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Analysis of Nonconducting Materials by dc Glow Discharge Spectrometry

ANNEMIE BOGAERTS, WIM SCHELLES
and RENÉ VAN GRIEKEN

University of Antwerp, Department of Chemistry,
Wilrijk, Belgium

11.1 INTRODUCTION

The concept of an analytical glow discharge, in which the material to be analyzed acts as the cathode of the glow discharge cell, seems to restrict the field of application to the analysis of conducting materials. This is, indeed, the most straightforward and routine application, but nonconducting materials can also be analyzed. Three different methods have successfully been applied for the analysis of nonconductors by glow discharges, namely:

- The use of a radio frequency (rf) glow discharge instead of the direct current (dc) source. In a dc glow discharge source, a constant voltage is applied between the cathode and anode, leading to a constant current to the cathode, which yields charging-up of the nonconducting sample, preventing it from further being sputtered. In an rf source, however, a time-varying voltage (with rf frequency) is applied between the electrodes. This protects the nonconducting sample from charging-up, since the positive charge accumulated due to positive ion bombardment is neutralized by negative charge accumulation due to electron bombardment during one half of the rf cycle. This method was first applied to analytical glow discharges in 1971 by Coburn and Kay [1], but it

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received much wider attention in the late 1980s, mainly as a result of work of Marcus's group [2].

- The mixing of a nonconducting powder with a conducting host matrix, which was developed in 1972 for glow discharge optical emission spectrometry (GD-OES), by Dogan *et al.* [3] and later also applied to glow discharge mass spectrometry (GDMS) and glow discharge atomic absorption spectrometry (GD-AAS).
- The use of a conducting secondary cathode in front of the nonconducting solid sample, which was first introduced in 1993 for GDMS by Milton and Hutton [4].

Since the basic principles and applications of rf discharges will be discussed in detail in another chapter, we will focus here on the two other techniques, which can be used in the case of dc glow discharges.

11.2 USE OF A CONDUCTING HOST MATRIX

11.2.1 METHODOLOGY

When the nonconducting sample is in powder form, it can readily be mixed with a conducting host matrix (mostly also in powder form), according to a certain sample-to-host mass ratio (see below). The mixing is usually accomplished by means of a mechanical shaker or grinder. A detailed description of this sample preparation procedure is given, among others, in ref. [5]. In our laboratory [6], a fraction of the sample + host mixture (e.g. 0.5 g) is usually inserted in a polystyrene vial with a glass ball pestle added. Thorough homogenization of the mixture is achieved by use of a Wig-L-Bug (Spex, Edison, NJ, USA) for several minutes. About 0.15 g of the homogenized mixture is then transferred into a polyethylene slug and pressed at a pressure of several tons per square centimeter, usually into the form of a pin (or a disk). The latter can then be directly inserted as the cathode in the glow discharge. This approach originates from experience gained with arc and spark discharges [7,8], and is relatively straightforward. However, several parameters have to be taken into account in order to perform successful measurements.

The Host Material

It is obvious that only high-purity powder can be used as the host matrix. Indeed, the host material is also sputtered and is introduced into the discharge, together with the material to be analyzed, and this results in a blank spectrum. Further, it has been proved that host materials with a good sputter yield are desirable to obtain a good overall sputtering of the compacted sample [5]. Other favorable characteristics of the host matrix include good mechanical strength upon pressing, low cost and availability in a variety of particle sizes (see below). In addition, interferences as a result of the matrix material should be avoided.

A number of materials have been evaluated as host matrix, such as Cu [2,9–27], Ag [2,9–12,28–34], Al [2,9,35,36], Ta [9,10,29–31,37], Ti [10,29–31], Fe [9,21], graphite [9,12,29,38], W [2,9], Bi [10], In [10,39], Pb [10], Sn [10], Zn [10], Ni [21] and Ga [40]. Gallium has the advantage of being available in extremely high-purity grade. Moreover, gallium has a melting-point of 30 °C. Therefore, if the gallium is mixed in the liquid state with the nonconducting material, it has been proved that only little gallium (<20% of the weight of the sample) is needed to produce a conducting electrode. It is believed that a very thin conducting gallium film is formed around each nonconducting particle. To obtain this effect, extremely thorough mixing is needed [40]. Experiments in our laboratory, however, have indicated that this sample preparation technique is not always reproducible. Another innovative technique has been applied with indium as host material [39]. Indium was used as a solid in which the nonconducting powder migrated in a high pressure vessel, thereby avoiding the trapping of residual gases.

The more classical technique, however, is based on the use of powdered host materials. The effect of different kinds of host materials has been investigated [e.g. 9,10,29]. From all these materials, tantalum has the advantage of being a getter material [9,29,30]. This means that it tends to form strong oxide bonds, effectively removing oxygen from the discharge, and therefore reducing molecular oxide interferences. Tantalum powder, however, generally is not available in such a pure form as, for example, silver and copper [41]. That explains why the latter materials are more often used as the host matrix [2,9–34]. Copper, in particular, is very suitable, because of its wide availability, relatively low cost and high sputter rate [14]. Moreover, its high thermal conductivity and an excellent suitability for blending of finely dispersed powders are additional factors for choosing copper as the host material [42]. De Gendt [6] found for an albite sample (oxide-based geological material) comparable analytical signals for a copper and a silver matrix, but lower analyte signals were obtained with graphite as a binder (see Figure 11.1) [6]. This could be due to the very low sputter rate of graphite, resulting in a very low overall sputtering of the compacted sample. In some cases [35,36], aluminum was preferred as a host matrix, because it gives rise to relatively few interferences in the mass spectrum, e.g., in the vicinity of Pd, Rh and Pt [36]. Generally, one can state that the choice of the host material has to be made for each specific analytical problem, depending on, among others, the presence of spectral interferences for the elements of interest.

