The effects of traces of molecular gases (H\textsubscript{2}, N\textsubscript{2} & O\textsubscript{2}) in glow discharges in noble gases

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Abstract: A brief introduction is given on the use of glow discharges in noble gases for spectrochemical analysis, with particular emphasis on Glow Discharge Optical Emission Spectroscopy (GD-OES). This explains the relevance of investigations on the effect of small quantities of molecular gases on the performance of discharges in noble gases, mainly in argon. The chief effects are on the electrical characteristics, the sputtering rate and the spectrum emitted. Earlier work is briefly reviewed, the options for spectral investigations discussed and the current state-of-the-art described for some samples (cathodes) of analytical importance (copper, iron and titanium) The main emphasis is on the addition of hydrogen to discharges in argon, with brief comments on other gas mixtures. A great deal of work remains to be done, both to produce empirical data for analytical use and to gain a fuller understanding of the discharge processes involved.

1. Introduction

Optical Emission Spectroscopy (OES) has been used for the analysis of chemical samples for very many years; initially, arc and spark sources were used in conjunction with prism or grating spectrographs with photographic plates. Later, low pressure glow discharge sources, such as demountable hollow cathode sources, were used in industrial laboratories, but relatively few systems were available commercially. Hollow cathode discharges can be used for metals by making the cathode of the sample material, or by introducing small pieces of the metal into, e.g., a graphite hollow cathode; solid powders can also be introduced directly into a graphite hollow cathode; drops of solution may also be introduced into a hollow cathode and the cathode heated to form a deposit on the walls. [1] The hollow cathode is thus versatile, but not very convenient if a solid metallic sample has to be machined to form a hollow cathode.

1.1 The Grimm source

In the late 1960's W.Grimm [2] introduced a new form of discharge source, shown diagrammatically in figure 1. In the original design, the diameter of the anode tube was 8 mm; typical operating conditions were 800 V, 80 mA, with an argon pressure of \textasciitilde 500 Pa. The source proved very convenient for routine analysis of bulk metallic samples; in all cases, calibration with samples of known
composition is required. The bombardment of the sample by ions and fast atoms causes sample atoms to be sputtered into the discharge and excited and ionised there. It was found that if appropriate discharge parameters are chosen, the sputtering is uniform across the sample surface and the crater formed has a flat base. Under these conditions the source can be used for the compositional analysis of the layers of e.g. a coated or layered material [3].

Instrumentation based on this source and consisting of source, vacuum and gas system and spectrometer is available from a number of commercial manufacturers; calibration algorithms are built into such instruments so that the sample composition, or the depth profile of a layered sample, is displayed directly. Figure 2 shows a routine example of such an analysis; the steel cover for an unused flue outlet has a copper coating with an intermediate layer of nickel about 1 μm thickness. Figure 3 shows that it is possible to record very much thinner layers if sufficient care is taken.

In current instrumentation, anode tubes with various diameters are available; the standard diameter is usually 4 mm, though 2.5 mm or even 1.0 mm is possible. The pressure is controlled by a servo system, so that the voltage and current may be set, and the pressure is automatically adjusted to the correct value within a few milliseconds. It should be noted that in many cases, particularly with older equipment, the recorded pressure may be a reproducible parameter, but is measured at some

Figure 1. The Grimm source
A plane metallic sample acts as the cathode. Originally the anode tube had an inner diameter of 8 mm, but smaller diameters are now common. The gaps between the outside of the anode tube and the cathode block, and between the end of the anode tube and the sample are each ~ 0.2 mm, and are evacuated by pump 1, so that when a discharge is initiated, it is restricted to an area of the sample equal to the cross-sectional area of the anode tube and no discharge occurs on the outside of the anode tube.

