Radiofrequency Powered Glow Discharges: Opportunities and Challenges*

Plenary Lecture

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The development of radiofrequency powered glow discharge (rf-GD) devices for application in direct solids elemental analysis has been underway for over five years. At this point in the evolution process from speculation to implementation, it is time to look at where the devices fit in the marketplace of potential end-users. The devices possess a number of basic advantages over more traditional solids analysis techniques; however, further implementation must be justified through the analysis of real-world samples and the ability to solve real-world problems. The basic analytical characteristics of the devices as applied in this laboratory are presented along with 'demonstration' spectra/data for a number of projected areas of commercial application. The projected areas include the analysis of bulk non-conductors (*e.g.*, glasses and ceramics), oxide powders (e.g., geological materials, coal, catalysts, glasses and ceramics), layered materials (*e.g.*, metals, coatings, optical materials and electronic devices) and polymers (*e.g.*, bulk organics and metal-containing coatings and substrates). Some of the technical and analytical challenges posed by these specific sample types have been identified, with some methods of remediating deficiencies proposed and/or demonstrated. It is clear that the rf-GD has the capabilities to be a valuable problem-solving tool across a broad range of solids analysis applications, although much basic research and method development remains to be carried out.

Keywords: *Radiofrequency glow discharge; atomic emission spectrometry; mass spectrometry*

While the advances in instrumentation in the field of analytical atomic spectroscopy have been truly phenomenal over the last two decades, the challenges to the primary researchers and commercial manufacturers have also become more sophisticated. In many instances, enhanced analytical performance has driven these increased demands; thus this community has become a victim of its own successes. In addition, the traditional users of atomic spectroscopic instrumentation have been mandated (by federal or market forces) to characterize their 'products' better. For example, a newly demonstrated capability to detect heavy metals in aqueous systems with tenfold lower detection limits would lead to further environmental impact studies and most assuredly regulatory reform. Market forces dictate the standards in instances such as the semiconductor industry where costs are based on the assayed purity of the primary materials, such as sputtering targets.

Perhaps the most optimistic way to look at these challenges is that the enhanced capabilities have simply increased the scope of interest and application. These sorts of supply (researchers' and manufacturers' advances) and demand (end-

users) relationships lead to all sorts of interdisciplinary endeavours which heretofore were very rare. One example of this new synergism has come about due to the successful coupling of (HPLC) and (ICP-MS). We now have situations where atomic spectroscopists must learn the fine details of human nutrition and metabolism, while clinicians must be familiar with acronyms of our trade. While ICP-MS is a relatively mature technique, with the coupling of HPLC becoming more commonplace, these new applications are non-trivial and can require re-thinking of accepted strategies. In many respects, the evolution of new analytical techniques must have these sorts of 'tech transfers' in mind to justify their development towards more basic applications.

The development of practical, radiofrequency powered glow discharge (rf-GD) devices has been a major emphasis in this laboratory for the last six years.[1-3] At this point the source characterization process has progressed to where more applications-oriented developments are in order, targeting real-world applications and end-users. As noted by Slavin in an assessment of analytical atomic spectroscopic techniques, 'Any new competitive technique must have greater potential advantages, compared to existing techniques, to justify all of this effort (development of commercial GD instrumentation)'.[4] Thus, it is not enough to do traditional tasks a little better than existing technologies, there must in fact be new analytical systems (*i.e.*, end-markets) to be tapped to justify the effort. While Slavin was referring to the development of GD devices, this is true for any new technologies. I refer to this wellfounded philosophy as the 'Slavin criterion'. It must be kept in mind that it is not sufficient to demonstrate a new capability by 'running a sample', one must demonstrate a real problemsolving capability. The development of rf-GDs in a number of laboratories is now entering this demonstration stage.[5-8]

At some stage in the development of an analytical technique one must project the impact that such an instrument/methodology might have. In order to assess the possible utility of an analytical technique, a survey of those topics described in the bi-annual Application Reviews published in *Analytical Chemistry* is instructive. Table 1 is a compilation of the topics, and number of pages devoted to each topic, as they appeared in the 1995 addition.[9] These page counts probably give a reasonable indication of the level of interest and development in instrumentation and methodologies for the given areas. For example, clinical chemistry is far and away the largest area, for obvious reasons. Alternatively, steel analysis, while economically important, is a mature field with few new developments. This may be a case where the industry is not providing new analytical challenges (*i.e.*, sample types) or where new analytical techniques have not made sufficient impact to warrant further developments or the establishment of new analytical benchmarks. Those topics where direct solids analysis (elemental or organic) is involved have direct relevance to the

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Table 1 Topical coverage of the 1995 Application Reviews published in *Analytical Chemistry*[9]

Topic*	No. of pages
Pesticides	20
Steel and Related Materials	**12**
Coatings	**14**
Process Analytical Chemistry	24
Geological and Inorganic Materials	**16**
Pulp and Paper	**10**
Analysis of Synthetic Polymers and Rubbers	**30**
Food	28
Separation and Analysis of Peptides and Proteins	28
Air Pollution	16
Surface Characterization	**22**
Environmental Analysis	**36**
Particle Size Analysis	16
Forensic Science	**22**
Pharmaceutical and Related Drugs	20
Petroleum and Coal	**34**
Industrial Hygiene	28
Clinical Chemistry	**148**
Water Analysis	58

* Those topics where direct solids analysis (elemental or organic) is involved, and which have direct relevance to the discussion here, appear in bold type.

discussion here and appear in bold type in Table 1. These are the areas of potential impact for any new direct solids analysis technique.