Relative Percentages of Sample and Host in the Mixture

It is clear that the electrode has to contain enough conducting material to avoid instabilities in the discharge and to create enough sputtering, since high relative

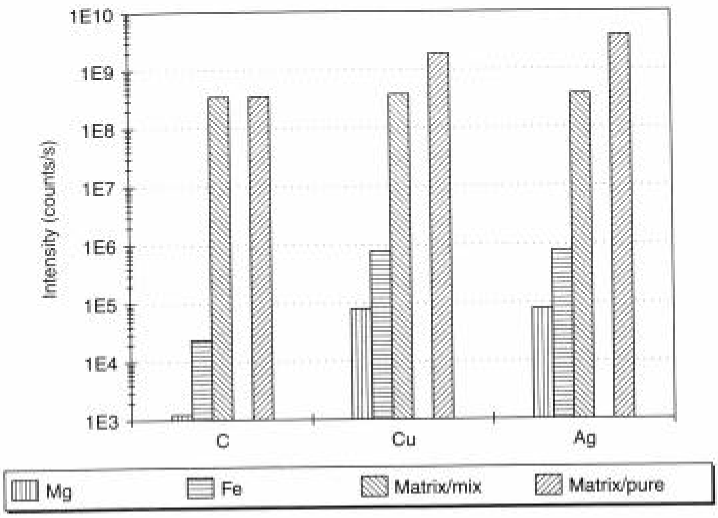

Figure 11.1 Comparison of the analyte (Mg and Fe) and host matrix ion intensities in compacted samples, in the VG9000 glow discharge mass spectrometer, for various conducting binders (graphite, copper and silver). The three bars on the left for each matrix are the analyte and matrix ion intensities in the compacted sample (nonconducting sample (albite) to conducting binder mixture of 1 + 4). The right bar for each matrix represents the matrix ion intensity in the pure matrix [6]

amounts of the sample result in low sputter yields, and thus in low signal intensities. In practice, this means that an excess of host material is needed [5,6], unless gallium is used, as discussed above. On the other hand, it is also obvious that a too high dilution of the nonconducting sample also results in low signal intensities.

Woo *et al.* [15] investigated the use of various mass ratios for an Al_2O_3 powder mixed with Cu powder, in analyses with a laboratory-built Grimm-type glow discharge quadrupole mass spectrometer.

Ratios of sample-to-host of 1 + 1 and 1 + 3 appeared to give unstable samples or unstable discharge conditions. Ratios of 1 + 5 and 1 + 10 yielded a stable discharge, and therefore a ratio of 1 + 5 (i.e. 17% sample content) was finally chosen to keep the dilution factor as low as possible [15]. In ref. [19], sample-to-host ratios were varied from 1 + 4 to 1 + 19 with some intermediate values, and the smallest sample content (i.e. 5%, in the ratio 1 + 19) was observed to give the highest sensitivity in GD-AAS. In most papers, mass ratios are reported to vary between 1 + 4 (i.e. 20% sample content) and 1 + 19 (i.e. 5% sample content).

In our laboratory, De Gendt investigated the use of various sample-to-host ratios (i.e. blank, 1 + 19, 1 + 9, 1 + 4, 1 + 2 and 1 + 1) in the analysis of a nonconducting sample (albite), mixed with high-purity copper [6]. The 1 + 1 mixture, which has the highest content of nonconducting material, led to problems when compacting the mixture into electrodes, and was not considered further. The 1 + 4 mixture (i.e. 20% of nonconducting sample) appeared to result in the highest analyte signal in GDMS (see Table 11.1), although the sensitivity in the case of the 1 + 19 mixture was found to be only about a factor of two lower. This conclusion is in line with observations of most other researchers for analogous analyses by means of GD-OES [43–45]. On the other hand, De Gendt also emphasized that the relative amount of nonconducting sample has an influence on the time required for stabilization [6]. As could be expected, in the case of a higher nonconducting fraction in the sample, the stabilization time is longer. For SiO_2 contents (in a copper host matrix) of 33, 17 and 9% (i.e. mixing ratios of 1 + 2, 1 + 5 and 1 + 10, respectively), stabilization times of about 3, 2 and 1 h, respectively, were found (see Figure 11.2) [6]. Although from the analyte

Table 11.1 Influence of the nonconducting material content in compacted samples on the sputtering rates and the ion intensities (Cu host matrix, and Mg and Fe analyte intensities) for various albite–Cu mixtures [6].

Mixing ratio in Cu	Sputtering rate (μg/s)	Ion intensity (counts/s)		
		Cu (host)	Mg (analyte)	Fe (analyte)
Pure Cu	2.4 ± 0.4	$(2.0 \pm 0.2) \times 10^9$	—	—
1 + 19	1.25 ± 0.01	$(6.6 \pm 0.6) \times 10^8$	$(3.5 \pm 0.4) \times 10^4$	$(2.9 \pm 0.2) \times 10^5$
1 + 9	1.13 ± 0.02	$(4.5 \pm 0.5) \times 10^8$	$(4.8 \pm 0.6) \times 10^4$	$(4.2 \pm 0.2) \times 10^5$
1 + 4	0.83 ± 0.09	$(3.8 \pm 0.6) \times 10^8$	$(8.1 \pm 0.2) \times 10^4$	$(7.7 \pm 0.9) \times 10^5$
1 + 2	0.65 ± 0.02	$(2.2 \pm 0.5) \times 10^8$	$(8.5 \pm 0.5) \times 10^4$	$(7.1 \pm 0.9) \times 10^5$

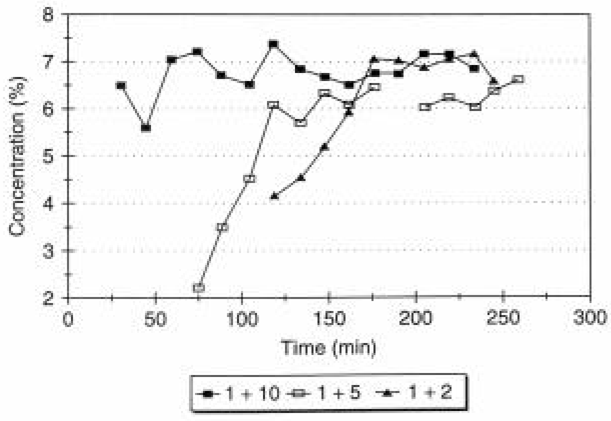

Figure 11.2 Calculated Si concentration as a function of sputter time, using Al as an internal standard, for compacted samples in a 1 + 10, 1 + 5 and 1 + 2 mixing ratio of a calcareous loam soil and Cu. The stabilization times appear to be of the order of 1, 2 and 3 h, respectively, in the VG9000 glow discharge mass spectrometer, at 3 mA and 1 kV [6]

signal (see Table 11.1) a 20% content was found to be optimum, the study on stabilization times demonstrated that, in practice, a 10% content of nonconducting material (i.e. a 1 + 9 mixture), or even less, was more convenient [6]. It should be mentioned, however, that these long stabilization times must also be partly attributed to the press, which was probably not working satisfactorily. Moreover, stabilization times in GD-OES are also typically shorter (see below).