Figure 2. Typical compositional depth profile of a copper coated steel sample. The nickel layer ensures that there is good adhesion of the outer copper layer. (Recorded using LECO GDS 850A, 4mm anode tube, 750V, 20 mA)

Figure 3. Illustration of the use of GD-OES to provide information of very thin layers on the surface of a stainless steel sheet. [4] The conversion of line intensity to composition by weight may not be accurate for such thin layers.
distance from the source and does not correspond to the actual pressure within the source. For a given voltage and current, the required pressure will depend on the sample material; nevertheless, it is found that such pressure variations have a smaller effect on recorded emission yields than current or voltage changes, so it is very common practice to work with fixed voltage and current — for a 4 mm diameter anode tube, 700 V and 20 mA are often described as “standard conditions”.

The relationship between the measured intensity and the concentration of a particular element E within a sample matrix is given by the “Standard GD-OES equation” [5]:

\[ I_{\lambda(E),M} = AR_{\lambda(E)} c_{E,M} q_M \]

where \( I_{\lambda(E),M} \) line intensity, \( \lambda(E) \) wavelength for line of element E, \( R_{\lambda(E)} \) "emission yield", \( c_{E,M} \) concentration of E in matrix M, \( q_M \) sputtering rate of matrix M, and \( A \) instrumental constant.

This simple equation must be modified in many cases to allow for interferences from overlapping lines of other elements, and at high concentrations for the effects of self-absorption [5]. The emission yield of a given line may be determined using samples of known composition and sputtering rate. Ideally \( R_{\lambda(E)} \) should be independent of the matrix used — “matrix-independent emission yield” but in many cases this does not hold — the calibration curves of \( C_{E,M} \) vs \( I_{\lambda(E),M} \) depend on the matrix used. For example, differing calibration curves are obtained for the analysis of zinc in copper and aluminium based zinc alloys [6].

1.2 Later developments

Since the first introduction of the Grimm source, the potential of the technique has steadily increased [7]. In ~1990, rf powered sources were introduced permitting the analysis of non-conducting layers and solids. This technique has been successfully employed for the analysis of, e.g. coated and painted steel sheets for the automotive industry. The source is usually capacitively coupled to the power supply via a matching network; the sample acquires a negative dc bias, and so is bombarded by ions and fast atoms and sputtered material enters the discharge in the usual way. However, the use of the matching network means that the only electrical parameter that can be conveniently measured is the power delivered by the generator. The rf voltage reduces if non-conducting samples are used and the dc bias voltage cannot be measured and thus changes in the plasma impedance are not recorded.

The problem is more serious when relatively thick non-conducting samples are analysed, rather than thin non-conducting layers. On the other hand, rf power supplies means that the discharge is more readily initiated. Samples may be coated with a very thin non conducting layer; this does not present a problem with rf excitation, but with dc excitation, the starting potential must be sufficiently high to break down the surface layer; the potential then requires a short time to adjust to stable conditions, and in addition very thin surface layers can be damaged.

In more recent years, very thin layers have been analysed using GD-OES. Angeli et al. [8] have demonstrated that layers of nm thickness can be detected routinely nowadays (see also figure 3). The analysis of layers in a multilayer stack can also be carried out with the same resolution as obtained in more traditional methods of layer analysis, but in a much shorter time and therefore at lower cost, and to greater depths. More recently, Shimizu [9] has shown that it is even possible to identify the position of the atomic layers when a very thin layer of molecular material is deposited on a sample.