It is important to note the diversity of possible matrices and types of (likely) desired information that are represented in Table 1. Table 2 lists some of the types of information that might be required in these situations. Beyond the basic need for bulk elemental analysis (*e.g.*, for a steel casting), solid sample dissolution for flame, furnace and atmospheric plasma analyses is not a viable option. Depth profiling applications tend to be more qualitative in nature than bulk analyses, as issues of pollutant identification and distribution are very important in assessing the integrity of a layered system. For example, the existence of oxygen at the interface of a galvanized coating is more important to ascertain than the exact stoichiometry of the Zn–Al coating. Surface mapping can be considered to be a specialized case of depth profiling as such analyses usually do not require inclusion of information from the bulk material. The identification of the speciation of 'elemental' analytes (*e.g.*, Fe^{2+} or Fe^{3+}) is also very important in the study of corrosion processes, for example. In addition, the molecular form of such analytes is crucial in electronics applications as well as polymer analyses. No single instrumental method is likely to be practical for each of these cases of sample types and information. Limitations are imposed from the point of view of basic physics (*e.g.*, the limited penetration depth of photons) and by questions of implementation (*e.g.*, cost and throughput). Probably more so than with solution-based atomic spectroscopic methods, direct solids analysis usually involves a number of compromises imposed by virtue of the large variety of sample types and types of desired information. Even so, the combination of sample types

Table 2 Types of information desired in direct solids analysis

1.	Elemental analysis —
	(a) qualitative
	(b) quantitative
2.	Depth profiling
3.	Surface mapping
4.	Speciation —
	(a) oxidation state
	(b) 'molecular' form

(Table 1) and types of information (Table 2) represent useful targets in methodology development.

Described here are representative examples of where rf-GD devices may find application. As mentioned previously, the practical viability of any technique must be established through thorough system optimization and rigorous analytical application. The data presented here are not necessarily in this latter case, but reflect those areas where the basic characteristics of the devices justify further investigation. Many of these possible applications are currently being pursued and have begun to pose real challenges to their practical worth. For example, the major driving force behind the development of rf-GDs was their inherent ability to sputter non-conductive samples such as glasses and ceramics; unfortunately, differences in the thickness of such samples lead to what would be considered substantial matrix effects. We illustrate here practical methods for assessing these difficulties as well as correcting for them. It is believed that these example data should provide sufficient evidence to interest 'non-traditional' users of solids elemental analysis, as well as shed some light on to how practical analyses can be performed.

EXPERIMENTAL

The instrumentation employed in this laboratory in the development of rf-GD optical and mass spectrometry sources has been described in detail elsewhere, so only general descriptions are necessary here.[10–13] All studies in rf-GD-AES have employed an external sample mount geometry, wherein the rf potential is applied directly to the back of the sample which is held against an O-ring to form the vacuum seal.[10] The sputtering area is defined by the inner diameter (typically 3 mm) of the limiting anode orifice plate. Optical intensity measurements are performed in the end-on manner, directly opposite the sample surface. Two optical spectrometer systems have been utilized. The first system is a 1.0 m J–Y 38 sequential scanning monochromator (Jobin–Yvon, Division of Instruments, Longjumeau, France) which is employed in single line diagnostic studies and in bulk solids analysis.[10] The spectrometer operates under the standard J-YESS control package for these traditional applications and under the IMAGE system for fast sequential (170–500 nm in 2 min) spectral recording. The high dynamic range detector (HDD) system accommodates the demands in this case for fast measurement (≈ 0.5 ms per point, for 264 000 points) of optical signals which can differ by more than nine orders of magnitude across the spectrum. A 14-channel polychromator system (J–Y RF 5000, Jobin–Yvon, Division of Instruments) is employed for the simultaneous, multi-element measurements required for in-depth profiling.[11] This system, which is expandable to include 64 photomultiplier tubes/wavelengths, operates at a 2 kHz sampling rate for each channel, sufficient to capture any optical transient produced as successive layers are ablated. The housing of the 0.5 m Paschen–Runge spectrometer is nitrogen-purgable, allowing access to transitions in the vacuum ultraviolet region of the spectrum, important for analysis of non-metals and gaseous sample constituents.

