputtering. When the original surface roughness was comparable to the film thickness, then almost total degradation of the depth resolution resulted [182].

4.1.4. Methods

4.1.4.1. Deconvolution. Beyond the immediate surface, the depth resolution in GDOES is largely determined by the crater shape. Observed CDPs are, therefore a convolution of the ‘true’ depth profile (i.e. the original in-depth compositions in the unsputtered sample), and the effect of crater shape. Evidence suggests that the form of the crater does not change greatly with depth in homogeneous materials, but simply grows with increasing depth (see, for example, Fig. 16 from a recent publication for a thick BPSG film [179]). For the same plasma conditions, however, the crater shape can vary significantly between different materials, determined largely by the electrical behaviour of the material surface in the plasma. These two variations with depth (i.e. a growing crater form and variations in shape from layer-to-layer), make deconvoluting the depth profile to remove the effects of crater shape quite difficult mathematically. Deconvolution routines normally assume a constant shape in the convoluting function. Prassler and his coworkers addressed these difficulties by assuming a time-invariant ion current density distribution function across the crater [188,189]. They then successfully applied an iterative deconvolution algorithm to the depth profile from a multilayer Cu/CrNi on Si sample to obtain a dramatic improvement in depth resolution (see Fig. 17). Their success makes deconvolution a real and exciting possibility for GDOES. The iteration uses information on the final crater shape to estimate the initial guess at the ion current density distribution; this is then refined during each iteration. Their calculated crater shape then shows the expected growth of the crater form. The algorithm, as described, requires a full two-dimensional scan of the final crater as input. This data input could be simplified by parameterizing the crater shape (e.g. inputting simply the depth and the ratio of center to edge), allowing the operator more flexibility in choosing the initial shape. This would also

Fig. 17. Composition depth profile of 100 nm thick Cu/CrNi multilayers on Si: (a) after deconvolution with a constant crater shape (the result being little changed from the unconvoluted profile); (b) after deconvolution with iteration to determine the uneven crater shape. (Fig. 8 in Ref. [188]; reproduced with kind permission of the authors and the publisher, Springer-Verlag.)
make deconvolution available to those without computerized profilometers.

4.1.4.2. Quantification. The similarities in emission characteristics between rf and d.c. plasmas mean that any quantitative schemes developed for one could be adopted for the other, the difference lying in the choice of control parameters rather than in concepts [136,140,190]. The principle reason for different control parameters is that voltage and current mean different things in d.c. and rf. In d.c., the voltage is the time-invariant potential difference between the two electrodes, and since most of this potential drops across the cathode dark space, it is approximately the time-invariant cathode fall voltage. In rf, the applied voltage is time-varying with a time-invariant amplitude, \( V_{\text{HF}} \), and a time-invariant offset \( V_{\text{DC}} \), the d.c. bias voltage. Because of the asymmetric design of the source, \( V_{\text{HF}} \approx V_{\text{DC}} \). As in the d.c. case, most of the d.c. bias voltage drops across the sheath adjacent to the sample surface, and \( V_{\text{DC}} \) can be taken as an rf analogue to the d.c. voltage. In d.c., the current is the net electron current between the electrodes. It is assumed that the net current is proportional to the total electron current. In rf, because of the blocking capacitor, the net current is zero. This is why rf works for both conductive and non-conductive samples, since, unlike the d.c. case, no net current has to flow through the sample. But during each cycle there are particle currents (electrons and ions) flowing in the plasma. The rf plasma power is the sum, over one cycle, of the product of the instantaneous applied voltage (without the d.c. offset) and the instantaneous total particle current. At the sample surface, the voltage is negative for much of the rf cycle and positive for only a small part of the cycle. During the large negative part of the cycle the instantaneous total current is mostly ion current, while during the short positive part of the cycle it is mostly electron current. The power is therefore dominated by ion current, and indeed rf power could be considered as the product of \( V_{\text{DC}} \) (or \( V_{\text{HF}} \)) and the average ion current. Since, in rf, there is no net current, the average ion current equals the average electron current, hence the average ion current is the analogue of d.c. current. Unfortunately, at present there is no routine way to monitor average ion current, hence power is commonly used in place of current. If \( V_{\text{DC}} \) (or \( V_{\text{HF}} \)) and plasma power are both kept constant, then the average ion current will be approximately constant. Alternatively, if the plasma power is kept constant and \( V_{\text{DC}} \) (or \( V_{\text{HF}} \)) increases then the average ion current will decrease in proportion.

In algorithms for compositional depth profiling, and indeed for some bulk analyses, sample compositions are multiplied by the sputtering rate to give elemental sputtering rates [191]. These elemental sputtering rates are proportional to the number of atoms of each element entering the plasma. Rather than such ‘absolute’ sputtering rates, it is also possible to use relative sputtering rates, ratioing all absolute sputtering rates to the sputtering rate of a reference sample [192]. The advantages of relative rates will be discussed below. If there are no changes in emission yield, then measured intensities will vary linearly with the relative elemental sputtering rates. The instantaneous sputtering rate of any sample can then be calculated easily by converting measured intensities into relative elemental sputtering rates, summing these, and multiplying by the absolute sputtering rate of the reference sample. Compositions are then determined by dividing the elemental sputtering rates by the instantaneous sputtering rate. Sputtered depths are estimated by dividing the instantaneous sputtering rates at each point in the depth profile by the calculated density at each point and summing from time zero.

Unfortunately emission yields do not remain constant. For any set of control parameters, changes in the sample matrix, either from changing the sample or from different layers in the sample, cause changes in the plasma and optical spectrum that affect emission yields [193]. Corrections are then introduced to account for these changes so that, in effect, an emission yield is determined as if these changes were not present. Note: these do not include sputtering rate changes, which are already included in the elemental sputtering rates.

4.1.4.3. Corrections. Corrections are conveniently divided into additive and multiplicative corrections. Some authors refer to the latter as matrix corrections. In additive corrections, a number is added to the intensity and in multiplicative corrections the intensity is multiplied by a number. In GDOES, additive corrections are mostly due to spectral interferences, and multiplicative corrections are mostly due to changes in the plasma, though sample reflectivity, if it becomes a necessary parameter in the future, would be a multiplicative correction. Other than self-absorption, multiplicative corrections can generally be treated as a perturbation of the form \( \left\{ 1 + r_i(p-p_b) \right\} \), where \( r_i \) and \( p_b \) are constants—though \( r_i \) may vary with the element \( i \) or wavelength \( \lambda \) and \( p \) is the parameter that is varying [136]. From d.c. work, multiplicative corrections are available to account for the effects of changes in current, voltage, or pressure, and the effects of H [163,193]. Multiplicative corrections may also be necessary for O and N. Self-absorption is usually treated as a polynomial or exponential expansion of intensity [155,176,194].

4.1.4.4. Relative sputtering rates. Relative sputtering rates are often used in calibration and analysis, rather than absolute sputtering rates, because relative sputtering rates are much less sensitive to changes in the GD plasma and differences between instruments. They are, for example, nearly constant with changes in applied rf
power or pressure [192]. They should therefore be similar for different source control modes (see, for example, Fig. 18, using data from Perez et al. [148]). They should also be similar between rf and d.c. (see Fig. 19, using data from Pisonero et al. [150]), at least within the rather large uncertainties in measured relative sputtering rates that currently exist. Work by Marshall et al. suggests absolute sputtering rates per effective watt in the plasma may also be the same in rf and d.c. [151].

These uncertainties in relative sputtering rates are the largest source of error in GDOES analysis. Several ways to deal with this problem are being considered. Much of the variation may be due to the lack of a standard describing how best to measure them. An interlaboratory test on relative sputtering rates is currently underway within the European GD community [195]. It is hoped that this study will identify how much variation occurs between laboratories, as well as the parameters responsible for the variations, so that uncertainties can be reduced and reliable measured values for relative sputtering rates can be shared among laboratories. One way forward may be ‘sputter factors’, i.e. relative sputtering rates determined directly from calibration curves [136,196]. Another approach is to calculate relative sputtering rates from semi-empirical theory, where relative sputtering rates are based on sample composition. Fig. 20 shows calculated sputtering rates for Cu–Zn alloys using this approach compared with the data from Winchester [197].

4.1.4.5. Density. Another source of uncertainty in sputtered depth in CDP analysis is the calculated density at each point in the depth profile, especially when strong covalent bonds are present, as in oxides and nitrides. Payling, Michler, and Aeberhard have presented an improved means for calculating densities when such compounds are present [193]. A table of oxide and nitride densities is used to calculate the fraction of the density due to these compounds, and the remainder is calculated in the usual manner by assuming constant atomic volumes.

4.1.5. Recent applications of rf-GDOES


![Fig. 18. Comparison of relative sputtering rates (RSRs) measured in rf with two different operating modes, for a wide range of metals and metal alloys. Data from Perez et al. [148].](image1)

![Fig. 19. Comparison of relative sputtering rates (RSRs) measured in rf and d.c., for a wide range of metals and metal alloys. Data from Pisonero et al. [150].](image2)

![Fig. 20. Sputtering rates (SRs) for Cu–Zn alloys, calculated with the approach of Payling et al. [192], including 95% confidence limits, and compared with data from Winchester [197].](image3)
4.1.5.1. Bulk analysis. Hartenstein and Marcus studied the analysis of low levels of gaseous elements (N, O, and H) in solids [198]. They found that care was needed in the construction of the vacuum and gas-handling systems in order to avoid air leaks, that 99.999% pure argon was insufficient, necessitating additional purification, and that care was needed in changing samples to minimize air ingress into the source. They achieved detection limits for N in iron of between 2 mg kg\(^{-1}\) to minimize air ingress into the source. They achieved detection limits and R.S.D.s -y\(^1\) comparable to or better than other analytical techniques (including Al, Mg, Cu, Fe, and Sr).

Glow discharge methods also show promise for applications related to health care. For example, in an exploratory study, Martinez et al. investigated the rf-GDOES spectra obtained from bone using several different means for preparing the samples [202]. A procedure is already well established in clinical laboratories to encapsulate thin slivers of bone (0.5 mm to 1 mm thick) in poly(methylmethacrylate) and paste them to a flat support. The procedure is used to reduce the amount of a patient’s bone required for analysis. This method proved to be the best for rf-GDOES, as well. At typical rf GD conditions, 35 W and 800 Pa, Martinez et al. found intense lines for Ca, Na, Mg, P, and C, and concluded that rf-GDOES could be suitable for biological and medical studies, such as determining P/C or Ca/C ratios for the diagnosis of osteoporosis.

In another study, Luaiswong and Marcus successfully fused coal ash powder with lithium compounds for rf-GDOES analysis [203]. Coal ash is a difficult material to analyze with competing solid sampling techniques. Their preparation method is suitable for other oxide-powder specimen types. Davis et al. also successfully dispersed either coal ash or cement in acid-catalyzed sol–gel films for rf-GDOES analysis [204].

Baude et al. have reviewed the possibilities for GDS in the analysis of environmental samples [205]. Samples considered included powders from soils, rocks, and sediments after mill-grinding, animal and plant tissues, liquids, and gases. One of the drawbacks for GDS in...