Discharge Conditions

It is obvious that the discharge voltage, which is a measure for the energy of the particles bombarding the sample, and the discharge current, which is proportional to the number of bombarding collisions on the sample and to the number of ionization/excitation collisions in the plasma, have an influence on the sputter rate and the analyte signal intensity. Generally, one can state that a higher discharge power yields higher signal intensities. De Gendt [6] found a certain threshold for the power, under GDMS conditions, which is needed to achieve reproducible results for the concentrations of components in the nonconductor. It is clear from Figure 11.3 that below a discharge power of ca 1.5 W, the concentration of Mg obtained in the nonconducting sample (i.e. albite mixed with Cu) is not very reproducible [6]. At higher power levels, more or less reproducible concentrations at the level of 40–50 ppm were obtained, for different conditions of pressure and power (ranging from 1.5 to 5 W). This threshold for reproducible quantitative

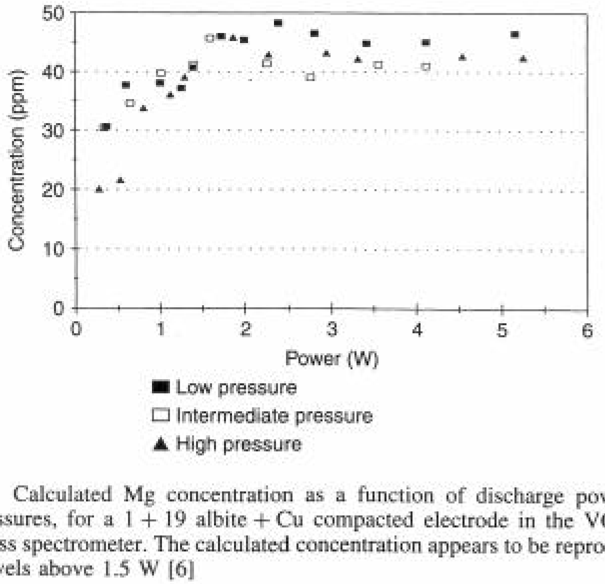

Figure 11.3 Calculated Mg concentration as a function of discharge power at three different pressures, for a 1 + 19 albite + Cu compacted electrode in the VG9000 glow discharge mass spectrometer. The calculated concentration appears to be reproducible only for power levels above 1.5 W [6]

results might be understood from the lower kinetic energy of plasma particles bombarding the cathode at low power, and hence low voltage. Indeed, it is likely that the conducting host and the nonconducting oxide-based sample have different threshold values for sputtering, and that at low power and voltage the conducting components are being sputtered more efficiently than the nonconducting sample components, which results in a too low calculated concentration of analytes [6].

Furthermore, Mai and Scholze demonstrated for compacted powder samples that a higher discharge power required a shorter stabilization time [46,47]. At 100 W, stable signals were obtained after a few minutes of sputtering only, whereas at lower power levels increasing stabilization times were required (e.g. ca 11 min at 30 W and more than 30 min at 14 W). It should be mentioned, however, that a power of 100 W might be a realistic value for Grimm-type GD-OES, but commercial GDMS instruments usually operate at much lower power levels (e.g. 3 W), so that typical GDMS stabilization times will rather be of the order of 1 h [6] (see Figure 11.2). In practice, one can state that the time required for reaching steady-state sputtering conditions can be somewhat reduced by optimizing the power, mixing ratio, etc., but a certain stabilization time appears to be inherent to the sputtering of compacted and multi-component samples.

Particle Size

It is stated that the particle sizes in the compacted sample must be small compared with the sputtering rate of surface layers, in order to obtain a discharge with gas-phase compositions which are representative of the bulk sample [5]. Moreover, small particles appear to result in more stable discharge conditions [5,46]. Generally, small particle sizes are therefore preferable, with respect to both the achievable accuracy and precision. On the other hand, a disadvantage of small particles is that they imply a larger surface area and thus a greater chance of trapping of gases in the final compacted sample. Nevertheless, most researchers agree that small particle sizes (i.e. below 50–60 μm in diameter) are preferable [16,20,21,26].

Presence of Trapped Gases

It is obvious that the sample preparation method of mixing a nonconducting sample with a conducting host matrix can give rise to contamination problems, most commonly due to the trapping of gases such as N_2, O_2, H_2, H_2O, CO_2, CO, NO, N_2O and CH_4. These gas species often result in a lower sputtering. Moreover, they can cause quenching of metastable argon atoms, thereby reducing the efficiency of Penning ionization. Both effects will result in lower analyte intensities [48]. Furthermore, the presence of residual gas species is a source of interferences in the mass spectrum. Not only the molecular species itself, but also clusters (hydrides, nitrides, oxides, etc.) can affect the determination of certain elements. Finally, the trapped gases generally lead also to longer stabilization times.

Some precautions during sample preparation can help in preventing the trapping of gases, e.g. heating of the sample materials before mixing, applying a mild vacuum to the sample mixture during pressing, and outgassing of the compacted sample under vacuum and/or mild heat treatment prior to analysis [5,14,26]. Furthermore, the use of host materials with gettering abilities has also been demonstrated to be useful [9,29]. Cryogenic cooling of the glow discharge cell has also been found to be successful in reducing the effects of the inevitable residual gases [49]. The most effective and generally usable method to limit the effects of trapped gases is to apply a suitable presputtering period prior to data acquisition [14]. If high discharge currents and powers are necessary to attain acceptable sensitivities [14], it is usually advantageous to increase the current from an initially low value to the desired analysis value in several steps. The presputtering sequence employed in ref. [14], for example, was as follows: (i) 60 mA during 20 s, (ii) 150 mA during 20 s, (iii) 225 mA during 15 s and (iv) 300 mA during 210 s.

11.2.2 SOME APPLICATIONS AND ANALYTICAL FIGURES OF MERIT

The host matrix technique has been used extensively since the 1970s, first mainly in GD-OES and later also in GDMS and GD-AAS. Various kinds of nonconducting materials have been analyzed, such as iron ore materials [6,11], rare earth oxides [6,9,29,31,32], other oxides [13,21], soils [10,28,34,35], rock sediments [9,22,34], marine sediments [17,18], vegetation [34], ceramic samples [15,24,25], automotive catalyst materials [14,36], medieval glass relics [26], historical ferrous ore and slag samples [27], nuclear samples [30] and biological materials [44]. Moreover, the technique might also be particularly suitable in cases where limited amounts of samples are available (e.g., archeological findings or meteoritic residues) [39]. Finally, the host matrix technique has also been applied to solution residues, e.g. for the determination of trace metals in petroleum [33], where 50–500 μl of the solution (which corresponds approximately to 0.05–0.5 g) were pipetted into 1.0 g of Ag powder. The resulting slurry was then dried at 100 °C for at least 2 h, mixed to obtain homogeneity and then pressed into a pin [33].