The development of rf-GD-MS sources has been undertaken on a VG GloQuad (FI Elemental, Winsford, Cheshire, UK), single quadrupole instrument.[12] The conventional dc-powered discharge source commercially available with this instrument was replaced with a simple direct insertion probe (DIP) apparatus. The DIP permits ready mounting of the sample, transfer into the high vacuum chamber, and rf powering of the discharge. Two basic source configurations have been developed to permit analytical flexibility: one which holds pin-type samples of less than 5 mm diameter[12] and another for flats of greater than 5 mm diameter.[13] The latter geometry is necessary for samples requiring in-depth analysis, as well as for bulk

polymers. The GD ion volume is operated at a temperature of $-160\,^{\circ}C$ by use of the standard VG cryo-cooling cell. Cryo-cooling is important in all applications of GDMS, but it is particularly necessary in rf-GDMS when sputtering samples such as compacted oxide powders (*e.g.*, glasses, catalysts and geological materials) which tend to outgas and have high moisture content, and polymers whose mass spectra would be greatly affected by gas phase ion–molecule reactions. The GloQuad is equipped with a dual detector (Faraday cup/Channeltron) system capable of operation over an ion current range of 10^{-18}–10^{-9} A with all scan functions and data manipulation under the control of a 386-Type microcomputer.

In all of the work described here, the rf-GD plasmas are operated with high purity (>99.9995%) argon as the discharge gas. Discharge gas pressures are monitored by use of Pirani-type gauges for the optical sources and with a specially designed DIP fitted with a thermocouple gauge for the MS source. The rf-GD sources are operated in a constant-power mode (up to 50 W). The sources coupled to the sequential optical and mass spectrometers are powered by RF Plasma Products (Voorhees, NJ, USA) RF-5s generators with their mate AM-5 automatching networks. The commercially available RF 5000 system is equipped with the manufacturer's GD source and rf generator.

RESULTS AND DISCUSSION

Throughout the primary rf-GD source development processes, a basic set of analytical characteristics have been realized. The characteristics listed in Table 3 have been determined for both AES and MS applications involving bulk samples including high-purity metals, alloys and glass standards. Comparison of these figures of merit for metallic samples with those of traditional bulk solids techniques (arc, spark and GD-AES/MS) suggests that the rf-GD spectrometries are competitive alternatives. In some cases, the enhanced limits of detection would be important, while the lower analytical throughput and sheer novelty of rf-GD-AES would be seen as negative attributes in the possible displacement of spark emission in foundry applications for example. Of course, the ability to analyse non-conductive samples directly is novel amongst the above-cited methods. Foundries do not generally need this capability, so major headway into markets serviced by those traditional solids analysis instruments would not be expected (*i.e.*, failure of the 'Slavin criterion'). Alternatively, this capability in combination with the figures cited in Table 3, would be very attractive to the glass, ceramic and speciality materials industries. The practical competition here is with either XRF or wet-chemical methods for bulk analysis. Laser ablation ICP-AES and MS, which have not competed successfully with arc and spark spectrometries for the bulk metals analysis market, are also being increasingly applied in these industries.

The following sections set out to illustrate the problem-solving opportunities afforded by rf-GD atomic emission and mass spectrometries. The application of rf-GD devices to the direct, bulk analysis of non-conductive samples represents just one opportunity for application. However, other possible applications do not come without challenges, *i.e.*, there is no free lunch. Within each section, realized and projected challenges to the practical application of these devices are discussed. For those applications where this laboratory has focused its efforts, potential methods for overcoming those challenges are detailed.

Bulk Glasses and Ceramics

As has been shown in many publications dealing with rf-GDs, one can obtain 'meaningful' mass and optical spectra from oxide-based samples without matrix modification. Bulk glasses and ceramics represent a very large and increasingly important segment of the materials industry. Owing to the difficulties presented in the dissolution of such materials, flame and plasma source spectroscopies have not enjoyed wide acceptance. XRF spectrometry has been the workhorse in this area because of its high degree of automation and low capital costs. Matrix effects and limited sensitivity are areas where XRF is found lacking. Glass sample analysis by rf-GD has a great deal of potential here, but matrix effects based on sample thickness are a major challenge. Fig. 1 illustrates the respective rf-GDMS spectra (single scan, mass calibration mode) obtained for two NIST SRM 610 Trace Elements in Glass samples which are (A) 1 and (B) 3 mm thick, respectively. These two sets of spectra are qualitatively the same, and are typical of rf-GDMS data of bulk solid glasses. The spectra are fairly simple in structure, with the characteristic isotopes of argon singly and doubly charged species, atomic and molecular oxygen, and silicon easily seen on the Faraday cup detector (>10^{-12} A). Further scale expansion reveals the lead (426 ppm) and bismuth (450 ppm) signals detected by the ion multiplier. From close inspection of the ion current axes, the proportional loss of ion beam intensity in going from the 1 to the 3 mm thick samples is illustrated although the relative analyte peak heights are not appreciably affected, at least within the expected experimental error. The approximately two-fold loss of analyte intensity across the board suggests a reduction in signal based on atomization. Differences in sputtering rates (based on absorbance measurements) can be of the order of a factor of ten for oxide/glass samples ranging from 0.8 to 5.3 mm in thickness.[14] (A practical limit of a 10 mm sample thickness is the rule-of-thumb in this laboratory.) Basically, the thickness of a dielectric sample directly affects the propagation of rf energy through the sample and thus thicker samples run at a fixed rf power level exhibit reduced sputtering rates. Reductions in sputtering rates obviously lead to lower concentrations of analyte in the gas phase and thus reduced analytical signal. In addition, it would not be unrealistic to expect that plasma excitation/ionization conditions would also be affected by sample thickness.