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<th>Type of analysis</th>
<th>Material</th>
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<td>Bulk</td>
<td>Iron and steel</td>
<td>[112,198,199]</td>
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<td></td>
<td>Cu–Zn alloys</td>
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<td></td>
<td>Glass and ceramics</td>
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<td>Coal ash</td>
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<td>Depth profiling</td>
<td>Surfaces</td>
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<td>Hard coatings</td>
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<td>Oxides, nitrides and oxynitrides</td>
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<td>Electrodeposited Ni–P</td>
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<td>Prosthetic implants</td>
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<td>Polymer coatings</td>
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<td>Glass/ceramics films</td>
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<td>Speciation</td>
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<td>Gases</td>
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<td>Fish tissue</td>
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these areas is the lack of suitable certified reference materials (CRMs) for calibration. The review indicates that various rf- and d.c.-GDOES studies have been published in all these areas of environmental analysis. However, competition is strong, since this is an area where many analytical techniques are applicable [e.g., ICP-OES and -MS, with or without laser ablation, ETV (electrothermal vaporisation), graphite furnace AAS, and XRF (X-ray fluorescence)].

Finally, some limited work has been directed towards the analysis of liquid samples. Low-pressure GDs are not very tolerant to the introduction of liquid aerosols, so Rodriguez, Periero, and Sanz-Medel developed a technique by which chloride in solution is first converted to volatile chlorine, extracted as a gas through a membrane using He as the carrier gas, and injected into a He rf-GD [174]. The selectivity of OES allows such a technique to distinguish the halogens, Cl, Br, and I, indistinguishable in conventional titration methods.

4.1.5.2. Depth profiling. ‘True’ surface techniques are capable of analyzing the outer atomic layer (<1 nm) of a solid. The work of Shimizu et al. is approaching this limit for rf-GDOES. They have analyzed a ~4-nm thick surface film on electropolished, high-purity, alumina, as predicted by the Gibbs free energy following either electropolishing, etching, pickling, or detect it. Next, Mato et al. considered a Ta–Cu alloy to surface technique, including SIMS, had been able to air after electropolishing. This enrichment of Cu had Cu-enrichment resulting from exposure of the aluminum (these areas is the lack of suitable certified reference coatings, with particular reference to depth resolution and interface studies, and the determination of Fe in Zn–Fe coated steel. Passetemps has reported work on the carburizing and carbonitriding of steel surfaces, obtaining excellent visual agreement between rf-GDOES depth profiles and SEM cross-sectional images [207].

In a related area, Payling and co-workers have provided several papers on the analysis of typical hard coatings, such as TiN and TiCN, and slip coatings, such as MoS2, produced either by chemical vapor deposition (CVD) or physical vapor deposition (PVD) [193,207,211,215]. An important part of this work is the use of V[DH], H corrections, and improved density calculations. The inclusion of a H correction, for example, is necessary to obtain stoichiometric analysis in CVD coatings. These coatings often contain significant amounts of H from furnace gases. Mitsuo and Aizawa monitored Cl distributions in a TiN hard coating with rf-GDOES [216]. The Cl reduces friction and wear. The measured Cl depth profiles, confirmed by TEM, peaked between 40 nm and 90 nm, depending on the preparation conditions, and extended to depths of 200 nm.

Dreer compared the analytical figures of merit of a variety of analytical techniques for the bulk analysis of silicon/aluminum oxynitride thin films [217]. The study found major problems in the accurate evaluation of O in these films with rf-GDOES, indicating that substantial improvements are needed, if the advantages of rf-GDOES (e.g. high speed and low cost) are to attract users. Hodoroaba et al. compared rf-GDOES with hfm-SNMS (high frequency mode secondary neutral mass spectrometry) for the evaluation of various SiO2/TiO2 and Si3N4/SiO2 multilayers on glass substrates [108]. Both techniques were successful in resolving the layers, with SNMS having better depth resolution, but being very much slower. Suchaneck et al. studied lead zirconate–titanate (PZT) thin films, using RBS (Rutherford backscattering spectrometry) to characterize calibration materials for rf-GDOES [218]. Marcus and Schwartz also studied PZT thin films, produced by sol–gel techni ques [219]. They were able to distinguish differences in pyrolysis conditions based on the rf-GDOES depth profiles for C, H, and O. Dorka, Kunze, and Hoffmann used the optical interference effect, mentioned earlier, to determine the thickness or refractive index of SiO2 films on silicon wafers [181]. The thicknesses of 1965 nm films were determined with an uncertainty (1 S.D.) of 5 nm and a 95% confidence interval of 15 nm, with the uncertainty arising from variations in film thickness rather than from the rf-GDOES measurement. Rother compared alumina coatings deposited on high-speed steel by reactive d.c. magnetron sputtering with rf-GDOES to verify the uniformity of the coatings [220].

Anodic films have become a major area of interest for rf-GDOES analysis. Shimizu et al. have studied the impurity distributions (electrolyte anions) in various
barrier anodic films on aluminum, including those formed in sodium tungstate, sodium molybdate, and sodium chromate solutions [221]. The rf-GDOES results agreed well with high resolution TEM photographs and were superior to SIMS results with these films. Shimizu et al. also studied thick, porous, alumina films with controlled distributions of coloring species (Cu and Ni) in the inner 1 μm of the film next to the Al substrate [222]. Despite some variations in thickness of the coloring material, rf-GDOES showed the distributions, with widths close to calculated values and with a depth resolution of approximately 100 nm, superior to results obtained with EPMA (electron probe microanalysis). Using rf-GDOES depth profiles of the distributions of sulfate ions in amorphous anodic aluminum films, compared with a boron species marker, Shimizu et al. were able to determine the inward migration rate of SO2 ions relative to O2 ions through the films [223]. They then studied the generation of oxygen gas bubbles a few nanometers in size in the subsurface of anodic aluminum [224]. Details in the rf-GDOES depth profiles provided key evidence for a complex model involving the oxidation of migrating O2 ions, as well as the role played by metal ion impurities (Cr3+ and W6+). In Al-0.2%Mg alloys, rf-GDOES shows incorporation of Mg in the residual alumina film and the absence of Fe and Si trace impurities, as well as enrichment of Cu at the alloy/film interface [225]. Habazaki et al. and Mato et al. have extended the rf-GDOES study of anodic films to titanium alloys [226,227], NbN, alloys [228], and Mg-Ta alloys [229]. Anodic films on aluminum have also been studied by Snoogan et al., where rf-GDOES was used to monitor the S distribution in the film formed by sulfuric acid [230].

In other research, Campestrini et al. have studied chromate conversion coatings on Al with a variety of techniques, including rf-GDOES [231,232]. Spectroscopic ellipsometry, SEM cross-sections, and rf-GDOES all gave similar film thicknesses. Nordlien et al. studied newer zirconium–titantium based conversion layers on Al, also with a variety of techniques, including rf-GDOES [233].

Shimizu et al. used rf-GDOES to study a Ni–P alloy film, approximately 0.5 μm thick, electrodeposited on Cu [234]. The depth profiles showed compositional variations in Ni and P, with the peaks in P corresponding to amorphous regions revealed by cross-sectional TEM.

In research pertinent to health care issues, Hartenstein, Compton, and Marcus used rf-GDOES to study the N depth distributions for nitried, wrought, Co–Cr–Mo alloys used for the production of prosthetic implant hip joints. They found differences in N distributions in the first 15 μm related to nitriding time [235].

A particularly interesting application area for rf glow discharge methods is the analysis of polymeric materials. In his review of direct polymer analysis by GDS, Marcus showed two rf-GDOES depth profiles of thick, pigmented and clear polymer coatings used in the automotive industry [15]. Similarly, Fernandez et al. have analyzed painted galvanneal sheets used for car bodies [236]. The very different electrical characteristics of the external pigmented polymer layers and the inner galvanneal Zn–Fe coating posed a special challenge in optimizing depth resolution. Also, operating at constant pressure and applied power, they successfully included Ar intensities as an internal standard to correct for changes in emission yield between the very different materials. An Ar I and several Ar II lines in the range 389.0 nm to 400.0 nm were found to be suitable. Passepetemps and Payling have obtained CDPs of electroplated Cd layers, using specially prepared in-house reference samples for calibration [207]. Xhoffer and Dillen have discussed rf-GDOES applications in the steel industry, including organic paint systems on galvanized steel sheet [237].

Finally, Rother and Mucha reported the rf-GDOES depth profiles of two graded glass/ceramic (SiO2 and Al2O3) protective coatings on light metal car wheels [238]. Jardin, Bourgeois, and Crener have examined various coatings on glass substrates, such as SiO2/TiO2 multilayers on borosilicate glass [207]. They described in detail the difficulties in analyzing these materials with rf-GDOES, including their propensity to shatter under mechanical and thermal stress and their hygroscopic nature.

4.1.5.3. Speciation. While rf-GDOES is most widely used for the direct elemental analysis of solids, it also offers possibilities as an element-specific detector in speciation analysis [241]. Centineo et al. investigated the capabilities of rf-GDOES for the analysis of gases, where rf may have an advantage over d.c. [239]. They introduced volatile organic compounds (containing C, Br, Cl, or S) into a He plasma through the side of the anode tube. They found linear responses over four orders of magnitude, with good precision and accuracy, and higher sensitivities than provided by other techniques, including microwave induced plasma OES (MIP-OES) and inductively coupled plasma OES (ICP-OES). Their comparison of detection limits with MIP-OES [242], ICP-OES [243], d.c.-GDOES [244], and capacitively coupled microwave plasma (CMP) OES [245] is shown in Table 4.

Continuing this work, Oreallana-Velado, Pereiro, and Sanz-Medel combined capillary gas chromatography with a He rf-GD for Hg speciation [240]. The Hg was removed from solution after derivatization with a Griegard reagent. The Hg was then transported to the GD with He flowing at 2.3 ml min−1. They used the technique to determine methylmercury in fish tissue. They found detection limits and accuracies similar to competing techniques. Advantages for their system
inherent analytical qualities. In addition to the capability of analyzing solids directly in the solid state, these inherent qualities include excellent sensitivities and detection limits, reasonable accuracies and precisions, wide elemental coverage, and relative lack of matrix effects and interferences compared to most other direct solids analytical techniques. Moreover, variation of analytical sensitivities across a wide range of elements within a given matrix generally does not significantly exceed one order of magnitude [4,246–248].

Rf-GDMS is characterized by the same analytical qualities as its d.c. counterpart. Additionally, it is directly applicable to electrically insulating sample materials, as noted before. Even with such considerable analytical potential, rf-GDMS has not yet been used widely for real world applications. In part, this is due to the fact that some important technical challenges remain to be solved. Also, commercially available rf-GDMS instruments and relevant documentary standards do not yet exist.

Before proceeding with an in depth discussion of rf-GDMS, it should be mentioned here that d.c.-GDMS can in fact be applied to the analysis of non-conductive solid materials in at least two well-known ways. First, insulating powder samples can be thoroughly mixed with electrically conductive host powders (e.g. high-purity graphite, Cu, Ag, or Ta), and the resulting mixture can be formed into a rigid solid under high pressure [e.g. 4,205,249–254]. While this approach can be useful, it is prone to sample contamination associated with the host matrix material. Also, pressing of powders often incorporates gases and water into the solid that is produced, serving as an additional source of unwanted contamination in the glow discharge. Another unfortunate characteristic of this approach is that sample components are necessarily diluted, usually by a factor of at least 5, resulting in a potential loss of analytical signal. Finally, it is often difficult to achieve uniform mixing of the sample and host matrix components prior to pressing, and so analytical precision can be poor. One potential advantage of this approach is that the use of the host matrix material inherently provides an internal standard element of known mass fraction in the pressed solid (i.e. the host matrix itself, provided that it is not also present in the unknown sample in significant amounts).