As mentioned above, the sample + host mixture is most often pressed in the form of a pin or disk, to be used in standard commercial GDMS cells, in Grimm-type GD-OES cells or in coaxial cathode source configurations. However, the technique has also been applied in hollow cathode glow discharge configurations, either as a pellet placed at the bottom of the cathode cavity [17] or directly pressed into the form of a hollow cylinder [44]. Moreover, Marcus and Harrison also used the host matrix technique for the analysis of geological samples with GD-OES in the hollow cathode plume configuration [12].

In general, internal precisions were found to be better than 10% RSD, whereas external precisions below 20% RSD are commonly reported [11,13,14,21,25,36,44]. Concerning the accuracy, the suitability of the use of relative sensitivity factors (RSFs) in GDMS has been investigated. Duckworth *et al.* [28] applied a set of standard RSFs (based on metal analysis) and reported errors up to ca 100% for the obtained concentrations adjusted by the RSFs. De Gendt *et al.* thoroughly investigated the influence of several parameters on the RSFs for iron-rich and other oxide-based samples in GDMS: the effect of cryo-cooling, the nonconducting matrix, sample geometry and conducting binder were evaluated [6,11]. With the exception of the sample geometry (pin or flat cathode), the RSFs hardly seemed to be affected. However, significant differences have been found between the set of RSFs for nonconductors and the 'standard' set of RSFs, such as that used in ref. [28]. In practice, this suggests that RSFs have to be determined for each type of nonconducting matrix in order to obtain accurate results. In ref. [14], typical accuracies for GD-AAS were reported to be in the range 2–3%, whereas Wayne [36] reported GDMS precisions and accuracies better than 10% [36]. Detection limits are generally in the ppm range for GD-OES [25] and in the sub-ppm to ppb range for GDMS [34].

11.3 USE OF A CONDUCTING SECONDARY CATHODE

11.3.1 METHODOLOGY

The above-mentioned mixing technique requires samples in powder form. Certain types of samples, such as geological samples and ceramic precursors, are available in this form, but many others are available as a compact solid, e.g. a glass plate, sintered ceramic material, polymer foils, etc. These types of samples can hardly be ground and, if so, serious contamination can be introduced. A direct solid sampling technique for the analysis of nonconductors by dc glow discharges was therefore sought. The so-called 'secondary cathode technique', used for this purpose, was introduced by Milton and Hutton in 1993 for dc-GDMS [4]. To our knowledge, it has not yet been applied to other glow discharge spectrometric detection systems (GD-OES, GD-AAS, GD-AFS). Since this is a rather new technique, which has not yet been described in other recent books about glow discharge spectrometry [5,42], it is necessary to explain this concept in some more detail.

The secondary cathode is a thin conducting diaphragm (or mask) placed in front of the sample. The nonconductor is thus exposed to the discharge through the aperture (typically 3–10 mm in diameter) of the secondary cathode. A similar concept was used before for the analysis of nonconducting materials with secondary ion mass spectrometry (SIMS) and sputtered neutrals mass spectrometry

(SNMS) [50], although in this case the aperture had a maximum diameter of 500 μm. Secondary electron emission from the conducting mask, induced by ion bombardment, then provided charge compensation. Hence, in the case of SIMS and SNMS, the diaphragm acts as a bombardment-induced electron source.

The principle of the secondary cathode technique for GDMS, as described by Milton and Hutton [4], differs significantly from that described for SIMS and SNMS [50], since it relies on the fundamental processes in the glow discharge. Indeed, the secondary cathode is (partially) exposed to the glow discharge and, consequently, it is sputtered and atoms are released. It has been found that more than 60% of the sputtered atoms are redeposited on the sample surface [4,51]. In the case of a secondary cathode, this means that mask atoms are being redeposited not only on the secondary cathode, but also on the part of the nonconductor that is exposed to the discharge. This results in the formation of a conducting film on the surface of the insulating sample. Consequently, this area will also attract bombarding ions and does not suffer from charge building-up. It is suggested [4] that the sputtering process is energetic enough to penetrate through the thin metallic film and to remove atoms from the underlying insulator. This sputtering–redeposition process is presented schematically in Figure 11.4. As soon as an equilibrium is established between the redeposition of metal atoms and the removal of sample atoms by sputtering, the glow discharge reaches a steady state. The plasma, and consequently also the obtained mass spectrum, is comprised of ions representative of both the insulating material and of the metallic secondary cathode. Successful application of this technique relies, therefore, on the appropriate thickness of the deposited metallic layer. When the layer is too thin or incomplete, discharge instabilities may occur. On the other hand, when the metallic layer is too thick, it prevents the underlying nonconductor from being sputtered.

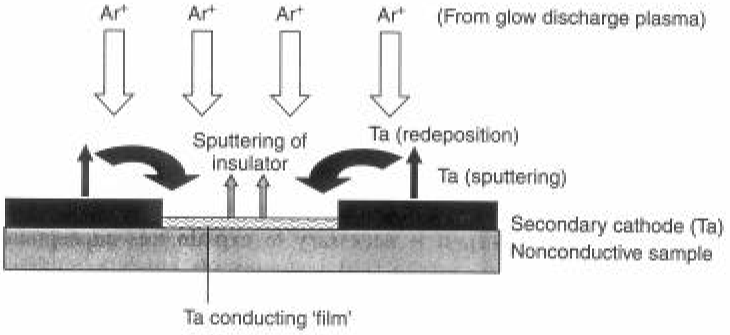

Figure 11.4 Schematic representation of the formation of the film by sputtering and redeposition of a film on the nonconducting sample surface, with the secondary cathode technique [55]

It should be emphasized, however, that the picture of a thin conducting film on top of the insulator may be not very appropriate, and that it should rather be interpreted as 'islands' of conducting material, as is described in the literature for the deposition of thin films [52]. Indeed, material arrives at a substrate mostly in atomic form. Atoms can be adsorbed and possibly also re-evaporated. After a certain time, the atom will combine with another atom, forming an atom pair, which is more stable and therefore it tends less to re-evaporate. The doublets will be joined by other single atoms to form triplets and so on. This is the *nucleation stage*, leading to the formation of relatively stable islands, each containing tens or hundreds of atoms. During the next stage, i.e. the *island growth stage*, the islands grow in size, rather than in number. Eventually, they grow large enough to touch each other, in the *agglomeration stage*. This proceeds until the film reaches continuity. It has been reported that this mostly happens after the film has reached an average thickness of several tens of nanometers. This would already be too thick to enable the underlying nonconducting sample to be sputtered, since the sampling depth is reported to be ca 0.5 nm [53]. Accordingly, one can assume that, in the case of a successful use of the secondary cathode technique, the 'thin film' that allows sputtering of the underlying nonconducting sample actually consists of hills and valleys, and that the nonconducting samples are not necessarily covered completely [54,55].