Two alternatives exist for addressing the differences in sputtering rates of dielectric samples. First, one could in principle match the thickness between the reference standards and the samples. Given the scarcity of glass and ceramic reference materials, this is not a viable option. Grinding of

Table 3 Basic analytical characteristics for rf-GD atomic emission and mass spectrometries

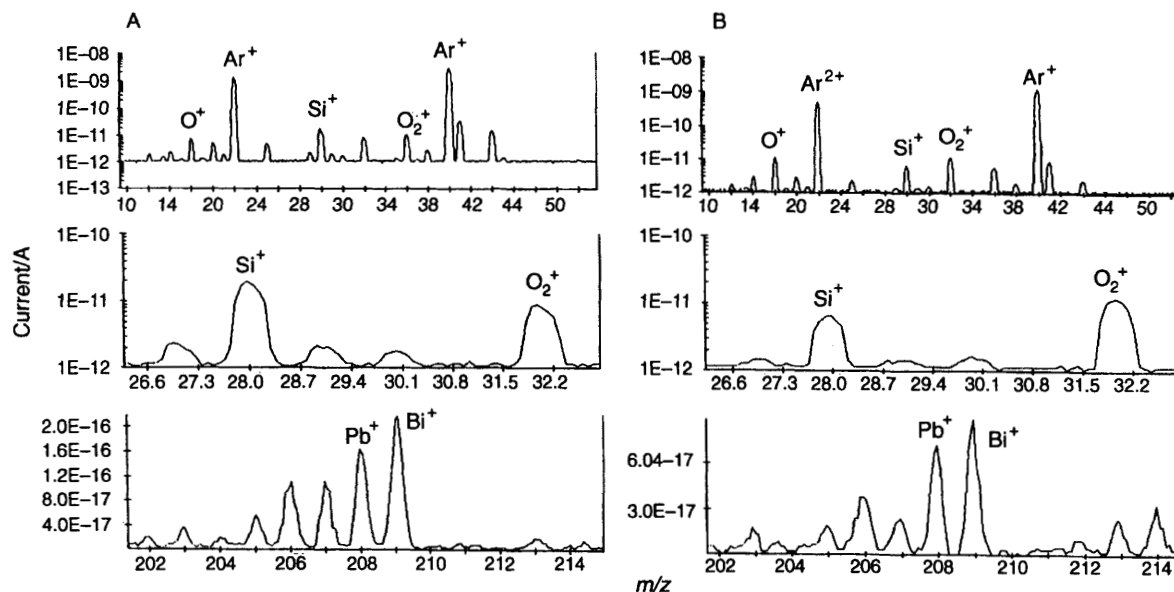| Technique/sample type	Stabilization to 5% RSD/min	Short-term precision (% RSD)	Long-term precision (% RSD)	External precision (% RSD)	Limit of detection
Atomic emission —					
Metals	0.5	0.5	2	4	1–50 ppb
Non-conductors	0.5	0.8	2	5	0.1–5 ppm
Mass spectrometry —					
Metals	3	<1	<2	<5	1–100 ppb
Non-conductors	≈30	<2	<3	<7	1–500 ppb

Fig. 1 Rf-GD mass spectra of NIST SRM 610 Glass samples of A, 1 and B, 3 mm thickness (rf power = 35 W, argon pressure = 70 mTorr)

samples down to the thickness of the standards is not practical and of course making samples thicker to match standards is impossible. The second approach to better quantification is to identify a measurable parameter within the analytical plasma which represents the energy being delivered to the sample surface, after passage through the sample. Early studies in Grimm-type GDs showed that sputtering rates were directly related to applied voltage, within a family of alloys.[15,16] The same sort of relationship has been found regarding the dc-bias potential in rf-GD systems.[17] Therefore, it is logical to expect that dc-bias potentials may be a good indicator to assess sputtering rates of insulating samples.

The approach used in this laboratory to counter matrix effects has involved the generation of a response function of analyte intensity *versus* sample thickness/dc-bias. The slope of this function is indicative of the energy loss due to differences in sample thickness. The general process of this approach is depicted in Fig. 2, where the emission intensity for the Mg I 285.1 nm transition is plotted as a function of dc-bias potential (sample thickness) for a series of Macor (Corning Glass Works) samples. The dc-bias values represent those measured for the discharges operated at powers of 30 W and argon pressures of 6 Torr, for samples ranging in thickness from 10 to 0.9 mm. As can be seen, a direct relationship exists between the measured dc-bias potential and the observed optical emission intensity. This relationship between emission and dc-bias voltage allows for the calculation of a corrected intensity (I_c) based on the slope of the line and the observed bias potential of the

analytical sample:

$$I_c = I_m + (m \times u) \qquad (1)$$

where I_m is the measured intensity, m is the calculated slope of the intensity *versus* dc-bias curve and u is the voltage deficit between the measured dc-bias of each sample and that of the thinner sample/standard. The product ($m \times u$) provides a correction factor for the power losses as is shown in Fig. 2 by the corrected emission intensities. Analytical quantification has been performed based on calibration graphs with CRMs, where the analytical response of the target elements is corrected for the effects of sample thickness. This basic approach has been used, with slight variations in implementation, in atomic absorption,[14] emission[18] and mass spectrometry[13] applications, resulting in analytical accuracies of the order of 5–10% error for samples which differ in thickness from the standards by many millimetres. The fact that this approach is successful in these applications suggests that the plasma energetics are not greatly affected by the thickness of the non-conducting samples, which is counterintuitive. Langmuir probe studies performed in this laboratory confirm that this is indeed the case.[19] In fact, charged particle (electron and ion) densities are reduced with increasing sample thickness, while electron temperatures and average electron energies are unaffected.

Glass and Oxide Powders

The ability to analyse oxide powders directly touches many applications including glass and ceramic primary materials, catalysts and geological materials.[20–22] Compaction of such samples with metal powders (binders) has been used in dc-GD applications for over 20 years. Those early works pointed to the importance of uniform grinding and mixing, thorough drying, and the use of good vacuum practices to minimize the deleterious effects of residual gases and water vapour on the plasma energetics. The presence of such species also adds to the complexity of the analytical spectra. These same considerations are even more important for direct pressing of sample discs from the sample powders without a binder as afforded by rf operation. In fact, such an approach relies heavily on the compaction properties of the sample in terms of it binding with itself as opposed to the relatively easy binding in metal powders.

Studies have recently begun towards the direct analysis of powder samples of simulated, vitrified nuclear defence waste
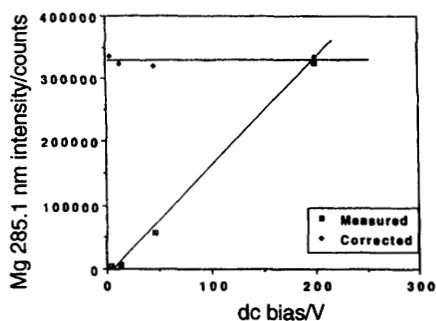

Fig. 2 Effect of dc-bias voltage on Mg I 285.1 nm emission intensities from Macor samples ($\approx 8.5\%$ Mg) (sample thickness = 10–0.9 mm, rf power = 30 W, argon pressure = 6 Torr)

glass. In this application, the goal is to take the primary powders, grind them to appropriate sizes, and press them into pellet form similar to those used in IR spectrophotometry. Challenges have arisen from the determination of proper powder mesh size (a function of grinding time), the pressing conditions (pressure and duration), and the most appropriate discharge conditions (power and pressure). Fig. 3 illustrates the extremes in the types of optical spectra that can be obtained in the analysis of powder samples, in this case a zeolite, molecular sieve. Zeolites are basically Si, Al and Mg clays with well defined pore sizes. This particular zeolite is used as a drying agent in flowing gas streams and so has a very high affinity for water vapour and other atmospheric gases. Fig. 3(a) is the spectrum derived from simple drying of the initial powder at 100 °C followed by grinding and pressing of the sample disc. The rf-GD-AES source operates stably with this sample, but the spectrum is dominated by water and molecular nitrogen associated band structure. Fig. 3(b) is the spectrum obtained by drying the sample at 300 °C following the same grinding step, pressing the sample in a vacuum die, and exposing the sample to a short (≈ 1 min) flux of the argon discharge gas before ignition of the plasma. Given the hygroscopic nature of this material, such a drying step is necessary in any case to obtain a proper weighing. The latter spectrum is clearly atomic in nature, with carbon seen as the dominant emitting species. The presence of the carbon was at first puzzling, but is easily attributed to the indicator dye with which this material is coated. Another key realization in this sort of application is the need to have the primary vacuum seal to a bulk metal surface rather than the sample disc itself, as this results in a poor seal and the introduction of atmospheric gases into the plasma. Therefore, the sample disc holder originally developed by Winchester and Marcus[23] has to be implemented such that the sample is press-fit into the water-cooled brass holder and that assembly held against the vacuum O-ring. The comparison between the two spectra shown in Fig. 3 illustrates the utility of the IMAGE data acquisition mode as this allows ready diagnostics of plasma operating conditions, spectral archiving and the direct comparison of spectra across wide wavelength ranges.