The second approach to analyzing insulating solids with d.c.-GDMS is the secondary (or sacrificial) cathode technique [e.g. 13,252,255–264]. An electrically conductive mask containing a hole (i.e. the secondary cathode) is placed over the surface of the insulating sample. Part of the material sputtered from the secondary cathode deposits onto the insulating surface, creating a thin surface layer. Because this layer is electrically conductive, it is then sputtered in the d.c. discharge, resulting in the incidental sputtering of the sample surface underneath. The conductivity of the deposited surface layer also prevents charge build-up on the non-conductive sample. The secondary cathode material must
be carefully chosen. A key factor is purity relative to the expected composition of the unknown samples. This is because ion intensities originating from the secondary cathode material can often be at least 4 times more intense than even the matrix ion intensities originating from the non-conductive sample [265]. Also, it is helpful to use a material that sputters rapidly enough to provide the necessary surface layer, but slowly enough to prevent that surface layer from becoming too thick. Tantalum is often selected. Judicious choice of discharge conditions is also limited and critical to the success of the analysis. One advantage of the secondary cathode approach compared to rf-GDMS is that the thickness and shape of the unknown insulating sample are much less important. As we shall see later, analytical signals from non-conductive solids sputtered in rf-GDMS instruments can depend dramatically on these geometric factors.

4.2.1. Instrumentation

Proliferation of GDMS in the d.c. mode has been facilitated by the availability of several commercial instruments over the years. Dedicated instruments have included the VG GloQuad quadrupole mass spectrometer and the VG 9000 double-focusing instrument (Thermo Elemental, Cambridge, United Kingdom), as well as the glow discharge version of the Concept double-focusing mass spectrometer (Kratos, Ramsey, New Jersey, USA). Direct current glow discharge devices have also been sold as accessories for instruments that were designed principally as inductively coupled plasma (ICP) mass spectrometers. Such instruments have included the TS SOLA quadrupole instrument and the Element double-focusing mass spectrometer (both Finnigan MAT, Bremen, Germany).

Unfortunately, no commercial rf-GDMS instruments have ever been available. This partially explains why rf-GDMS has not been nearly as well developed or widely used for real-world applications, despite the potential utility. In the absence of commercial rf-GDMS instruments, researchers and practitioners have been forced to design and build their own instruments. Some have chosen to interchange an rf glow discharge device with the ionization source that came with a commercial mass spectrometer that was obtained for some other purpose. Others have built their rf-GDMS instruments from scratch using original equipment manufacturers (OEM) mass spectrometer components. Either way, the rf glow discharge ionization source must be custom designed and built, since no such analytical devices are commercially available.

Rf glow discharge devices have been coupled to several different types of mass spectrometer. These include single [e.g. [10,56,251,266–268], double [57], and triple [269] quadrupoles, double-focusing instruments [265,270,271], time-of-flight (TOF) mass spectrometers [272], Fourier transform ion cyclotron resonance (FT-ICR) instruments [62], and ion traps [60]. Quadrupole mass spectrometers offer the advantages of relatively low cost, as well as relatively rapid $m/z$ (mass-to-charge ratio) scanning and selective peak hopping capabilities. Unfortunately, they provide only unit mass resolution, and are, therefore incapable of resolving many isobaric interferences. Double and triple quadrupoles are sometimes used in attempts to reduce isobaric interferences through collision-induced dissociation (CID), also known as collisionally-activated dissociation (CAD) [57,273]. Detection limits (DLs) for instruments based upon quadrupole mass filters are generally in the sub- to low microgram per gram range. Double-focusing instruments are significantly more expensive than quadrupoles and have relatively slow scanning and no true peak hopping capabilities. However, they provide good spectral resolution, with mass resolving powers approaching 10 000. As a result, many isobaric interferences commonly encountered in rf-GDMS can be resolved. DLs are typically in the sub- to low nanogram per gram range. TOF mass spectrometers offer true simultaneous sampling of ions of different $m/z$, making them especially suitable for coupling to pulsed glow discharge sources [274–277] or for depth profiling applications [276,278,279]. These instruments have not yet been used much for analytical rf-GDMS, but are likely to become more important as pulsed rf glow discharge sources and depth profiling develop further. Finally, FT-ICR and ion trap instruments are not likely to be used for routine rf-GDMS analytical applications, but have found utility for more fundamental studies [60,62]. In a general sense, a noteworthy advantage of FT-ICR and ion trap instruments is that the accessible $m/z$ range is inherently limitless. Moreover, FT-ICR mass spectrometers provide the highest of all spectral resolving powers, with values approaching $2 \times 10^6$.

4.2.1.1. Source design. Both d.c.- and rf-GDMS are applicable to pin and flat samples. It is also possible to analyze oddly shaped samples [e.g. [15]] and thermally unstable samples [e.g. [12]] with custom sample holders. Pin samples are typically introduced into the glow discharge cell by means of a direct insertion probe (DIP). One example of an rf-powered DIP is depicted in Fig. 21a [61]. Rf power is delivered from the rf power source, usually the combination of an rf generator and matching network, to the electrically conductive or non-conductive sample by means of the RG-213 coaxial cable. Though it may be difficult to see in the figure, this cable actually extends all the way from the HN connector, which is attached to the matching network output, through the probe body to the electrical feedthrough at the sample end of the DIP. The outer covering and shielding of the RG-213 cable was removed from the section corresponding to the stainless steel probe
Fig. 21. (a) Direct insertion probe (DIP) designed for rf-GDMS. (b) Rf glow discharge cell, adjustable bellows assembly, and vacuum interlock used in conjunction with the DIP. See text for further explanation. {Figs. 1 and 2 in Ref. [61]; reprinted with kind permission of the author and the publisher.}

Fig. 22. DIP designed specifically for coupling to the VG 9000 double-focusing mass spectrometer. (Reprinted with permission from Ref. [271]. Copyright 1993 American Chemical Society.)

body, in order to allow it to be inserted through the body. The outer body of the probe acts as the coaxial shielding for that section of the rf electrical pathway. Centering of the center conductor within the probe was effected by the retention of the native interior insulator of the RG-213 cable and the inclusion of the additional
glass tubing pictured in the inset of Fig. 21a. Sputtering is limited to the sample surface by means of the Macor and stainless steel sleeves located at the end of the DIP. These sleeves effectively isolate the plasma to the exposed sample surface. It is noteworthy that the Macor sleeve itself would sputter in the absence of the ground-
ed steel sleeve surrounding it. The solid sample, typi-
cally 1.6 mm to 4.8 mm in diameter, is slip-fitted into the Cu sample holder, which is attached to the electrical feedthrough by means of a set screw. Sample holders, Macor sleeves, and stainless steel sleeves of different sizes are used to accommodate samples of different diameters. Compacted powder samples could also be analyzed using this DIP design. A compacted sample would simply be mounted onto a Cu substrate using conductive silver paint. The Cu substrate would then be slip-fitted into the Cu sample holder as described above.

Previously published work had demonstrated that effective mass spectrometric sampling of glow discharge produced analyte ions requires proper positioning of the sample surface with respect to the sampling orifice of the mass spectrometer [56]. Analytical sensitivities are most favorable when the orifice is positioned close to the interface between the negative glow and the plasma sheath surrounding the sample surface. For this reason, the DIP illustrated in Fig. 21a was introduced into the rf glow discharge cell through an adjustable bellows assembly (see Fig. 21b). The bellows allowed the distance between the sample surface and the sampling orifice to be optimized. The vacuum interlock, consisting of the combination of the ball valve and three-way valve, enabled the introduction of the DIP into the discharge cell without loss of vacuum. This is important, because atmospheric contaminants are problematic in both d.c.- and rf-GDMS analysis [4,31,32,271,280–284].

At least one rf glow discharge device has been designed for the VG9000 double-focusing mass spectrometer [271]. This development is logical, since this particular instrument model, sold as a d.c.-GDMS, has been by far the most successful of all commercial GDMS instruments. The design of an rf-powered glow discharge DIP for the VG9000 is illustrated in Fig. 22. (This DIP has also been adapted for use with the VG GloQuad quadrupole mass spectrometer [285].) The DIP is designed to allow coupling to the instrument without modification of the d.c. source interface provided by the instrument manufacturer. This allows the rf and d.c. sources to be interchanged easily and rapidly. Complete conversion requires approximately 45 min, including evacuation and reconfiguration of electrical power. The DIP design illustrated in Fig. 22 is in most respects analogous to that presented in Fig. 21a, and so no detailed explanation will be given here. The interested reader may find a more complete description in Ref. [271]. The BN section in Fig. 22 serves three important functions in this device. First, it provides electrical insulation between the steel discharge cell and the grounded stainless steel outer body of the DIP. Second, the o-ring mounted within the BN effects the necessary vacuum seal. Finally, the high thermal conductivity of BN provides a good heat conduction path for cryogenic cooling of the sample mount assembly. A liquid N₂ cold finger surrounds the BN section for that purpose. The discharge cell of the VG9000 itself is also cooled with liquid N₂.

Cryogenic cooling of glow discharge sources has proved to be analytically beneficial for both d.c.- and rf-GDMS [271,281–284]. The benefits are effected by the removal of condensable contaminants from the discharge environment. Such contaminants, primarily water vapor, interfere with sputtering and gas phase processes in the plasma. For example, molecular gas phase species tend to quench the Ar metastables that play such an important role in glow discharge plasma processes, including being responsible for Penning ionization [286,287]. Gas phase contaminants may also react with analytes, reducing desired analyte ion signals and producing unwanted polyatomic isobars. They may also react with sample surfaces, thereby affecting sputtering yields. Finally, very light contaminant ions, such as H⁺, may carry a disproportionately large fraction of discharge current, yet produce very little sputtering [4,288]. Owing to the substantial analytical advantages associated with cryogenic cooling, some means of cooling is a standard feature of commercial instruments.

The benefits of cryogenic cooling for rf-GDMS have been studied. As an example, De Gendt et al. acquired mass spectra with and without the flow of liquid N₂ through a cryogenic coil immersed within the discharge environment [284]. Fig. 23a presents an rf glow discharge mass spectrum obtained without the flow of liquid N₂. The sample consisted of Macor powder compressed under high pressure into a sample disk. This spectrum is dominated by Ar species and ion signals originating from contaminant species present within the discharge environment. Fig. 23b contains a mass spectrum of the same sample obtained after 40 min of liquid N₂ flow. It is obvious that cryogenic cooling substantially reduced isobaric interferences arising from discharge contamination. The isotopic ratios for Mg (m/z 24, 25, and 26) and Si (m/z 28, 29, and 30) in the spectrum acquired with cooling approximately agree with expected natural abundances. It should be emphasized that the compacted oxidic sample characterized in this work represents a worst-case scenario. This is because contamination originates not only from vacuum leaks, adsorbed water on surfaces, and impurities in the discharge gas itself, but also from the oxidic nature of the sample components and trapped gases and water incorporated into the sample disk during compaction. Nonetheless, cryogenic cooling has also been shown to...
be beneficial for other sample types, including bulk insulators and even metallic solids [281,282].

There was a significant technical challenge associated with coupling the rf glow discharge device pictured in Fig. 22 to the VG9000 mass spectrometer. Double-focusing mass spectrometers usually employ high d.c. accelerating potentials, in order to improve ion extraction efficiencies. The VG9000 utilizes an adjustable accelerating potential of up to 8 kV. The ionization source is normally floated at this accelerating potential. As a result, it was necessary to find a way to superimpose the rf driving potential of the glow discharge on the high d.c. accelerating potential, while avoiding rf interference that might influence the mass spectrometer electronics.