Wayne *et al.* [54] tried to obtain more insight into the sputtering of nonconductors in a dc glow discharge using the secondary cathode technique, by characterization of the conducting film of the secondary cathode material (Ta in this case) on the analytical surface. Examination of the sample surface by micro-X-ray fluorescence and scanning electron microscopy indicated that the Ta film formed by sputtering and redeposition is nonuniform, with a thicker accumulation of sputtered Ta in the outermost 0.25–0.5 mm of the sputtered area, where the Ta cathode is in physical contact with the nonconducting sample under it. Rutherford backscattering spectrometry was then used to characterize the thickness of the Ta film, and it was found that this may vary from $<10^{15}$ to $\sim 9 \times 10^{15}$ atoms/cm^2 for different materials. The results indicated that both crater shape and film thickness depend on the glow discharge sputtering parameters and on the nature of the material being sputtered. Finally, it was speculated that the electrical properties at the analytical surface may be very different from those expected in the bulk material [54].

Since the secondary cathode technique is a relatively young technique, which, to our knowledge, has only been used in GDMS up to now, only a few groups have been working in this field. A thorough methodological evaluation was, as far as we know, mainly carried out by Milton and Hutton [4] and in our laboratory by Schelles and co-workers [55–58]. The results of these investigations, with respect to the parameters which need to be optimized for good analytical practice, are described below. It may be important to note first that the three major criteria for a good analysis are (i) a stable (steady-state) atomization of the nonconducting sample, (ii) high signal intensities of the nonconducting sample and (iii) a low blank contribution due to the sputtering of the secondary cathode material.

Secondary Cathode Material

The choice of the secondary cathode material is important for several reasons. First, it must be sufficiently pure to avoid too high blank levels due to the secondary cathode material. Second, its sputtering characteristics have an influence on the formation of the metallic layer: the sputtering efficiency should be high enough to produce a stable discharge, but it should not be too high, in order to avoid a complete coating which would protect the underlying nonconducting sample from being sputtered. Finally, the price and mechanical properties of the secondary cathode material, such as its suitability to machine a diaphragm out of it, are also of importance.

Various materials have been evaluated by Milton and Hutton [4]. Al, Cu and Ag, which are characterized by a high sputter rate, resulted in a rapid coating of the glass sample, under all discharge conditions. Also Pb and In were subject to too much sputtering and, moreover, they were found to be too soft, causing a short circuit. Finally, it was concluded that only a Ta secondary cathode, which has a low sputter rate, produced a stable discharge [4].

Schelles and co-workers [55,56] also investigated the use of several secondary cathode materials. Mo, Ni and Al were characterized by too much sputtering and consequently by too much redeposition. Both Ta and W appeared to be suitable as secondary cathode materials, as they have a similar sputtering efficiency and price, but Ta was favored because it yields better detection limits than W, as a result of higher sample-to-mask intensity ratios, and W appeared to be more brittle than Ta and therefore more difficult to machine.

Secondary Cathode Geometry

Given the cylindrical geometry of the discharge cell, a circularly symmetric secondary cathode resulting from a hole in a metal plate is the most obvious geometry. However, the use of a grid secondary cathode, as in SIMS [50], has also been evaluated [55]. It always resulted in vacuum leaks, because the edges of the front plate of the sample holder were not suitably sealed. Multi-aperture secondary cathodes, consisting of a metal plate with, for example, three symmetrically drilled holes, were also evaluated, but mostly an unstable discharge and low sample signal intensities were found. Therefore, a circular secondary cathode was found to be the best geometry.

In addition to the geometry, the size of the hole and the thickness of the secondary cathode also affect the analytical performance. A hole size of 4 mm diameter was found to be optimal in the investigations both of Milton and Hutton [4] and of Schelles [55]. Larger hole sizes appeared to give rise to discharge instabilities, whereas smaller sizes resulted in high blank values due to the sputtering of the mask. The thickness of the secondary cathode was varied [55,58] between 0.12 and 1 mm. It appeared to have only a minor effect on the sample signal intensity obtained. However, the weight of the blank values due to the sputtering of the secondary cathode appeared to be more pronounced for thick secondary cathodes. Therefore, the use of a thin secondary cathode (i.e. 0.12–0.25 mm thick) was preferred to reach low detection limits [55,58]. On the other hand, it was also found that the thickness of the secondary cathode indirectly affects the obtained crater shape, and a thick secondary cathode (1 mm) appeared to favor a flat crater [55,58]. Because the secondary cathode technique works only under restricted discharge conditions (see below), which are not necessarily the best for obtaining a flat crater, it should be mentioned that rf-GDMS or GD-OES seem to be more appealing for depth profiling analysis.

Discharge Conditions

Milton and Hutton [4] investigated the effect of the gas pressure in the secondary cathode technique, and they found that only a limited pressure regime yielded a good balance between a stable discharge, because for enough redeposition the pressure should not be too low, and a sufficiently high sample-to-mask intensity ratio, because for not too much redeposition the pressure should not be too high. Schelles and co-workers [55–57] found that, in addition to the gas pressure, the discharge current and voltage are also of crucial importance for the amount of redeposition of secondary cathode material. They found that only specific combinations of voltage, pressure and current yielded stable discharge conditions. Since these combinations may depend on the type of sample to be analyzed, the optimum discharge conditions need to be investigated prior to analysis, which is considered a disadvantage of the secondary cathode technique.

Electrical Resistivity of the Sample

It is obvious that the general term 'nonconducting samples' includes sample types of varying electrical resistivity, and that the latter characteristic has some effect on the analytical performance of the secondary cathode technique. Schelles and co-workers [55,56] investigated samples of varying electrical resistivity. They found that samples with a resistivity higher than the critical barrier of about 10^{10} Ω cm, such as glass and most soils (see Table 11.2) [55,56], can be considered as 'nonconducting'. For these types of samples, the secondary cathode is essential to create a stable discharge. Only Ta and W could be used as a secondary cathode material, and the aperture diameter was limited to 4 mm. This results in low sample-to-mask intensity ratios, and hence a high blank contribution for certain elements. Samples with a resistivity lower than the critical barrier

Table 11.2 The specific electrical resistivity and the behavior of different materials when used directly as a cathode (i.e. without secondary cathode) in the VG9000 glow discharge [55].