For the analysis of such thin layers, a very flat clean sample is obviously required. In addition, the spectra must be recorded from the initiation of the discharge, and any contamination on the sample or in the source may lead to the transient presence of molecular species, which may influence both the discharge conditions and the intensity of individual lines. Moreover, analyses are often required of layers containing compounds such as oxides and nitrides, where the sample itself contains an element forming a molecular gas. When the sample is sputtered, this gas enters into the discharge. The problem is particularly acute for the analysis of non-conducting solids such as glasses with a very high oxide content.
2. The effects of molecular gases - previous work in the field
Fischer, Naoumidis and Nickel [10] investigated the effect of nitrogen and oxygen on one or two lines of each of a number of elements (the lines available on a commercial GD-OES system) and found major intensity changes. The effect of hydrogen contamination on line intensities was first clearly demonstrated by Bengtson et al. in 1998 [11]. With a standard GD-OES system, a bulk sample of a chromium containing steel was analysed; two chromium lines were available. At the start of the discharge, these lines behaved in different ways until they came to a common value for the Cr content. Bengtson demonstrated that the presence of hydrogen increased the intensity of one Cr line, whilst decreasing that of the other. After the start of the discharge, the hydrogen arising from contamination is removed and the correct chromium content was obtained. Clearly the values obtained for a thin layer might be incorrect.

Hodoroaba [12-15] carried out a detailed study of the effect of hydrogen on the intensity of copper lines, using controlled additions of hydrogen in the range 0-0.6 % H₂ v/v. A large number of Cu I, Cu II, Ar I and Ar II lines were selected using a monochromator, and the relation between line intensity and hydrogen concentration measured for each line. He operated using a fixed voltage (1000V), fixed pressure (~7.70 hPa) mode with a 2.5 mm diameter anode tube. The introduction of hydrogen caused an increase in plasma resistance, and hence a fall in the current. The sputtering rate also fell, but the sputtering rate per unit current for copper remained almost constant – other elements show major changes in sputtering rate. In some cases, the shape of the crater profile changed. Allowing for the changes in current and sputtering, Hodoroaba showed that the behaviour of each line – or rather lines from each upper energy level – investigated was different, but general trends could be identified: the intensity of Cu I lines tended to increase, whilst that of Cu II lines fell dramatically. Ar I lines tended to be less intense, whilst Ar II lines increased in intensity. Hodoroaba [13] also compared the electrical parameters and line intensity for a titanium sample sputtered with various hydrogen concentrations in the plasma gas with those for a titanium hydride sample sputtered in pure argon, and was able to show that the latter case corresponded to using about 0.2% v/v H₂ in pure argon. The exact H₂ concentration will depend on the details of gas flow in the source, but he showed that his data corresponded to the appropriate range of hydrogen concentrations.

Hodoroaba [14] also made some mass spectrometry measurements, and showed that whilst the intensity of Ar II lines increased, i.e. the population of excited Ar ions increased, the total number of argon ions fell greatly (and the number of ArH⁺ ions increased). On the other hand, whilst the population of excited Cu⁺ ions fell greatly, the total population of Cu⁺ ions increased. This work showed the importance of obtaining data by mass spectrometry as well as by OES. Using standard GD-OES instrumentation, Hodoroaba [13] also investigated the behaviour of the one or two lines available for each of a number of other elements, and obtained a wide range of intensity variations. In all cases, when hydrogen was introduced, the hydrogen continuum was observed; with standard GD-OES instrumentation, this means that signals may be observed at the wavelength corresponding to an element X, although this element is not present in the sample.

Subsequently, further investigations have been carried out by the Oviedo group on the effects of hydrogen, nitrogen and oxygen [16]; the majority of their OES work has involved studies on the one or two lines of each element available using commercial GD-OES systems. Wagatsuma has published a review on glow discharge plasmas [17] covering use of mixed noble gases as well as the presence of molecular gases in noble gas plasmas. Bogaerts [18] has undertaken modelling studies on analytical glow discharges containing hydrogen but the experimental conditions were those for the VG9000 cell for mass spectrometry (1000V, ~5 mA) but a paper dealing with typical Grimm-type conditions has now been submitted [19].