Duckworth et al. found an elegant solution to this technical challenge through the implementation of the simple circuit depicted in Fig. 24 [271]. The inductor between the d.c. high voltage source and the glow discharge cell allows the application of the d.c. accelerating potential to the cell. This causes the plasma to float at this accelerating potential, as desired. The d.c. high voltage is also transmitted to the sample through the conductance of the plasma. However, the capacitor between the matching network and the glow discharge device isolates and protects the rf electronics from the d.c. high voltage. If any d.c. should leak through this capacitor, the nearby inductor provides a ready pathway to ground. In terms of the application of the rf potential needed to sustain the glow discharge, the capacitor between the matching network and the discharge device provides a low-impedance path. The inductor between the discharge device and the d.c. high voltage supply protects the latter from the rf potential. Should any rf

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**Fig. 23.** Comparison of rf-GDMS mass spectra of a compacted Macor ceramic powder sample obtained (a) without and (b) with liquid N\(_2\) flowing through a cryogenic cooling coil immersed within the discharge environment. The applied rf power and the Ar pressure were 50 W and 50 Pa, respectively. The sample-to-exit orifice distance was 7 mm. [Reprinted with permission from Ref. [284]. Copyright 1995 American Chemical Society.]
leak through, the nearby capacitor provides a conductive pathway to ground.

Rf glow discharge sources for the mass spectrometric analysis of flat samples have also been developed. Such a source for coupling to the commercially available VG GloQuad quadrupole mass spectrometer is depicted in Fig. 25 [289]. This rf glow discharge source basically consists of the same DIP design given in Fig. 21a, but with the addition of a flat sample holder that attaches to the end of the DIP. A flat sample is mounted for analysis by placing the sample and the insulator spacer against the anode plate in such a way that the spacer is completely shielded from the discharge. This is possible, because the inner diameter of the spacer is slightly larger than that of the anode plate. The grounding cap is then inserted through the Teflon back plate until it makes firm contact with the back of the sample. It is then locked into position by means of the set screw shown in the figure, thereby holding the sample and insulator spacer in place. The DIP is then inserted through the grounding cap to make rf electrical contact with the back of the sample. Finally, the DIP and the attached sample holder assembly are positioned against the stainless steel discharge cell, in order to form the enclosed discharge volume. The insulator spacer is machined from BN, in order to provide sample cooling by the conduction of heat away from the sample to the cryogenically cooled discharge cell. The entire assembly seen in Fig. 25 is contained within a larger vacuum chamber during operation. Nominally flat samples with diameters in the range 6 mm to 38 mm could be analyzed with this rf device, so long as the sample thickness did not exceed 26 mm. Thicker samples could be accommodated, however, with the use of longer Teflon support rods and a longer grounding cap.

4.2.1.2. Magnetically-enhanced sources. Another type of rf-powered glow discharge device that has been investigated for analytical rf-GDMS is the magnetically-enhanced, or magnetron, source [265,266,290–293].

Such devices are usually designed for the analysis of flat samples. They are in most respects very similar to the more common flat sample devices, such as the one pictured in Fig. 25. The principle difference is that one or more magnets are usually placed against the sample on the side opposite to the plasma. The associated magnetic field helps to confine electrons within the plasma, producing increased ionization efficiencies. One result is that the plasma can be operated at lower pressures than non-enhanced rf glow discharges. Some data have shown that the use of extremely low operating pressures can reduce isobaric interferences in some cases [265]. Sample sputtering rates and ion intensities have also been improved with the use of magnets [265,292]. One disadvantage of magnetron sources is that sputtering tends to be very localized to the shape of the magnets. This normally results in extremely non-flat craters, limiting the utility of magnetron sources for depth profiling [292,293].
4.2.1.3. Pulsed sources. Other types of rf-GDMS sources that have been pursued include pulsed devices [269,294,295]. There is nothing inherently different in the design of such devices compared to the sorts of devices already described. Obviously, some means of pulsing the rf power delivered to the glow discharge device must be provided. One of the analytical advantages associated with pulsing the rf source is that instantaneous discharge powers can be very high, resulting in very strong analytical signals. At the same time, time-averaged discharge powers can be kept low, avoiding sample overheating and associated instabilities. Moreover, pulsed rf glow discharges often exhibit ‘pre-peaks’ and ‘afterpeaks’ in mass spectra [294], similar to those observed with optical emission. Given the presence of these prepeaks and afterpeaks, time-gated detection can sometimes be used to discriminate analyte ion intensities from undesired ion signals [294]. Another possible use of pulsed sources is for depth profiling of very thin surface layers, owing to the high sensitivities and low sputter penetration rates associated with pulsing. However, optical emission detection has an advantage over mass spectrometry, in that the transport of glow discharge generated ions to the sampling orifice of the mass spectrometer naturally induces mixing that may degrade depth resolution [295].

4.2.1.4. Experimental parameters. As with any other technique, obtaining good analytical results with rf-GDMS requires the optimization of experimental parameters. These include parameters associated with the rf glow discharge device, such as the support gas pressure and rf power, as well as those associated with the mass spectrometer. Regarding the mass spectrometer, some parameters of interest are the settings of the ion optics that govern the extraction of ions from the plasma and the focusing of those ions into the mass analyzer. Careful optimization of these parameters is necessary, in order to accommodate the kinetic energies of ions originating in the rf glow discharge [296].

4.2.1.5. Memory effects. Finally, we should mention that memory effects can be problematic in both d.c.- and rf-GDMS, especially in trace and ultratrace analysis [35]. For this reason, it is often important to clean adequately the equipment between analyses of different matrices. In other attempts to control memory effects, GDMS practitioners may reserve specific glow discharge cells and sample holders, and sometimes even sampling orifices and lens stacks, for use with specific matrices.

4.2.2. Methods and applications

To date, most of the development of rf-GDMS has been directed toward bulk analysis of solid materials. The types of solid materials include electrical conductors [56,57,60,61,271,272,285,289,297,298], semiconductors [270,299–301], insulators [10,12,15,16,56,57,60,265,271,285,289,292,293,302–304], and powders [251,284,294,305]. A small amount of work has been directed toward the use of rf-GDMS for depth profiling of layered surfaces [10,15,16,306–308]. Finally, rf-GDMS has been investigated as a means for the determination of elemental speciation [241,267,309–312]. The published research papers are categorized according to application area in Table 5.

4.2.2.1. Bulk analysis. For both d.c.- and rf-GDMS, quantification for bulk analysis is usually accomplished through the use of relative sensitivity factors (RSFs) [4,246–249,251,303,313]. To be very specific, an RSF mathematically expresses the sensitivity of a particular GDMS instrument for a given analyte in a specific matrix relative to the sensitivity for a standard element in that matrix. However, RSFs are not strongly dependent upon matrix or instrument, allowing standard RSF tables to be applied in routine analysis with good success. Such tables are normally provided for a GDMS instrument model by the instrument manufacturer. Analysts do not usually measure RSFs for a particular matrix and a specific GDMS instrument unless the best possible analytical accuracy is desired. When such accuracy is needed, the appropriate RSFs should be measured with CRMs that are as closely matrix-matched to the unknown samples as possible. It is also noteworthy that within a given matrix RSFs generally do not vary by significantly more than one order of magnitude across a wide range of elements. Consequently, semi-quantitative survey analysis of solid materials can be performed simply by utilizing raw ion beam ratios.

<table>
<thead>
<tr>
<th>Type of analysis</th>
<th>Material</th>
<th>Refs.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulk</td>
<td>Iron and steel</td>
<td>[289]</td>
</tr>
<tr>
<td></td>
<td>Cu-based alloys</td>
<td>[56,57,60,61,271]</td>
</tr>
<tr>
<td></td>
<td>[272,289,297,298]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Al-based alloys</td>
<td>[57,284,298]</td>
</tr>
<tr>
<td></td>
<td>Ni-based alloys</td>
<td>[272,285,298]</td>
</tr>
<tr>
<td></td>
<td>Semiconductors</td>
<td>[270,299–301]</td>
</tr>
<tr>
<td></td>
<td>Ceramics</td>
<td>[284,292,302–304]</td>
</tr>
<tr>
<td></td>
<td>Glasses</td>
<td>[56,57,60,265,271]</td>
</tr>
<tr>
<td></td>
<td>[285,289,292,293,298]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Polymers</td>
<td>[10,12,15,16]</td>
</tr>
<tr>
<td></td>
<td>Oxide powders</td>
<td>[56,251,305]</td>
</tr>
<tr>
<td></td>
<td>Soil</td>
<td>[271]</td>
</tr>
<tr>
<td>Depth profiling</td>
<td>Surfaces of polymers</td>
<td>[15,16,306]</td>
</tr>
<tr>
<td></td>
<td>Oxide surfaces</td>
<td>[307,308]</td>
</tr>
<tr>
<td></td>
<td>Conductive layers</td>
<td>[10,306]</td>
</tr>
<tr>
<td></td>
<td>Insulating substrates</td>
<td>[306]</td>
</tr>
<tr>
<td></td>
<td>Conductive multilayers</td>
<td>[306]</td>
</tr>
<tr>
<td>Speciation</td>
<td>Organotins</td>
<td>[267,309–311]</td>
</tr>
<tr>
<td></td>
<td>Selenoamino acids</td>
<td>[312]</td>
</tr>
</tbody>
</table>
(IBRs). In essence, the IBR method assumes that all RSFs are unity.

The actual analytical accuracy characterizing a given d.c. or rf GDMS bulk analysis depends not only upon the selected quantification approach, but also upon a myriad of other factors. Examples of such factors include analyte identity, the level of analyte in the sample, sample heterogeneity, sample matrix characteristics, interferences, sample preparation procedures, instrumental operating parameters, operator skill and experience, and laboratory environmental conditions. As a result, it is difficult to predict reliably the accuracy of a particular analysis. Nevertheless, it is helpful for the purposes of this review to attempt to make general statements regarding the level of analytical accuracy attainable with the different quantification approaches. Allowing for variability associated with the sorts of factors listed above, uncertainties on the order of 30\% relative may be obtained for minor and trace constituents when RSFs are evaluated using matrix-matched calibrants. The use of non-matrix-matched calibrants may provide uncertainties in the range of 2\% to 5\% for such analytes. Finally, the IBR method usually allows order-of-magnitude determinations to be performed.

An example rf glow discharge mass spectrum of an electrically conductive sample, SRM 1103 Free-Cutting Brass [National Institute of Standards and Technology (NIST), Gaithersburg, Maryland, USA] is presented in Fig. 26 [271]. This mass spectrum was acquired using a pin that was machined from the disk SRM and mounted into the DIP depicted in Fig. 22. The DIP was interfaced to a VG 9000 double-focusing instrument using the electrical circuit in Fig. 24, and a mass resolution of approximately 2000 was employed. The certified mass fraction of Sn in this sample is 0.88 \( \mu g \ \text{g}^{-1} \), giving a \( ^{115}\text{Sn} \) mass fraction of 31.7 \( \mu g \ \text{g}^{-1} \). Based on this spectrum and 3 times the standard deviation of the background, the DL for Sn was estimated to be approximately 15 ng g\(^{-1}\). These results demonstrate the excellent sensitivity of rf-GDMS for conductive samples using a double-focusing mass spectrometer.

Using the same equipment, rf and d.c. RSFs for several analytes in SRM 1103 were compared (see Table 6) [271]. Both the d.c. and rf data were acquired with the same DIP assembly, simply by interchanging the rf power supply and matching network with a d.c. power supply. A small adjustment of discharge gas pressure was necessary once the power supplies were interchanged. As shown, the difference between the d.c. and rf values for a given analyte is generally smaller than a factor of two, with the single exception of the matrix element, Zn. These data, which can be considered representative, provide further evidence of the similarities between rf and d.c. glow discharges in terms of analytical characteristics.