Material	Electrical resistivity (Ω cm)	Behavior in the glow discharge
Aluminum	2×10^{-6}	Normal intensity (5×10^{-10} A) at 3 mA, 1 kV
SiC	1×10^{3}	Lower intensity (5×10^{-11} A) at 3 mA, 1 kV
Iron ore sinter	4×10^{9}	Very low intensity (5×10^{-16} A) at 3 mA, 1 kV Stable discharge
Soil	4×10^{10}	Unstable discharge
Glass	3×10^{11}	No discharge

of 10^{10} Ω cm, such as specific iron ore sinters, should be classified as 'poorly conducting'. A stable discharge here could be created without the secondary cathode, but the sample signal intensity was extremely low. This intensity could, however, be increased significantly by the use of a secondary cathode, leading to signal intensities which were comparable to those of conducting samples [55,56]. In this case, larger hole sizes could be applied, and a detailed knowledge of the properties of the nonconducting material was not so crucial.

Surface Characteristics of the Sample

Because the deposition of metal atoms on the surface of the nonconducting sample is essential in the secondary cathode concept, it is straightforward that the surface of the sample can have an influence on the operating conditions required for stable atomization. First, it appears that the surface roughness has a distinct effect [57], i.e. rough surfaces require clearly more redeposited metal atoms, and hence a higher pressure, than smooth surfaces, so as to ensure a certain conductivity. This is illustrated in Figure 11.5 and in Table 11.3. Second, samples with a similar electrical resistivity and a similar surface roughness, such as Macor, which is a glass ceramic, and glass, can still require different optimum discharge conditions. This can be understood from differences in the affinity between the metal atoms and the nonconducting sample [55].

11.3.2 SOME APPLICATIONS AND ANALYTICAL FIGURES OF MERIT

As mentioned before, the secondary cathode technique was developed for GDMS only in 1993, and we are not yet aware of its use in GD-OES and GD-AAS. A

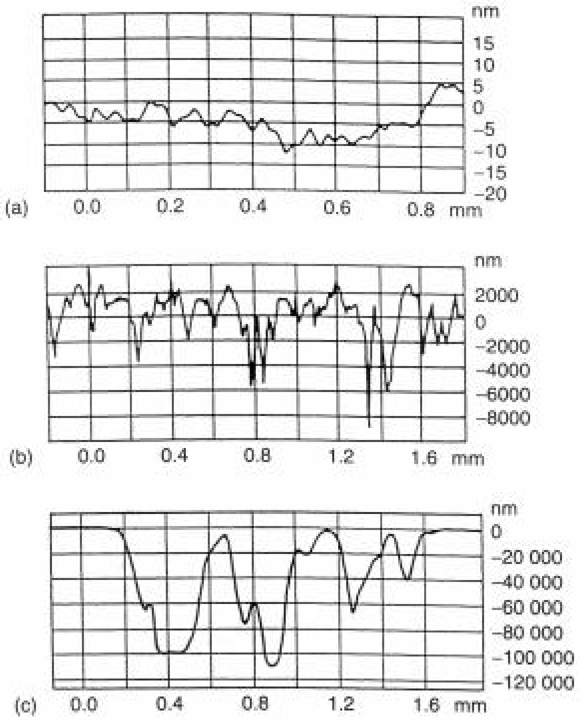

Figure 11.5 The surface roughnesses of three different sample types: (a) glass; (b) marble; (c) limestone [55]

Table 11.3 Overview of the influence of the surface roughness on the required discharge conditions in the VG9000 glow discharge mass spectrometer with a Ta secondary cathode with 4 mm aperture, for glass, marble and limestone [55].

Material	Surface roughness	Optimum discharge conditions	Pressure, % redeposition
Glass	Smooth	3 mA, 600 V	Normal
Marble	Rough	3 mA, 400 V	High
Limestone	Very rough	3 mA, <300 V	Very high

possible reason for the fact that this technique has not yet been applied in GD-OES might be the generally higher pressure in GD-OES, which yields too much redeposition of secondary cathode material, preventing the underlying nonconductor from being sputtered. On the other hand, commercial rf-GD-OES instruments are also available, which can be used for the analysis of nonconductors, and therefore the need for using the secondary cathode technique is not as high as for GDMS, where no commercial rf-GDMS instrument is yet available.

Based on the above considerations, it is obvious that the number of papers describing applications of the secondary cathode technique is much more limited than for the host matrix technique. Nevertheless, the technique has been shown to be successful for the analysis of glass [4,54–58], iron ore sinter [55,56], marble [55,57], Teflon [55,57], ceramic materials [54,55,57,59–61], atmospheric particulate matter [62], polymers [63], soil [34], sediment [34], vegetation [34] and nuclear samples [30,64]. Most of these applications have been performed with the VG9000 double-focusing glow discharge mass spectrometer (VG Elemental, Thermo Instruments) [4,30,34,55–64], although the technique has also been used with the double-focusing magnetic sector instrument manufactured by Kratos [54].

Milton and Hutton [4] developed the secondary cathode technique for glass samples. They obtained an analytical precision of typically 5% RSD at ppm levels and detection limits in the sub-ppb to ppb range [4]. Also Schelles and co-workers [55–58] performed most of their methodological work with solid glass samples. They found internal precisions (without changing the samples) of 2–10% and external precisions (with changing the samples) of 5–25%. The practical detection limits were between 0.1 and 1 ppm, but they could be further improved by working in the low-resolution mode. If no interfering peaks were present, detection limits down to 10 ppb could then be obtained.

A comparison between the analysis of massive, solid glass samples, which are really nonconducting, and compacted iron ore sinters, which are poorly conducting, has also been described [56], showing the influence of electrical resistivity of the samples. It was found that iron ore sinters could in principle also be analyzed without the use of a secondary cathode, but the latter enhanced the signal intensity to a level comparable to that commonly reached for conducting samples. The high sensitivity and the negligible blank values as a result of a very low mask-to-sample signal intensity ratio, because a mask with larger aperture could be used, made it possible to determine concentrations of ca 100 ppb on a routine basis [55,56].

The suitability of the secondary cathode technique for the analysis of ceramic materials has been demonstrated for Nd:YAG [54], for potassium titanyl phosphate [54], for Al_2O_3 [55,57], for Macor [55,59] and for ZrO_2 [55,60,61]. Although sample characteristics such as the electrical conductivity and surface roughness for Macor are closely comparable to those of glass, the optimum discharge conditions for Macor analysis were found to be significantly different from those of glass [59]. This illustrates that the discharge conditions need to be optimized for each new type of sample. The limits of detection were found to be in the sub-ppm range. The internal precision was found to be 5.7% RSD, whereas the external precision was typically better than 10% RSD [59]. For ZrO_2, the internal and external precisions were also found to be better than 10%

RSD in most cases, and the accuracy without using standards, and thus assuming 'uniform sensitivity', was within a factor of 2–3 the known concentration. Limits of detection for most elements were in the range between 10 ppb and 10 ppm, depending on high or low elemental sensitivity and the integration times. In practice, blank contributions due to the Ta secondary cathode material restricted the detection limits to a level of about 100 ppb or even higher. Generally, it could be concluded that 85% of the elements could routinely be determined at the sub-ppm level [60].