3. Work by present authors on the effects of molecular gases
All the authors of the current paper have been collaborating for some years in investigations on the effects of molecular gases in the plasma gas, with the majority of our work has been with hydrogen and nitrogen. This study is now taking place within the EC Marie Curie Analytical Glow Discharge
Research Training Network “GLADNET” [20], and we have started to investigate the effects of oxygen. To get a clearer understanding of the processes involved we have also used neon and in some gases krypton as the plasma gas, but most of results presented involve argon. All the results presented in this paper have been obtained with dc excitation, usually in the constant voltage, constant current mode, though the exact conditions vary. Preliminary investigations have shown that similar general trends are observed when rf excitation is used, but there may be differing effects on specific energy levels.

It had already been shown by Hodoroaba [13] that similar results are obtained when molecular gases are added to the plasma gas and when the element forming the molecular gas is sputtered from the sample. The former method has been used in most of our work. Normally commercially supplied argon containing 2% v/v of the molecular gas is mixed with pure argon using a system of mass flow controllers (MKS Instruments) In this way, accurate mixtures are obtained even at small levels of the molecular gas. When other noble gases (neon, krypton, xenon) have been the main plasma gas, it has been necessary to mix the noble gas with the molecular gas directly. All the gas piping is stainless steel; nevertheless, some traces of OH bands have been sometimes observed in the spectra; these have been eliminated by introducing a cooled trap after the mass flow controllers and immediately before the inlet valve of the Grimm source.

3.1 Electrical parameters

![Figure 4](image1.png) **Effect of addition of 2% v/v H\textsubscript{2} to Ar** (Fe cathode, 5 mm diam. anode tube).

![Figure 5](image2.png) **Effect of addition of 2% v/v N\textsubscript{2} to Ar** (Fe cathode, 5 mm diam. anode tube).

![Figure 6](image3.png) **Effect of addition of 2% v/v H\textsubscript{2} to Ne** (Fe cathode, 8 mm diam. anode tube).

![Figure 7](image4.png) **Effect of 0.25 % v/v O\textsubscript{2} added to Ar.** (Fe cathode, 4 mm diam. anode tube).
In all cases with the typical discharge conditions used for spectrochemistry, the addition of hydrogen or nitrogen to argon causes an increase in the discharge resistance, so that under constant voltage, constant pressure conditions (as used by Hodoroaba) the current falls; under constant current, constant pressure conditions, the voltage rises whilst it is necessary to increase the total gas pressure to hold voltage and current constant, as in the majority of our work. The magnitude of the changes required depends to some extent on the cathode material. Changes in the V-i characteristics at various pressures caused by the addition of hydrogen and nitrogen to argon are shown in figures 4 and 5, respectively.

On the other hand, when hydrogen is added to neon, the discharge resistance changes are much smaller, and may be positive or negative (figure 6). The magnitude of the change depends on the discharge conditions. Similarly, when oxygen is added to argon, then, at a constant pressure, the sign of the resistance change may depend on the current (figure 7).

3.2 Sputtering rate
It has already been noted that the sputtering rate per unit current does not change much with hydrogen addition for copper; the situation is very different for iron and titanium; for a N$_2$ or H$_2$ content of about 1%v/v the sputtering rate falls to about 30% of the rate in pure argon for iron and about 15% for titanium [21]; these changes should be borne in mind when considering intensity changes. Correcting for sputtering rate changes by dividing the intensity by the sputtering rate, or using emission yields instead of measured intensities may give a more realistic picture of the intensity changes.

3.3 Spectral changes – interpreting the results
Two approaches may be used to investigate the spectral effects produced by a molecular gas.

(1) If a commercial GD-OES system with a polychromator is used, then only one or two lines can be investigated for each element; often a scanning monochromator can be used to select an additional line, but even so only a very limited number of lines can be investigated for each element. This may provide data for empirical corrections for analytical work, but as different lines of the same element may be affected in very different ways by a particular molecular gas, a full understanding of the effects cannot be obtained in this way. It is possible to use a monochromator to make a series of sequential measurements, but this is a slow and time-consuming experimental procedure, and may well give rise to a misleading impression if an error is made in the gas mixtures used for a particular line.