The rf-powered DIP coupled to the VG9000 instrument was also used to acquire a low-resolution mass spectrum of a non-conductive powder sample, NIST SRM 4355 Environmental Radioactivity, Peruvian Soil (see Fig. 27) [271]. A portion of the soil sample was compacted in a die under high pressure into a shape that could be mounted for analysis. The uncertified elemental mass fraction of Pb in SRM 4355 is 129 \( \mu g \ \text{g}^{-1} \). The corresponding value for Bi is 12 \( \mu g \ \text{g}^{-1} \). Given the natural abundances of the Pb isotopes, the isotopic mass fractions of \( ^{204}\text{Pb} \), \( ^{206}\text{Pb} \), \( ^{207}\text{Pb} \), and \( ^{208}\text{Pb} \) are approximately 2 \( \mu g \ \text{g}^{-1} \), 31 \( \mu g \ \text{g}^{-1} \), 29 \( \mu g \ \text{g}^{-1} \), and 68 \( \mu g \ \text{g}^{-1} \), respectively. Since Bi is naturally monoisotopic, the uncertified isotopic mass fraction of \( ^{209}\text{Bi} \) is the same as the uncertified elemental mass fraction, 12 \( \mu g \ \text{g}^{-1} \). Given these isotopic mass fractions for the Pb and Bi isotopes, the data in Fig. 27 illustrate that, even for electrically insulating powder samples, rf-GDMS using a double-focusing instrument can provide excellent sensitivities and DLs.

Example data sets illustrating the level of analytical precision characterizing rf-GDMS for electrically conductive and insulating samples are presented in Tables 7 and 8, respectively [298]. The conductive sample consisted of a pin that was machined from NIST SRM 1243 Waspaloy, while a pin machined from NIST SRM 610 Trace Elements in Glass served as the insulating sample. Both pins were mounted in the DIP illustrated in Fig. 22 coupled to a VG GloQuad quadrupole mass spectrometer. One important difference between running the two samples is that the glass sample required a 30 min preburn to reach a reasonable level of signal stability, while the metallic sample required only a few minutes. This behavior, which is typical of rf-GDMS, is related to the much slower sputtering rates associated with insulating samples. Also, such samples are often hygroscopic, thereby introducing water into the glow discharge source. Finally, insulating samples may be porous and contain trapped gases and water within their structures.

In Tables 7 and 8, ‘within-burn’ precision refers to the observed R.S.D. of three mass scans acquired in peak-hopping mode during a single burn over a time period of approximately 20 min. When more than one such burn was undertaken, pooled R.S.D.s are reported. ‘Between-burn’ precision refers to the observed R.S.D. for four separate burns, with the sample extracted and exposed to the atmosphere between burns. In this way, the between-burn R.S.D.s reflect all sample handling and source equilibration processes. As indicated in the tables, the within-burn precision afforded by rf-GDMS is good, with median R.S.D.s for the Waspaloy and glass samples of 0.9\% and 1.4\%, respectively. Similarly, the between-burn precision is also acceptable, with median R.S.D.s for the conductive and insulating samples of 4.8\% and 6.2\%, respectively. Finally, we should
mention that for both d.c.- and rf-GDMS, sample heterogeneity can be problematic when measuring analytes of very low mass fraction. This is because only a small amount of sample material is actually removed during signal integration.

Detection limits provided by rf-GDMS instruments have also been investigated [e.g. Refs. [272,289, 290,298,301]]. As an example, DL values measured for a high-purity (99.9999%) Al pin introduced into a VG GloQuad by means of the DIP pictured in Fig. 22 are presented in Table 9 [298]. Each DL was computed as the known mass fraction for the element of interest divided by the average peak ion intensity for three replicate measurements within a single burn multiplied by three times the standard deviation of that average intensity. This approach to DL computation was
Table 6
Comparison of rf and d.c. glow discharge RSFs (relative to Fe) for several analytes in NIST SRM 1103 Free-Cutting Brass. [Reprinted with permission from Ref. [271]. Copyright 1993 American Chemical Society.]

<table>
<thead>
<tr>
<th>Analyte</th>
<th>rf</th>
<th>d.c.</th>
</tr>
</thead>
<tbody>
<tr>
<td>P</td>
<td>6.64</td>
<td>5.39</td>
</tr>
<tr>
<td>Fe</td>
<td>1.00</td>
<td>1.00</td>
</tr>
<tr>
<td>Ni</td>
<td>1.67</td>
<td>1.65</td>
</tr>
<tr>
<td>Cu</td>
<td>2.16</td>
<td>3.36</td>
</tr>
<tr>
<td>Zn</td>
<td>1.72</td>
<td>3.75</td>
</tr>
<tr>
<td>Sn</td>
<td>1.65</td>
<td>1.98</td>
</tr>
<tr>
<td>Pb</td>
<td>2.04</td>
<td>2.06</td>
</tr>
</tbody>
</table>

Fig. 27. A portion of an rf glow discharge mass spectrum of NIST SRM 4355 Environmental Radioactivity, Peruvian Soil, acquired using the same instrumentation employed to collect the data in Fig. 26. The accelerating potential was 8 kV, and discharge conditions were 38 W applied rf power and approximately 190 Pa Ar pressure. [Reprinted with permission from Ref. [271]. Copyright 1993 American Chemical Society.]

Table 7
Precision data for a pin sample machined from NIST SRM 1243 Waspaloy. See text for explanation. [Adapted from Table 2 in Ref. [298]; reprinted with kind permission of the author and the publisher.]

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Certified mass fraction (%)</th>
<th>Within-burn R.S.D. (%)</th>
<th>Between-burn R.S.D. (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>0.024</td>
<td>2.6</td>
<td>4.9</td>
</tr>
<tr>
<td>Al</td>
<td>1.23</td>
<td>1.7</td>
<td>3.8</td>
</tr>
<tr>
<td>Si</td>
<td>0.018</td>
<td>0.8</td>
<td>7.5</td>
</tr>
<tr>
<td>P</td>
<td>0.003</td>
<td>0.6</td>
<td>5.1</td>
</tr>
<tr>
<td>S</td>
<td>0.0018</td>
<td>2.0</td>
<td>5.1</td>
</tr>
<tr>
<td>Ti</td>
<td>3.06</td>
<td>1.3</td>
<td>2.9</td>
</tr>
<tr>
<td>V</td>
<td>0.12</td>
<td>2.0</td>
<td>6.6</td>
</tr>
<tr>
<td>Cr</td>
<td>19.20</td>
<td>1.1</td>
<td>1.7</td>
</tr>
<tr>
<td>Mn</td>
<td>0.019</td>
<td>0.4</td>
<td>6.0</td>
</tr>
<tr>
<td>Fe</td>
<td>0.79</td>
<td>0.9</td>
<td>3.7</td>
</tr>
<tr>
<td>Co</td>
<td>12.46</td>
<td>0.3</td>
<td>4.0</td>
</tr>
<tr>
<td>Ni</td>
<td>58.78</td>
<td>0.4</td>
<td>1.8</td>
</tr>
<tr>
<td>Mo</td>
<td>4.25</td>
<td>0.9</td>
<td>4.8</td>
</tr>
</tbody>
</table>

Table 8
Precision data for a pin sample machined from NIST SRM 610 Trace Elements in Glass. Mass fraction values in parentheses are uncertified, while those in brackets were computed from the nominal composition of the matrix. See text for further explanation. [Adapted from Table 3 in Ref. [298]; reprinted with kind permission of the author and the publisher.]

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Certified mass fraction (µg/g)</th>
<th>Within-burn R.S.D. (%)</th>
<th>Between-burn R.S.D. (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>(351)</td>
<td>1.2</td>
<td>5.0</td>
</tr>
<tr>
<td>O</td>
<td>[46.31 %]</td>
<td>1.1</td>
<td>2.8</td>
</tr>
<tr>
<td>Na</td>
<td>[10.39 %]</td>
<td>0.5</td>
<td>4.9</td>
</tr>
<tr>
<td>Al</td>
<td>[1.06 %]</td>
<td>0.7</td>
<td>2.8</td>
</tr>
<tr>
<td>Si</td>
<td>[33.66 %]</td>
<td>1.1</td>
<td>3.2</td>
</tr>
<tr>
<td>K</td>
<td>(461)</td>
<td>13.3</td>
<td>27.0</td>
</tr>
<tr>
<td>Ca</td>
<td>[8.58 %]</td>
<td>1.6</td>
<td>4.6</td>
</tr>
<tr>
<td>Ti</td>
<td>(437)</td>
<td>1.4</td>
<td>6.3</td>
</tr>
<tr>
<td>Mn</td>
<td>485±10</td>
<td>1.6</td>
<td>2.6</td>
</tr>
<tr>
<td>Fe</td>
<td>458±9</td>
<td>1.6</td>
<td>4.4</td>
</tr>
<tr>
<td>Co</td>
<td>(390)</td>
<td>1.5</td>
<td>7.8</td>
</tr>
<tr>
<td>Ni</td>
<td>458.7±4</td>
<td>1.6</td>
<td>6.1</td>
</tr>
<tr>
<td>Zn</td>
<td>(433)</td>
<td>1.3</td>
<td>4.7</td>
</tr>
<tr>
<td>Rb</td>
<td>425.7±0.8</td>
<td>1.1</td>
<td>6.9</td>
</tr>
<tr>
<td>Sr</td>
<td>515.5±0.5</td>
<td>1.4</td>
<td>7.6</td>
</tr>
<tr>
<td>Au</td>
<td>(25)</td>
<td>4.0</td>
<td>12.7</td>
</tr>
<tr>
<td>Ti</td>
<td>(61.8±2.5)</td>
<td>2.0</td>
<td>10.1</td>
</tr>
<tr>
<td>Pb</td>
<td>426±1</td>
<td>1.3</td>
<td>7.9</td>
</tr>
<tr>
<td>Th</td>
<td>457.2±1.2</td>
<td>1.1</td>
<td>11.8</td>
</tr>
<tr>
<td>U</td>
<td>461.5±1.1</td>
<td>1.1</td>
<td>11.7</td>
</tr>
</tbody>
</table>

Table 9
Detection limits obtained for a high-purity (99.9999%) Al pin using a quadrupole mass spectrometer. See text for further explanation. [Adapted from Table 4 in Ref. [298]; reprinted with kind permission of the author and the publisher.]