An interesting application of the secondary cathode technique has been reported [62] for the analysis of atmospheric particulate matter. The sample preparation was simple and time-saving. The air was sucked by a pump through a single-orifice impactor stage, in which the aerosols were impacted on a metal support, forming a central spot (see Figure 11.6) [62]. This metal plate was directly used as a cathode in the VG9000 glow discharge mass spectrometer,

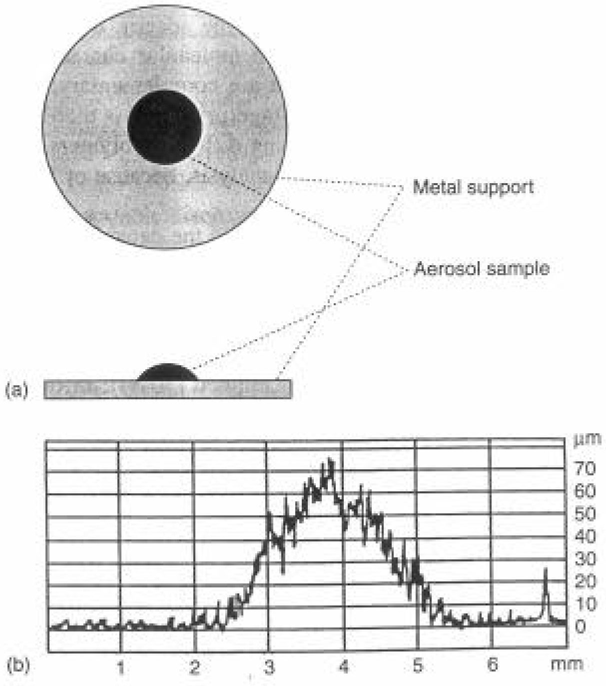

Figure 11.6 Aerosol sample spot, impacted on the metal support. (a) Schematic front view and side view; (b) thickness of the sample spot, as measured with the aid of a mechanical profilometer (Dektak 3030, Veeco Instruments, USA) [55,62]. Reprinted with permission from Schelles, W., Maes, K. J. R., De Gendt, S. and Van Grieken, R. E., *Anal. Chem.*, 1996, **68** 1136–1142. Copyright 1996 American Chemical Society

and it played the role of secondary cathode for the analysis of the atmospheric particulate matter. By careful evaluation of the sample loading and of the discharge parameters, the signal could be optimized and the drop in intensity as a consequence of its consumption during continuous sputtering could be minimized. The available aerosol analysis time could be prolonged to more than 3 h, a time span necessary to perform a multi-element analysis with the VG9000 instrument. A NIST reference aerosol was analyzed to evaluate the potential for quantitative analysis. The internal reproducibility was better than 10% RSD, and the limits of detection were estimated to be in the low-ppm or sub-ppm region [62].

The secondary cathode technique has also been applied in our laboratory for the elemental characterization of different types of polymers [63], i.e. polytetrafluoroethylene (PTFE), polycarbonate (PC), and poly(vinyl chloride) (PVC). The mass spectra obtained were predominantly characterized as atomic (see Table 11.4) [63]. It should be mentioned that the VG9000 cell here was generally cryogenically cooled, to reduce molecular peaks in the mass spectra due to residual gases. The mainly atomic mass spectra obtained with the secondary cathode technique are clearly different from the spectra of polymers obtained with rf-GDMS [65], which have a definite molecular character. Therefore, it appears that the dc- and rf-GDMS spectra are complementary: the rf spectrum shows molecular cluster peaks forming a fingerprint, and is therefore particularly suitable for characterizing and distinguishing different polymers, whereas the dc spectrum facilitates quantitative elemental analysis, because of less interferences from cluster peaks.

Betti and co-workers [30,34,64] demonstrated the capability of the secondary cathode technique for the detection of trace radioisotopes in soil, sediment and vegetation [34], and for the analysis of samples of nuclear concern [30,64]. For the latter purpose, the VG9000 instrument was placed in a glove-box [30,64]. Depending on the type of samples, a combination of the host matrix method and the secondary cathode technique was applied [30,34], in order to decrease the dilution effect of the host matrix material for determinations at the trace

Table 11.4 Average abundances for the main clusters present in the VG9000 glow discharge mass spectrum of various polymers, relative to the elemental matrix signal intensities, measured with the secondary cathode technique [55,63]. Reprinted with permission from Schelles, W. and Van Grieken, R. E., *Anal. Chem.*, 1997, **69** 2931–2934. Copyright 1997 American Chemical Society.

PTFE (relative to $C^+ + F^+$)		PVC (relative to $C^+ + Cl^+$)		PC (relative to $C^+ + O^+$)	
$^{24}C_2{}^+$	1.8×10^{-3}	$^{13}CH^+$	4.9×10^{-2}	$^{13}CH^+$	1.3×10^{-2}
$^{31}CF^+$	3.4×10^{-2}	$^{24}C_2{}^+$	3.3×10^{-3}	$^{24}C_2{}^+$	1.2×10^{-3}
$^{43}C_2F^+$	2.4×10^{-5}	$^{47}CCl^+$	6.3×10^{-4}	$^{28}CO^+$	3.2×10^{-3}
$^{50}CF_2{}^+$	2.4×10^{-3}	$^{59}C_2Cl^+$	1.0×10^{-5}	$^{44}CO_2{}^+$	1.6×10^{-4}
$^{62}C_2F_2{}^+$	7.0×10^{-5}				
$^{100}C_2F_4{}^+$	1.3×10^{-3}				

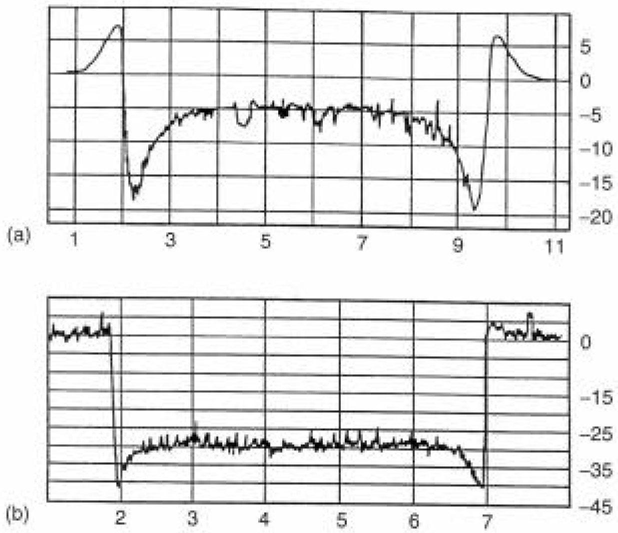

Figure 11.7 Optimized crater profile for a Cu CRM 074 sample obtained with the VG9000 glow discharge mass spectrometer. (a) Without Ta mask (850 V, 1.9 mA); (b) with Ta mask (850 V, 3.5 mA) [67]

level and to obtain a stable discharge. Detection limits in the ppb range could be obtained when integrating up to 1 h. By optimizing the integration time and mass resolution, e.g. by selecting the low-resolution mode, the detection limits could be reduced down to ppt levels for U and Th [34]. However, it should be mentioned that there are virtually no interferences in this high-mass range, and that these excellent detection limits therefore cannot be generalized. The obtained accuracy was typically 9–30%, whereas the internal and external precisions amounted to 3–7 and 5–20%, respectively [34].