Much work remains to be carried out in the methodology development for powder sample analysis. The ease of this procedure, along with the wide variety of possible applications, make this an attractive line of investigation. Key to any application in this area is the ability to produce discs that are free from excess waters of hydration. This is particularly true for water scavenging matrices such as the zeolites and those samples that have inherently small particle sizes, such as coal. A cursory study has been performed where coal samples have been ground and sputtered directly for rf-GDMS analysis, producing mass spectra that have high, stable ion beam currents.[24] Great care must be taken to dry the samples at each stage of preparation, prior to grinding, weighing, compaction and analysis. The use of a quadrupole mass filter made this particular analysis difficult in the low mass range (<44 u) due to the high abundance of residual gases. Nevertheless, the beam currents for the analyte metals in the NIST SRM 1632b Trace Elements in Bituminous Coal were acceptable, with the relative sensitivity factors falling within a reasonable range. In practice, a high resolution mass analyser would be most beneficial to eliminate the many isobaric interferences introduced by combinations of N, O and S species which are ubiquitous in coal samples.

Conductive/Non-conductive Layered Systems

One of the earliest projections as to the future applications of GD spectrometries, atomic emission to be specific, was in the area of in-depth analysis. Belle and Johnson showed in 1973 that fast, effective depth profiling of metallic layers was possible with a Grimm-type GD–AES source.[25] Since that time, depth profiling of 'thick' (>1 µm) films such as galvanized coatings has been the largest application of these devices. Alternatively, MS applications have centred on the bulk analysis of high-purity metals with relatively few applications in depth-resolved analyses. Extensive studies by the groups of Bengtson,[26] Hocquaux[27] and Payling[28] and others, have made great strides into the quantification of depth profiles. Specifically, one records the data in the intensity *versus* time domain, which must be translated into the concentration *versus* depth format. In addition, studies by groups including those of Gijbels,[29] Raith[30] and Angeli,[31] have shown how discharge parameters (particularly gas pressure and voltage) affect the shape of the sputtered craters. In the ideal case, a three-dimensional cylinder with an atomically flat bottom will evolve as successive layers are removed. In general, these groups have shown that high voltages (low pressures) result in craters that are convex in shape (*i.e.*, edges deeper than the centres), while high pressures (low voltages) produce concave craters.[27,29–31]

Studies in this laboratory towards the quantitative implementation of rf-GD-AES for depth-resolved analysis have begun, with the determination of how discharge parameters affect crater shapes having recently been completed. Studies of the sputtering of metallic (brass and stainless steel) and non-conductive (Macor) materials have shown similar types of influences as noted for the dc plasmas cited above. For the rf-GD, which is typically run in a constant-power mode, increases in dc-bias voltage increase the amount of crater convexity. Sputtering rates are seen to increase from 1 to 12 µm min^{-1} with powers from 10 to 50 W for a brass target, while the rates for Macor samples (1.2 mm thick) vary from only 0.2 to 0.5 µm min^{-1}.[11] Very importantly, while the absolute roughness (actually the RSD of the depth) of the crater

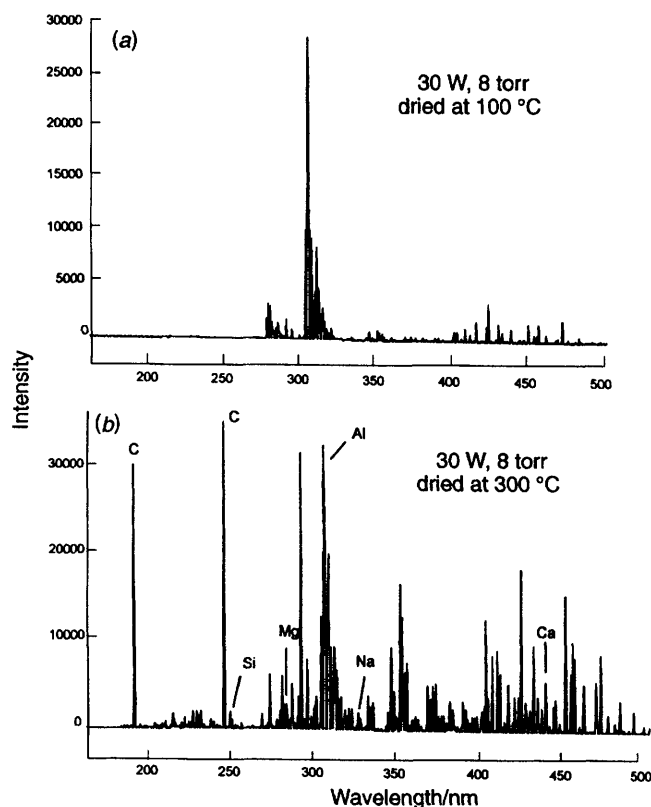**Fig. 3** Rf-GD atomic emission spectra of zeolite, molecular sieve powders prepared by (a) simple drying at 100 °C and (b) drying at 300 °C and use of vacuum pressing (rf power = 30 W, argon pressure = 6 Torr)