<table>
<thead>
<tr>
<th>Analyte</th>
<th>DL (µg/g)</th>
<th>Analyte</th>
<th>DL (µg/g)</th>
<th>Analyte</th>
<th>DL (µg/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>&lt;0.060</td>
<td>Mo</td>
<td>&lt;1</td>
<td>Dy</td>
<td>&lt;0.045</td>
</tr>
<tr>
<td>Be</td>
<td>&lt;0.001</td>
<td>Rh</td>
<td>&lt;0.18</td>
<td>Ho</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>B</td>
<td>&lt;25</td>
<td>Ru</td>
<td>&lt;0.109</td>
<td>Er</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>Mg</td>
<td>&lt;3</td>
<td>Pd</td>
<td>&lt;0.312</td>
<td>Tm</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>Sc</td>
<td>&lt;2</td>
<td>Cd</td>
<td>&lt;0.1</td>
<td>Yb</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>Ti</td>
<td>&lt;2</td>
<td>Ag</td>
<td>&lt;14</td>
<td>Lu</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>V</td>
<td>&lt;1</td>
<td>In</td>
<td>&lt;0.013</td>
<td>Hf</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>Cr</td>
<td>&lt;7</td>
<td>Sn</td>
<td>&lt;1</td>
<td>Ta</td>
<td>&lt;0.152</td>
</tr>
<tr>
<td>Mn</td>
<td>&lt;1</td>
<td>Sb</td>
<td>&lt;0.055</td>
<td>W</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>Fe</td>
<td>&lt;4</td>
<td>Te</td>
<td>&lt;0.15</td>
<td>Re</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>Co</td>
<td>&lt;2</td>
<td>Cs</td>
<td>&lt;1</td>
<td>Os</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>Ni</td>
<td>&lt;5</td>
<td>Ba</td>
<td>&lt;0.083</td>
<td>Ir</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>Ga</td>
<td>&lt;1</td>
<td>La</td>
<td>&lt;0.026</td>
<td>Pt</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>Ge</td>
<td>&lt;1</td>
<td>Ce</td>
<td>&lt;0.037</td>
<td>Au</td>
<td>&lt;1</td>
</tr>
<tr>
<td>As</td>
<td>&lt;1</td>
<td>Pr</td>
<td>&lt;0.032</td>
<td>Hg</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>Se</td>
<td>&lt;4</td>
<td>Nd</td>
<td>&lt;0.124</td>
<td>Tl</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>Rb</td>
<td>&lt;1</td>
<td>Sm</td>
<td>&lt;1</td>
<td>Pb</td>
<td>&lt;3</td>
</tr>
<tr>
<td>Sr</td>
<td>&lt;0.044</td>
<td>Eu</td>
<td>&lt;0.006</td>
<td>Bi</td>
<td>&lt;0.09</td>
</tr>
<tr>
<td>Y</td>
<td>&lt;0.028</td>
<td>Gd</td>
<td>&lt;0.001</td>
<td>Th</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>Zr</td>
<td>&lt;1</td>
<td>Tb</td>
<td>&lt;0.001</td>
<td>U</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>Nb</td>
<td>&lt;1</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

employed, because spectral background characteristics immediately adjacent to peaks are not generally measurable with quadrupole mass spectrometers, owing to
the inherently unit mass resolution. Therefore, DL methodologies that rely upon signal-to-background ratios and relative standard deviations of the background are not useful. It should be noted that the DLs reported here are instrumental detection limits, because they reflect only within-burn precision. Other experimental approaches that would reflect additional potential sources of imprecision would likely produce somewhat poorer values.

As shown in Table 9, the DL values provided by the quadrupole rf-GDMS instrument for this sample are good, ranging from 1 ng g \(^{-1}\) to 25 \(\mu\)g g \(^{-1}\). A more careful perusal of the data indicates a strong dependence of DL upon analyte mass. Specifically, the first row transition metals generally have the poorest values, while the rare earth elements are characterized by the best DLs. Additionally, analytes with mid-range masses seem to be generally characterized by mid-range DLs. This behavior is explained as the result of the combined effects of isobaric interferences resulting from discharge contaminant species and the poor resolution of the quadrupole mass filter. Such isobaric interferences are most problematic for the first-row transition metals, but have very little effect on the heavier elements. The authors state that some minor instrument modifications, including more effective cryogenic cooling of the discharge cell and better shielding of the mass spectrometer detector electronics from rf interference, would likely improve these DLs. Nevertheless, the values reported certainly imply the utility of rf-GDMS for routine analysis of such samples, even with the quadrupole instrumentation. Notably, a double-focusing mass spectrometer would circumvent many of the problems with isobaric interferences observed here, resulting in substantially lower DLs (i.e. nominally, up to three orders of magnitude), especially for the analytically important first-row transition metals.

Similar studies of the DLs provided by rf-GDMS for an electrically insulating sample have also been published by the same research group [289]. For these studies, NIST SRM 616 Trace Elements in Glass was mounted for analysis in the VG GloQuad using the sample introduction assembly diagrammed in Fig. 25. This sample presents a somewhat more difficult challenge than the high-purity Al sample discussed above, because of the greater propensity for isobaric interferences. Nevertheless, as shown in Table 10, the DLs measured in these studies are again very useful for many analytical purposes, ranging from 1 ng g \(^{-1}\) to 6 \(\mu\)g g \(^{-1}\). The sample was allowed to presputter for 2 h prior to the measurement of the DLs, in order to clean up the discharge as much as possible. Also, the efficiency of cryogenic cooling of the source used here was thought to be somewhat better than that of the source used to obtain the data in Table 9. As for the Al sample, substantially lower DLs would be expected with the use of a high resolution mass spectrometer, owing to better interference discrimination.

Studies have also been conducted to evaluate the analytical utility of rf-GDMS for the analysis of semiconducting samples [270,299–301]. Shown in Table 11 are comparative results for the determination of several analytes in a SiC powder sample using inductively coupled plasma atomic emission spectrometry (ICP-AES), laser ionization mass spectrometry (LIMS), and rf-GDMS [301]. For the two latter techniques, a portion of the SiC powder was compacted in a die under high pressure to form a flat solid sample. The ICP-AES analysis was performed on the powder by means of slurry sampling with acid dissolution. The rf glow discharge device was designed to accept flat samples and was mounted to an SM1B (Varian MAT, Germany) double-focusing mass spectrometer of Mattauch-Herzog geometry. Because of a lack of suitable reference materials for calibration, the IRB method was used for rf-GDMS quantification, meaning that all RSFs were assumed to be unity. The matrix element, Si, was employed as an internal standard. As the data in the table indicate, the agreement among the three methods is generally within a factor of six, and there are no systematic trends between methods.

### Table 10
Detection limits obtained for SRM 616 Trace Elements in Glass using a quadrupole mass spectrometer. See text for further explanation. [Adapted from Table IV in Ref. [289]; reprinted with kind permission of the author and the publisher.]

<table>
<thead>
<tr>
<th>Analyte ion</th>
<th>Certified elemental mass fraction (µg/g)</th>
<th>DL (µg/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>⁶⁰Cu⁺</td>
<td>(0.80±0.09)</td>
<td>0.081</td>
</tr>
<tr>
<td>⁷¹Ga⁺</td>
<td>(0.23±0.02)</td>
<td>0.033</td>
</tr>
<tr>
<td>⁸⁶Sr⁺</td>
<td>41.72±0.05</td>
<td>6</td>
</tr>
<tr>
<td>¹²¹Sb⁺</td>
<td>(0.078±0.007)</td>
<td>0.001</td>
</tr>
<tr>
<td>¹⁹⁷Au⁺</td>
<td>(0.18±0.01)</td>
<td>0.006</td>
</tr>
<tr>
<td>²⁰⁸Pb⁺</td>
<td>1.85±0.04</td>
<td>0.28</td>
</tr>
<tr>
<td>²³²Th⁺</td>
<td>0.0252±0.0007</td>
<td>0.001</td>
</tr>
<tr>
<td>²³⁸U⁺</td>
<td>0.0721±0.0013</td>
<td>0.003</td>
</tr>
</tbody>
</table>

Table 11
Comparison of the mass fractions of several analytes in SiC powder measured by inductively coupled plasma atomic emission spectrometry (ICP-AES), laser ionization mass spectrometry (LIMS), and rf-GDMS. [Table 2 in Ref. [301]; reprinted with kind permission of the author and the publisher.]

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Mass fraction (µg/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ICP-AES</td>
</tr>
<tr>
<td>B</td>
<td></td>
</tr>
<tr>
<td>Al</td>
<td>180</td>
</tr>
<tr>
<td>Ti</td>
<td>150</td>
</tr>
<tr>
<td>V</td>
<td>80</td>
</tr>
<tr>
<td>Cr</td>
<td>10</td>
</tr>
<tr>
<td>Cu</td>
<td>10</td>
</tr>
<tr>
<td>Zr</td>
<td>20</td>
</tr>
</tbody>
</table>
The same rf-GDMS instrumentation was also employed to determine Si in GaAs semiconducting crystals [301]. The high mass resolution of the double-focusing instrument was needed to discriminate $^{28}\text{Si}^+$ from common residual gas species, including CO$^+$ and N$_2^+$. The results are presented in Table 12, along with determinations performed with secondary ion mass spectrometry (SIMS). The SIMS instrument was calibrated using ion implanted reference materials. Comparison of the rf-GDMS and SIMS data in the table shows that the two methods agreed to well within a factor of two for three separate GaAs crystals. Preliminary DLs for a large number of analytes in a single crystal GaAs wafer, measured according to the 3σ criterion, are given in Table 13 [301]. The authors emphasize that these are initial values that should improve with further development. Both the SiC and GaAs data imply the potential utility of rf-GDMS for the analysis of semiconducting solids.

In addition to the comparisons discussed above, determinations of several elements in a ceramic solid using rf-GDMS have also been compared to determinations measured using laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) [304]. In this case, the ceramic sample was a perovskite ($\text{La}_{0.65}\text{Sr}_{0.3}\text{MnO}_3$) layer sputtered onto a number of elements at mass fractions approaching 100 μg g$^{-1}$. Perovskites are important as components of solid oxide fuel cells [302,304,307,308]. Once again, the rf glow discharge source coupled to the SM1B double-focusing mass spectrometer was employed. The LA-ICP-MS instrument was a quadrupole mass spectrometer with much lower mass resolution. The results of the comparison, presented in Table 14, show that rf-GDMS and LA-ICP-MS agreed well within a factor of two, with the single exception of Al. For this particular analyte, the LA-ICP-MS determination of Al was affected by an unresolved $^{58}\text{Mn}^{2+}$ isobaric interference. These results illustrate the potential utility of rf-GDMS for analysis of insulating solids, such as glasses and ceramics.

A particularly interesting area of potential utility for rf-GDMS is the direct analysis of polymeric solids [10,12,15,16,306]. Such materials are important, and becoming more so, in many areas of modern science and technology. Some analytical methods that can be applied to the chemical characterization of polymers directly in the solid state currently exist (e.g., SIMS, XRF, and LA-ICP-MS). However, there is a need for additional and better methods. Research into the applicability of rf-GDMS to the evaluation of polymers is just beginning. Nonetheless, this method has already been shown to provide a means of obtaining both elemental and molecular information on polymeric materials relatively rapidly and inexpensively. Moreover, rf-GDMS can be used to acquire much of the spatial information that may be critical in real-world applications.

As an example, an rf-GDMS mass spectrum of a 1.5 mm thick polytetrafluoroethylene (PTFE) sample disk is presented in Fig. 28 [10]. This spectrum was obtained using the flat sample mount device illustrated in Fig. 25 coupled to a VG GloQuad. Notably, the spectrum contains both atomic and molecular fragment peaks.

### Table 12
Comparison of Si mass fractions in three GaAs crystals measured using rf-GDMS and secondary ion mass spectrometry (SIMS). [Table 3 in Ref. [301]; reprinted with kind permission of the author and the publisher.]

<table>
<thead>
<tr>
<th>Sample no.</th>
<th>rf-GDMS (at./cm$^2$)</th>
<th>SIMS (at./cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$3.2 \times 10^{19}$</td>
<td>$5.7 \times 10^{18}$</td>
</tr>
<tr>
<td>2</td>
<td>$2.5 \times 10^{19}$</td>
<td>$1.7 \times 10^{19}$</td>
</tr>
<tr>
<td>3</td>
<td>$1.1 \times 10^{19}$</td>
<td>$1.2 \times 10^{19}$</td>
</tr>
</tbody>
</table>

### Table 13
DLs (3σ criterion) for analytes in a single crystal GaAs wafer measured using rf-GDMS with a double-focusing mass spectrometer. [Table 4 in Ref. [301]; reprinted with kind permission of the author and the publisher.]