Finally, it should be mentioned that a Ta secondary cathode or mask has also been applied successfully in GDMS depth profiling analysis of conducting [66,67] and nonconducting [61] samples. The mask appears to reduce significantly the crater edge effect, by which the crater is much deeper at the sides than in the center [66,67], as is illustrated in Figure 11.7 [67]. Moreover, the crater side walls become steeper and there is no deposition of material outside the crater, since the back-diffusing sputtered atoms are redeposited on the mask instead of on the sample [67].

11.4 CONCLUSION

The two techniques which can be applied with dc glow discharges to analyze nonconducting samples have been discussed in this chapter.

The host matrix technique, which consists of mixing a nonconducting powder with a conducting host matrix and pressing the mixture into an electrode, was first applied to GD-OES about 30 years ago and is nowadays being used routinely for the bulk analysis of nonconductors in GD-OES, GDMS and GD-AAS. Different kinds of host materials have been proposed in the literature, but Cu powder is most widely used, mainly because of its availability in pure form, its relatively low cost and its high sputter yield. On the other hand, Ta powder was used in some studies because it has the advantage of being a getter material, and accordingly removing oxygen from the discharge and reducing molecular oxide spectral interferences. The compacted electrode must contain an excess of conducting host material to avoid instabilities in the discharge and to ensure enough sputtering. Sample-to-host mass ratios reported in the literature usually vary between $1 + 4$ and $1 + 19$. The choice of discharge conditions necessary for good analytical practice is not so strict as in the secondary cathode technique (see below), but it is found that a high discharge power yields higher analyte signal intensities and more reproducible concentration results, as well as a shorter stabilization time. Moreover, most authors agree that the particle sizes in the compacted sample should be small and, of course, that the mixture should be homogeneous, to obtain good precision and accuracy. The major problem with the host matrix technique is the contamination which can occur during the mixing procedure. Further, trapped gases in the compacted sample, which yield lower signal intensities, can be a source of spectral interferences, and generally give rise to longer stabilization times (several minutes to hours). Therefore, some precautions should be taken during sample preparation and during the measurement in order to reduce the effect of these trapped gases. Another disadvantage of the host matrix method is the analyte dilution due to the mixing with the metal powder, which results in losses of sensitivity and, if the metal powder is not sufficiently pure, it may mask analyte trace element peaks. Finally, the powder compaction precludes the acquisition of certain types of data, such as concentration depth profiles.

The secondary cathode technique is a direct solid sampling technique, so that the above-mentioned type of information can in principle be acquired. It should be mentioned, however, that the secondary cathode technique can only be used for the analysis of flat samples and not for pin samples. It is a rather new approach, developed about a decade ago for GDMS, and is based on placing a thin conducting diaphragm (i.e. the 'secondary cathode') in front of the massive nonconducting sample before exposing it to the discharge. Since the secondary cathode is also partly exposed to the discharge, it is subject to sputtering and the sputtered atoms can be redeposited on the nonconducting sample, forming a conducting 'film' on the surface of the nonconductor. This film avoids electrical charging of the nonconductor, but it should be 'thin' enough to permit sputtering from the underlying insulator. Because it is a direct solid sampling technique, it is suitable for the analysis of solid samples, which are difficult to grind. Moreover, there are no problems of contamination during sample preparation, as in the case of the host matrix technique. The technique does, however, still suffer from dilution due to sputtering of the secondary cathode material. In addition, the latter should be sufficiently pure, to reduce the blank contribution and spectral interferences. Indeed, the detection limits in the case of this technique are mainly determined by the possible blank contribution of the secondary cathode material. Further, the sputtering rate of the secondary cathode material should be low enough to avoid complete coating of the insulator, which would prevent the latter from being sputtered. Therefore, Ta has been favored as secondary cathode material, also based on its price and mechanical properties.

The hole size and thickness of the secondary cathode also play an important role, in order to achieve sufficient redeposition to produce a stable discharge, and on the other hand, not too much redeposition to limit the 'mask' blank contributions. Generally, a hole size of 4 mm diameter and a thickness of 0.25 mm are preferred. In contrast to the host matrix technique, the discharge conditions appear to be crucial for a successful measurement. It was found that only specific combinations of voltage, pressure and current yield stable discharge conditions. Obviously, sample characteristics such as electrical resistivity, surface roughness, etc., have a distinct effect on the choice of the operating conditions. It appears that the latter need to be optimized, or at least 'fine-tuned', for each new matrix under investigation. Therefore, it cannot be guaranteed that a novel matrix can immediately be analyzed, which has to be considered a disadvantage of the secondary cathode technique. On the other hand, repeated experiments have indicated that, once the required measurement conditions have been found for a specific matrix in a given instrument, they are reproducible, even over a long time such as more than 1 year. Moreover, several types of matrices have already been successfully investigated with the secondary cathode technique, and except for porous materials and low-melting-point polymers, all materials which have been studied could be successfully analyzed. Nevertheless, it should be mentioned that with the secondary cathode technique, in principle, depth profiling analysis of nonconducting samples is possible, but practical realization is not straightforward because of the restricted discharge conditions for a stable discharge. Indeed, it is possible that the conditions which would yield a flat crater profile do not coincide with the conditions necessary for stable atomization of the nonconducting sample, and therefore a perfect depth profile might be difficult to achieve. The latter application is undoubtedly more possible with rf-GDMS or rf-GD-OES. On the other hand, a definite advantage compared with rf glow discharge analysis seems to be that the signal intensities do not depend on the thickness of the sample, a problem that, up to now, is inherent to most types of rf glow discharges. In summary, we can conclude that the secondary cathode technique, because of its simplicity and low cost, can be of interest, especially to those researchers who have no rf-GDMS or rf-GD-OES instrumentation available, and who want to extend their field of application towards nonconducting materials.

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