bottoms increases with sputtering depth, the relative degree of roughness (RSD variation/average depth) actually becomes better, which indicates that the depth resolution (based on the optical transients) will probably not deteriorate as a function of depth. Fig. 4 illustrates the primary advantage of using the rf-GD approach to depth-resolved analyses. Seen here are the rf-GD-AES profiles of the elements present in a laboratory-grown (via sputter deposition) layer of brass (≈ 1 μm thick) on a 1.2 mm thick glass flat. This sample would be representative of a mirrored surface used optical application. Seen clearly is the rapid stabilization of the emission signals of the brass constituents (Cu and Zn) followed by a reduction in their intensities at the transition region between the metallic and glass matrices. The absence of step functions for the decrease in the surface species and the increase in the glass constituents reflects the poor formation of a finite interface (i.e., we have much to learn about sputter deposition processes). Certainly, the opposite situation of a non-conductive coating on a metallic substrate (e.g., a paint coating) could be addressed in the same manner. In any case, these capabilities do not exist with dc powered GDs and thus represent new opportunities for rf-GD-AES and MS applications. As with the application of dc-GD-AES to depth profiling,[26–28] monitoring of dc-bias potential and argon discharge gas emission intensity as a function of time will be useful in monitoring the discharge energetics and sputtering conditions.

One additional area where the basic qualities of rf-GDs will be useful is in the profiling of very thin layers which may be conductive or non-conductive. Shown in Fig. 5 is a first-try temporal profile of a superlattice system consisting of a 100 nm Cu layer on top of nine alternating layers of Cr–Ni and Cu (each of which is 50 nm thick) on a silica substrate. The overall sample thickness is ≈ 0.5 mm. A similar temporal profile has been presented by PraBler et al.[32] for a Grimm-type rf-GD-
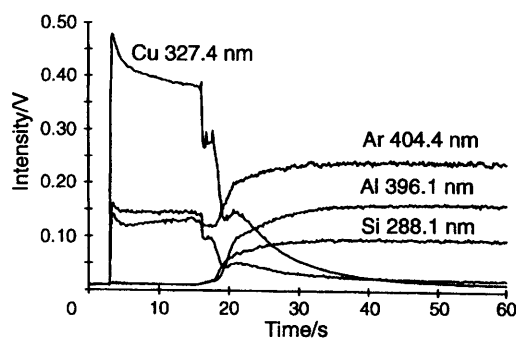

Fig. 4 Rf-GD atomic emission temporal profiles of an approximately 1 μm thick brass layer sputter-deposited onto a 1.2 mm thick glass flat (rf power = 20 W, argon pressure = 4 Torr)
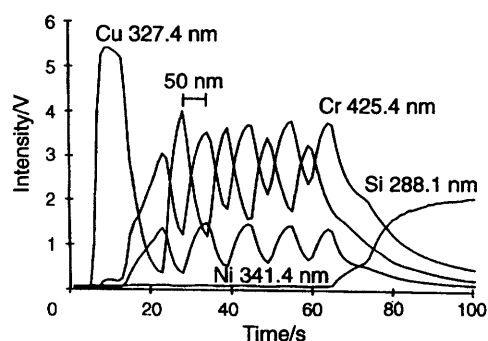

Fig. 5 Rf-GD atomic emission temporal profiles of a superlattice material consisting of a 100 nm thick Cu layer on nine alternating 50 nm layers of Cr–Ni and Cu deposited on an approximately 0.5 mm thick silica substrate (rf power = 10 W, argon pressure = 10 Torr)

AES device. The individual layers, while not baseline-resolved, are seen distinctly as the entire profile is completed in less than 1 min. No particular optimization of discharge parameters had been performed prior to this analysis. The rapid attainment of steady-state discharge conditions afforded by the rf source is paramount in these sorts of samples and points to fields of application which most researchers would not have imagined practical a handful of years ago.

Polymeric Materials

The final general area of opportunity for rf-GD devices is in the analysis of polymeric materials. Bulk polymers represent another fast-growing segment of materials research and production. Both very high density and electrically conductive polymers continue to push new applications. Normally, atomic spectrometrists do not have occasion to analyse polymeric materials which have traditionally been composed of little more than carbon, hydrogen, oxygen and fluorine. Metals (usually oxides) have always been added to polymer blends as colouring agents, having more to do with aesthetics than with structure and functionality. Metals are now being used as integral components in conductive polymers as well as electro-optic materials. In these cases, direct solids analysis is a necessity for qualitative as well as quantitative analysis as dissolution in plasma/flame compatible solvents is not a practical option, if possible at all. Ediger[33] presented preliminary studies of the use of a direct laser ablation–atomic emission system for the characterization of polymers. In this case, the polymer structure was broken down by the heating of the laser, with the resulting vapours dissociated and the analyte metals excited by the plasma plume. This was seen to be a promising approach to qualitative sorting of polymers based on metal content.