<table>
<thead>
<tr>
<th>DL (μg/g)</th>
<th>Analytes</th>
</tr>
</thead>
<tbody>
<tr>
<td>≤0.1</td>
<td>Li, Be, B</td>
</tr>
<tr>
<td>0.1 to 1</td>
<td>Na, Mg, Al, P, Cl, Sc, V, Cr, Mn, Co</td>
</tr>
<tr>
<td>1 to 10</td>
<td>Ti, Ni, Cu, Zn, Se, Rh, Sr, Y, Nb, Mo, Ru, Rh, Pd, Ag, Cd, In, Sn, Sb, Te, Cs, Ba</td>
</tr>
<tr>
<td>10 to 100</td>
<td>Si, S, Fe, Zr, Br, I, Hf, Ta, W, Re, Os, Ir, Pt, Au, Hg, Tl, Pb, Be, Rare earth elements</td>
</tr>
</tbody>
</table>

### Table 14
Comparison of the mass fractions of a number of elements determined using laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) and rf-GDMS. The LA-ICP-MS determination of Al was affected by an unresolved $^{58}\text{Mn}^{2+}$ isobaric interference. [Adapted from Table 4 in Ref. [304]; reprinted with kind permission of the author and the publisher.]

<table>
<thead>
<tr>
<th>Analyte</th>
<th>LA-ICP-MS (μg/g)</th>
<th>rf-GDMS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>18.5</td>
<td>90</td>
</tr>
<tr>
<td>Co</td>
<td>27.3</td>
<td>32</td>
</tr>
<tr>
<td>Ni</td>
<td>35</td>
<td>60</td>
</tr>
<tr>
<td>Cu</td>
<td>12</td>
<td>14.9</td>
</tr>
<tr>
<td>Zn</td>
<td>11.2</td>
<td>12</td>
</tr>
<tr>
<td>Ga</td>
<td>21.4</td>
<td>28</td>
</tr>
<tr>
<td>Ba</td>
<td>45.4</td>
<td>38</td>
</tr>
</tbody>
</table>
Prominent peaks with ion currents greater than 100 pA and that are associated with the components of the solid sample include \(^{12}\text{C}^+\), as well as numerous fragments of the general formula \(\text{C}_x\text{F}_y^+\). Rf-GDMS mass spectra of several other polymers have similarly exhibited both atomic and molecular characteristics. The ion currents observed while sputtering polymers in rf glow discharge devices are large, implying high sensitivity. As a practical matter, low-melting polymers require cryogenic cooling, not only of the discharge cell, but also of the sample itself. A special sample holder for this purpose has been reported [12].

At least some of the polyatomic ions observed while sputtering polymeric materials in rf-GDMS instruments seem to be sputtered as neutral polyatomic fragments from the sample surface and then ionized in the gas phase, rather than being formed in the gas phase through collisional association of sputtered atoms [10,12,15]. A particularly good piece of evidence supporting this contention has been provided through experiments involving the rf-GDMS analysis of low density polyethylene (LDPE). For this material, the mass spectral peaks associated with the two-C base repeating unit of the polymer and its dimer (containing four C atoms) were by far the most intense peaks related to C in the mass spectrum. In contrast, the atomic C peak was very weak [12].

The presence of both atomic and molecular fragment peaks in the rf-GDMS mass spectra of polymeric materials implies that the technique may be useful for such applications as the determination of molecular structure and polymer identification. An example of the latter is presented in Table 15, where the ratios of the intensities of certain ions are seen to depend upon the identity of the polymer being sputtered [10]. In this particular case, the two polymers, PTFE and PTFE-\(\text{co-PFA}\) (a copolymer composed of PTFE and perfluoromethyl vinyl ether), could easily be distinguished on the basis of these ratios.

Regarding the use of rf-GDMS for this sort of polymer ‘fingerprinting,’ it is useful to note that the prominence of polyatomic fragment peaks in the mass spectra can be selected to some degree by the choice of discharge conditions [10,12,15,16]. This aspect adds some flexibility to the methodology. Specifically, discharge conditions which tend to increase the kinetic energies of \(\text{Ar}^+\) bombarding the sample surface (i.e. lower pressures and higher voltages) tend to increase the prominence of molecular fragments in the mass spectra. These higher

![Figure 28](image-url)
energies of bombardment are required for the sputtering of larger fragments, because more chemical bonds must be broken. In contrast, when polymers were examined using d.c.-GDMS by means of the secondary cathode approach, the mass spectra observed were predominantly atomic. This was explained as the effect of the very low discharge power employed (2 W), resulting in the sputtering of very few polyatomic fragments [13].

Finally, there is an important problem associated with the application of rf-GDMS to the analysis of electrically insulating solids. Specifically, analytical signals depend dramatically on the geometric shape of the insulating sample, owing primarily to unwanted rf power losses. The most relevant geometric parameter is usually the sample thickness, because rf power is normally coupled to the sample from the back side, opposite the plasma [10,289,290]. The most obvious effect of these power losses is that ion intensities are reduced. However, in some cases, the very character of the mass spectra may also be noticeably affected. For example, rf-GDMS mass spectra observed for thicker PTFE samples tended to be characterized by fewer polyatomic fragments compared to mass spectra obtained with thinner samples. A possible explanation of this behavior is that the larger rf power losses associated with the thicker samples result in less energetic plasmas, which then lead to less efficient sputtering of larger polyatomic fragments [10].

4.2.2.2. Depth profiling. Generally speaking, as far as glow discharge analytical instruments are concerned, depth profiling of surfaces has to date been the business of GDOES, not GDMS. In part, this may be due to the fact that no commercial instrument manufacturer has demonstrated any significant interest in developing GDMS instrumentation and methods for depth profiling applications. However, a more important fact may be that the mass filters that have been commonly employed with glow discharge devices are not well suited for depth profiling, given their inherently sequential nature. This is true not only for high-resolution, double-focusing instruments, but also for quadrupole mass filters. While quadrupoles may provide relatively rapid \( m/z \) scanning and peak hopping capabilities, they are nonetheless too slow for monitoring more than a few analytes within a single glow discharge burn. A particularly interesting development in GDMS in recent years has been the coupling of glow discharge devices with time-of-flight (TOF) mass spectrometers. These instruments are capable of true simultaneous sampling of glow discharge generated ions, making them a suitable match to the requirements of depth profiling. Several papers have described the coupling of d.c. and rf glow discharge devices to TOFMS instruments [25,272,274–279,290,295,314]. However, very little work has been done specifically in terms of depth profiling, and what work has been reported has been concerned exclusively with d.c. glow discharge devices [276,278,279].

There appears to be no inherent reason why GDMS depth profiling cannot generally provide depth resolutions equivalent to those that are commonly observed in GDOES. Critical factors that must be given adequate attention include the design of the glow discharge source and the judicious choice of discharge parameters. As an example, Jakubowski and Stuewer investigated quantitative depth profiling using a d.c. glow discharge device coupled to a quadrupole mass spectrometer [315]. One of the samples studied was a multilayer stack of ten alternating Ni and Cr layers (each layer nominally 25 nm thick) on a polished, \( n \)-type, Si wafer. Depth resolutions in the 5 nm to 9 nm range were observed at the interfaces between the layers. Such depth resolutions are similar to those that would be expected with GDOES depth profiling.

In terms of other analytical figures of merit, GDMS depth profiling may offer enhanced sensitivities and lower DLs compared to GDOES depth profiling. Also, GDMS may in some cases be characterized by simpler spectra that are somewhat more interference free. A particularly important point to make is that GDMS depth profiling should be generally less applicable to thick layers, owing to the relatively slower sputtering rates.

Focusing again on \( rf \) glow discharge, a small number of papers have reported rf-GDMS depth profiling research [10,15,16,306–308]. A particularly good example of the potential utility of rf-GDMS for depth profiling applications can be taken from Gibeau and Marcus (see Fig. 29) [306]. The sample in this case was an automotive paint panel, comprised of an Al substrate with three polymeric paint layers. The primer coat,
which is placed directly on the Al, contained a methanol moiety, such that methoxy ion (CH$_3$O$^-$) could be used as an appropriate analyte. The next layer in the system consisted of the base coating containing a white pigment that could be detected by means of Ti$^+$. Finally, the CH$_3^+$/C$_2$H$_4^+$ ion ratio was taken to be indicative of the top clear coat. The total thickness of the layer stack was approximately 45 μm, with each layer estimated to be approximately 15 μm thick. The instrumentation used in this work consisted of the flat-sample holder pictured in Fig. 25 coupled to a VG GloQuad quadrupole mass spectrometer operated in peak hopping mode. Cryogenic cooling of the sample was effected by means of a special sample holder [12]. As shown in the figure, while the analysis time was rather long, all of the layers were nicely resolved. The ability to monitor both atomic and molecular analytes is a distinct advantage of GDMS as compared to GDOES. These data imply the potential usefulness of rf-GDMS depth profiling.

4.2.2.3. Speciation. Over the past 15 years or so, there has been significant interest in developing analytical instrumentation and methodologies for the evaluation of elemental speciation (i.e. the determination of not only the amount of an element present in a sample, but also of the chemical form of that element) in a variety of sample types. The growth of interest in elemental speciation has been driven by the diverse and developing needs of biochemists, geologists, environmentalists, nutritionists, toxicologists, and others. For example, it is well known that elemental toxicity in humans may be dependent on both the amount and chemical form of the element of interest. Therefore, toxicological studies may require information on both elemental aspects. While a number of well-established and powerful analytical techniques are available for elemental speciation studies [e.g. gas chromatography mass spectrometry (GC-MS)], not all of the questions relevant to modern society can be adequately answered. As a result, there is a need for additional and better elemental speciation techniques to be developed.

In efforts to develop additional instrumentation and methods for elemental speciation applications, the use of analytical plasma sources has been investigated [241]. The typical scenario involves the coupling of such a plasma source to some form of chemical separation instrument. As an example, a liquid chromatograph (LC) may be coupled to an ICP-MS instrument. In this case, the LC is used to separate the molecular analyte of interest from the sample matrix, and the ICP-MS is used essentially as a chromatographic detector. ICP sources developed specifically for atomic spectrochemistry operate at high rf powers and at atmospheric pressure, producing high plasma temperatures. As a result, the use of common ICP sources for this sort of application means that the ICP-MS data will provide only atomic spectrochemical information. In other words, no information on molecular identity can be obtained from the ICP-MS data, other than the possibility of evaluating simple stoichiometry through elemental ratios. For this reason, molecular identification must rely solely upon the calibration of chromatographic retention times. This is a major drawback of plasma based speciation instruments that employ plasma sources developed specifically for atomic spectrochemistry.

In efforts to overcome this limitation, there has been significant interest in the development of plasma sources for mass spectrometry that operate at much lower temperatures, usually implying lower powers and pressures. Examples from the scientific literature include ICPs that are designed for low powers and reduced pressures [316–320], MIPs [321–324], both d.c. [23.25–27,325–329] and rf [267,309–312] glow discharge devices, as well as other plasma sources [330–333]. Notably, many of these plasma sources have been demonstrated to provide both elemental and molecular spectrochemical information. Moreover, they have shown some usefulness for controlled fragmentation of molecular analytes, from more atomic to more molecular, through the judicious choice of operating parameters. Coupled with the molecular information available from the separation itself, the ability to control molecular fragmentation within the plasma source provides a potentially powerful approach to elemental speciation analysis.

Several papers have been published describing research directed toward the development of instrumentation and methods for elemental speciation analysis using rf-GDMS [267,309–312]. An example of appropriate instrumentation can be taken from Belkin et al. who investigated the coupling of an rf-GDMS instrument to a GC [309]. The rf-GDMS actually consisted of an rf glow discharge device mounted onto a VG Plasma-Quad II STE quadrupole ICP mass spectrometer (Fisons, Loughborough, Leicestershire, United Kingdom) in place of the normal ICP source. Schematic diagrams of the GC-rf-GD interface and the associated rf glow discharge device are presented in Fig. 30. Briefly, effluent from the GC column is carried through a deactivated silica capillary into the rf glow discharge, which is formed inside the 0.375 in o.d. glass cell body. The discharge is ignited by a 13.56 MHz rf potential difference placed across the cathode and the grounded front plate. The distance from the cathode to the 1-mm diameter sampling orifice in the plate is 2.5 mm. Ultra-high-purity He, used as the discharge support gas, is introduced through the Swagelock tee and directed through the stainless steel tube through which the capillary is threaded. This setup allows efficient introduction of GC effluents into the rf glow discharge device.
Fig. 30. Schematic diagrams of (a) an interface used to couple a GC to an rf-GDMS instrument and (b) the associated rf glow discharge device. [Fig. 1 in Ref. [309]. Reproduced by permission of The Royal Society of Chemistry.]

An example of an rf glow discharge mass spectrum of an eluting peak obtained using a setup similar to that pictured in Fig. 30 is presented in Fig. 31a [267]. The eluting fraction in this case was composed of (CH₃)₄Sn [tetramethyltin (TMT)]. It is noteworthy that the rf-GD mass spectrum contains peaks representing not only the elemental Sn isotopes at around m/z 120, but also various Sn-based molecular fragments. The peaks that are clumped in the vicinity of m/z 135 represent CH₃Sn. Those around m/z 150 represent (CH₃)₂Sn, and those at approximately m/z 165 are indicative of (CH₃)₃Sn. Moreover, peaks corresponding to the parent molecule, (CH₃)₄Sn, are observed at around m/z 180, though the abundances of the parent peaks are quite small at the chosen operating conditions. As mentioned above, it is possible to manipulate to some extent the molecular fragmentation observed in rf glow discharge mass spectra through prudent selection of operating conditions. Finally, comparison of Fig. 31a,b indicates that the rf-GD mass spectrum of TMT is similar to cataloged electron impact ionization (EI) mass spectra of this compound, though the relative intensities of the peaks are different. This similarity implies that the vast EI mass spectral libraries that are available may be of some use for compound identification.

5. Conclusions and future directions

Analytical radio frequency glow discharge spectrometries have come a long way since the beginning. Much has been learned about the fundamental physics of analytical rf plasmas, and rf glow discharge instrumentation and methods have reached the point of usefulness for ‘real world’ applications. The latter is especially true for rf-GDOES, which is now being used routinely in a fairly large number of commercial and industrial laboratories. In contrast, rf-GDMS and other rf glow discharge techniques, such as rf-GDAAS, are not used much at all in such laboratories. There may be many reasons for this difference, but one of the most important is that rf-GDOES instruments have been commercially available for a long time (and, indeed, are still available), while no rf instrumentation has ever been commercially available for any of the other glow discharge techniques. Additionally, driven by various technological and economic factors, rf-GDOES has become better developed, further enhancing the usefulness for ‘real world’ applications.

Over the years, developments in the practice of analytical rf glow discharge spectrometries have been accompanied and aided by significant growth in our understanding of the deceptively complex physical pro-
cesses that occur within these plasmas. Both empirical studies and computer modelling of analytical rf glow discharges have contributed to the increased understanding. For example, we now comprehend more completely and accurately the characteristics and roles of electron and ion populations averaged over time, as well as throughout the various portions of the rf cycle. As another example, the importance of symmetric charge exchange in producing fast atoms that sputter the sample surface has been revealed. The increased knowledge of such physical processes is important not only for academic reasons, but also because improvements in instrumentation and methods can sometimes be made based upon such new information. Therefore, these efforts should continue.

Focusing on rf-GDOES, the main areas of work represented in the scientific literature continue to be primarily the more traditional areas (e.g. iron and steel, metal coatings, and hard coatings), but with an increasing interest in thin oxide films, particularly anodic films. These films appear to be prime candidates for reference materials (RMs) and/or CRMs to support and expand the implementation of glow discharge methods. In addition to these areas of application, there continues to be considerable exploratory rf-GDOES research directed toward bulk and depth profile analysis of electrical insulators. Also, research is being conducted toward the analysis of samples of biological, medical, and environmental concern.

Compared to a few years ago, improved quantitative algorithms for rf-GDOES are now available, including H corrections and improved density calculations for solid samples composed of oxides and nitrides. A major area of development over the past few years has been in rf source control and operation, with many new possible ways to operate the source, including means for monitoring rf current–voltage characteristics, plasma impedance, real power, and effective power. While these sorts of developments are certainly important and welcome, there is much more work to be done.

An interesting area of rf-GDOES research currently being pursued involves pulsing the rf power in the millisecond-to-microsecond regime. Similar pulsed d.c. glow discharge devices are also being developed. Pulsed sources offer potential new applications, such as analyses of polymers, glasses, and low-temperature metals, that have been considered too heat sensitive to analyze with continuously powered glow discharge sources. Pulsed sources may also provide improved sensitivities for some of the more traditional applications. Pertinent properties of these pulsed plasmas appear to be similar to those of continuous plasmas, making the transition from continuous to pulsed operation an easy task for the operator. But much work is still to be done to find the optimum conditions (e.g. pulse width, repetition rate, peak power, pressure, source control, etc.) before pulsed devices can become routine tools.

Shifting focus to rf-GDMS, we note that some excellent research has been published over the years. However, the future of this technique seems somewhat less optimistic than the future of rf-GDOES. This is not because there are technical difficulties that are clearly unsolvable, but rather because it appears that rf-GDMS research interest may be dwindling, as noted earlier. Moreover, the lack of any commercial instruments tends to slow progress.

Among the research papers that have been published on rf-GDMS, the emphasis has been placed on bulk analysis of solid materials, including electrical conductors, semiconductors, insulators, and powders. Depth profile analysis has not been pursued as much with rf-GDMS as with rf-GDOES. The same is true, in fact, for the d.c. instruments. This is probably because even quadrupole mass filters, which have relatively rapid m/z scanning and peak hopping capabilities, are not truly simultaneous instruments, meaning that no more than a few analytes can be monitored within a single burn. Fortunately, TOF instruments have shown great promise for rectifying this situation by offering truly simultaneous detection capabilities. They are also especially suited for coupling to pulsed discharge devices, resulting in a potentially powerful combination. As a result, rf-GD-TOF-MS (as well as d.c.-GD-TOF-MS) instrumentation and methods should be developed further. Finally, rf-GDMS has been explored as a means of evaluating chemical speciation. In contrast to hotter plasmas, such as the typical atmospheric pressure ICP operating at approximately 1 kW rf power, the rf-GD allows some control over molecular fragmentation of analyte molecules through selection of discharge conditions.

The analysis of polymeric materials is an area of special promise for both rf-GDOES and rf-GDMS. Though some analytical techniques that can be applied to this important class of materials exist, there is a need for additional and better techniques. Comparing rf-GDOES and rf-GDMS, the latter has the advantage of being capable of providing both elemental and molecular information. Moreover, the relative amounts of atomic vs. molecular information can be selected to some extent through the judicious choice of discharge conditions. This should enable effective polymer ‘fingerprinting’ to be accomplished. Additionally, both rf-GDMS and rf-GDOES can potentially provide much of the spatially resolved information that cannot be provided through many other methods. An obvious example is the depth profile evaluation of polymeric layers and surfaces. However, if rf glow discharge methods are to find widespread application for such analytical problems, much research work remains to be done.

Further implementation of both d.c. and rf glow discharge spectrometries in commercial and industrial
laboratories depends in part upon the development of pertinent standards [i.e. documentary standards, such as those published by ISO, ASTM International, and other standards developing organizations (SDOs)] and reference materials (both RMs and CRMs). Many, especially those who work primarily in academic and other ‘pure research’ environments, underestimate the importance of this topic. Suitable standards and reference materials work together to help provide the technical infrastructure that is necessary for the effective and efficient application of glow discharge techniques within the global marketplace. In particular, they enable glow discharge practitioners to perform more meaningful analyses on a routine basis. In turn, this provides many benefits of industrial, technological, and economic importance. These include enhanced quality control and assurance, easier laboratory accreditation against recognized quality systems (e.g. ISO 17025), facilitated commercial transactions and business relationships, mitigation and easier resolution of legal and contract disputes, and others. As a result, appropriate standards and reference materials actually help to promulgate the implementation of glow discharge techniques in ‘real world’ laboratories [334].

For these reasons, there is a critical need for the further development of both standards and reference materials pertinent to glow discharge spectrometries, whether rf or d.c. Standard test methods are needed to guide the practitioner in the performance of various analyses of economic and technological importance, such as depth profiling of thin films. Standards are also necessary to provide guidance on the definitions of crater shape parameters, the estimation of detection limits, and sputtering rate measurement. While some efforts to develop such standards are currently underway, much more needs to be done.

Concerning reference materials, both layered RMs and CRMs are needed for depth profiling applications. Moreover, there is a notable lack of such materials with characteristics pertinent to glow discharge methods [335]. These materials are needed mostly as control samples for checking accuracy. However, they might also be utilized for establishing or adjusting calibration parameters. Generally speaking, production and characterization of layered reference materials is a difficult and expensive activity. Moreover, since glow discharge methods are inherently destructive, these kinds of reference materials may be quickly consumed. Therefore, layered reference materials specifically designed for GDS may not always be economically viable. This is of concern from the viewpoint of the national metrology institutes (NMIs, e.g. NIST), who must recover the actual costs of producing reference materials, and who are continually faced with an ever-increasing demand for reference materials, but with little or no increase in available resources. In at least one sense, it might be of even greater concern from the viewpoint of commercial reference materials producers, who must be concerned not only with recovering costs, but also with making a profit. As mentioned earlier, anodic films have characteristics that are particularly appealing for use in GDS applications. Since these can be produced relatively easily, quickly, controllably, and reproducibly, they may provide at least a partial solution and should be explored further.

Although a myriad of bulk solid RMs and CRMs exist, there is always a need for more. Specifically, bulk materials with well-known mass fractions of H, O, and N are notably lacking. These are required to enable good instrument calibration for these elements. Production and accurate characterization of these sorts of reference materials may be difficult. This is largely due to the fact that H, O, and N are among the most problematic elemental analytes to determine accurately, especially in solid materials, where they may exist chemically bound in solid phase or as trapped gases within voids. Nevertheless, it is hoped that such materials will become more available.

Finally, reference materials with well-known trace and ultra-trace analyte mass fractions would be very helpful for the practice of both rf- and d.c.-GDMS. An important reason is that accreditation of GDMS laboratories against recognized quality systems often requires characterization of accuracy and establishment of traceability to suitable points of reference, at least within a ‘fit-for-purpose’ context. This may be a difficult or impossible task without suitable reference materials. This is an especially relevant point when one considers that, at least for many applications, GDMS may be one of the most sensitive, if not the most sensitive, method available. Therefore, there may be few or no viable competing methods with which to confirm mass fractions determined with GDMS. As for other materials described above, the production and accurate characterization of reference materials for trace and ultra-trace analytes presents a challenging task for the reference materials producer.

References


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