The use of an rf-GD allows for the direct sputtering of polymeric materials as with metals or glasses. Fortuitously, the sputtering process here does not produce a solely atomic population, but rather discrete fragments of the monomer base unit are liberated. Gas phase molecules, more likely radicals, are then subject to collisional ionization by electron impact and Penning processes to produce mass spectra which reflect the composition of the polymer itself. Fig. 6 illustrates the type of mass spectrum obtained in the sputtering of a terpolymer film, THV (3M, St. Paul, MN, USA), consisting of PTFE, hexafluoropropylene, and poly(vinylidene fluoride). As would be expected, the mass spectrum includes $C_xF_y^+$ fragments that are assignable to PTFE and hexafluoropropylene, which have very similar SIMS fragmentation patterns; however, their signatures have different relative intensities.[34] The third component of THV, poly(vinylidene fluoride), yields characteristic peaks such as $C_2H_4F^+$ and $C_3HF_4^+$. Rf-GDMS spectra of the sort shown in Fig. 6, and others from this laboratory,[35] suggest that structurally similar polymers could be distinguished from one another by rf-GDMS in a manner similar to SIMS. In fact, the rf-GD mass spectra are very similar in character to those that have been observed for static SIMS employed on quadrupole mass filters.[36]

Preliminary studies into the applicability of rf-GDMS to the analysis of polymers have provided a good basis for continued exploration. In addition to the dual-mode (elemental and organic MS), the probable advantages of this approach over SIMS sources include: (1) simple sample preparation, (2) rapid sample introduction pump-down (< 1 min), (3) rapid plasma stabilization times (< 3 min), (4) high analyte ion beam currents (> 10^{-9} A) and (5) excellent signal stability (< 5% RSD).[35] The effects of discharge gas pressure and rf power were studied to provide further insights into the sputtering process and various ionization mechanisms. The relative contributions of large $C_xF_y^+$ fragments to the mass spectra are
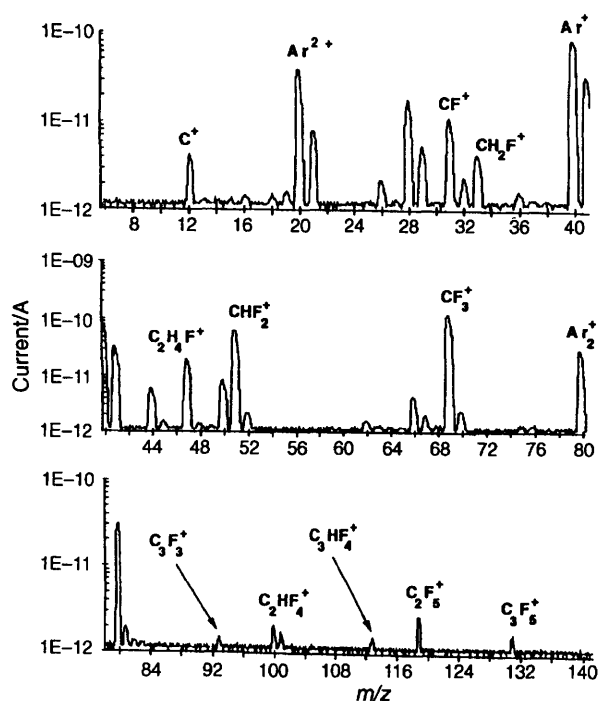
Fig. 6 Rf-GD mass spectrum of a THV terpolymer sample (rf power = 20 W, argon pressure = 0.10 Torr)

solids elemental analysis techniques, these are unique capabilities that are not presented by any other single spectrochemical device.

It is unclear whether the rf-GD will become a widely accepted, routine analytical source in the way that flame atomic absorption or the ICP spectrometries have evolved. Perhaps the rf-GD will be more of a problem-solving source, which will be applied more in research support and product development, such as in centralized analytical facilities. This paper has set out some of the basic opportunities and challenges of these future applications. The next few years will define where the devices will find application. Their ultimate commercial success will depend on whether or not they successfully fulfill the 'Slavin criterion' in real-world situations.

dictated by the relative dc-bias potential at the sample surface, such that situations of relatively low discharge pressures or high powers produce larger populations of high mass fragments. Similarly, sample thickness plays an important role in the spectral characteristics as the lower dc-bias generated for thick samples tends to exhibit more low mass fragments than for thinner samples. Future rf-GDMS studies will explore the utility of the technique in a wider range of polymer families and in end-applications involving the determination of residual additives and trace elements, structure determinations and depth-resolved analyses. Many challenges remain to be revealed for this application of rf-GD spectrometries. For example, many polymers are thermally sensitive, and so cooling of the sample is an important source design criterion. Gas purity will also affect system performance as ion–molecule reactions in the gas phase and on the sample surface will greatly complicate spectral interpretation for MS in particular. The cryo-cooling apparatus employed with the present system greatly minimizes these problems.

CONCLUSIONS

Rf-GD devices have evolved to the point where they must now demonstrate true analytical utility to justify further investments in time, energy and resources. Atomic emission and mass spectrometric sources have been designed to allow maximum flexibility in terms of letting the sample and the types of desired information dictate the form of sample presentation, without rigid geometric constraints imposed by the sample introduction systems. These sources have demonstrated analytical characteristics and figures of merit that would warrant their consideration to replace more established technologies. To be truly valuable though, the devices must be capable of performing analyses that extend the general scope of direct solids elemental analysis. The characteristics of the rf-GD devices that will probably contribute to expanding the realm of direct solids analysis include the ability to sputter non-conductive materials directly for both bulk and depth-resolved analyses and the ability to generate mass spectra that include both atomic and molecular information. In comparison with traditional direct

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