(2) The preferable method is to record large sections of spectra simultaneously, using a range of gas mixtures. As photographic methods are no longer used in general practice (and in any case intensity calibration was tedious), very few suitable instruments were available until recently. The high resolution uv-vis Fourier transform (FT) spectrometers at Imperial College [22] are very suitable for this purpose, and have been used for studies on GD sources since ~1990. The best limit of resolution is ~0.03 cm$^{-1}$, so that at 200 nm (50,000 cm$^{-1}$), the chromatic resolving power (CRP) is ~ 1.6 x 10$^6$; the CRP is less than this value at higher wavelengths but in very many cases the instrumental contribution to the line profile is very small and line shapes may be studied. If such studies are not required, a lower resolution with better signal/noise ratio and shorter recording time can be used. Various photomultipliers are used for detection, so that typical observation ranges are 200-300 nm, 300-600 nm, etc. Recording times are of the order of a few minutes per spectral range. Using high vacuum conditions in the spectrometer, lines can be observed down to ~140 nm; the high wavelength limit is determined by the photomultiplier used, but we have made measurements up to ~ 900 nm.

More recently, some GD-OES systems have been produced with spectrometers with CCD arrays, and a number of grating and echelle instruments with CCD detectors are now available commercially. Such instruments are very suitable for such studies, although the limited resolution of some commercial systems makes line identification difficult, particular for complex samples.

With both FT and CCD spectra, the intensities of a large number of spectral lines can be recorded simultaneously in a pure plasma gas, and similar data recorded for a number of gas mixtures. It is then possible to study (a) the variation of intensity with molecular gas concentration for selected lines, and
also (b) to plot the ratios of the intensity of a given line in a particular gas mixture to the intensity in pure noble gas against the energy of the upper level of the line. Such plots allow the identification of significant energies and excitation processes. The plots of intensity vs molecular gas concentration demonstrate that various upper levels show different responses to molecular gas concentration and also that the effects vary with different discharge parameters (voltage, current, pressure). The particular conditions (molecular gas concentration, discharge parameters) used for studies of type (b) will affect the clarity with which processes are detected.

The recording of complete spectra has also the great advantage that initially data from a limited number of lines can be evaluated, but data on other lines may subsequently be processed when significant effects have been observed.

We have used this method for extensive investigations on the effect of hydrogen and nitrogen on systems with a range of metallic cathodes (copper, aluminium, iron, titanium, vanadium, silver, zinc, etc, and alloys of known composition). In this paper, we use work with iron and titanium cathodes to illustrate typical effects.

3.4 Effects on the ionised spectra of the sample

Early work by Hodoroaba [12] and others had shown that the addition of hydrogen to argon causes the suppression of Cu II lines excited by charge transfer. This effect also occurs for Fe II lines [23], as shown in figure 9, where lines in the Fe II spectrum with a total excitation energy (TEE) (ionisation energy + excitation energy of the ion) ~15.8 eV (Group A) are suppressed.

Charge transfer (CT) is a resonant process and only small amounts of energy can be converted to or from kinetic energy so the TEE needs to close to the ionisation energy of argon (15.76 eV) or the nearby metastable $^2P_{3/2}$ state (15.94 eV). However, excitation is also possible from the metastable FeI levels close to the ground state, so additional energy levels can be involved. It was observed in 1998 that excitation by hydrogen CT also occurred [23], causing enhanced intensities for FeII states with TEE ~13.6 eV. Figure 8(a) shows the ratios of the intensity in an argon/hydrogen mixture to the intensity in pure argon, plotted against the energy of the upper state for a hydrogen concentration of 0.3% v/v, whilst the section of the plot figure 8(b) shows that the marked difference in the relative positions of groups B and C of levels for a hydrogen concentration of 0.08% v/v. This is wholly in agreement with the dependence shown in figure 10 of the intensity ratios for individual lines on the hydrogen concentration. Note that no allowance for changes in sputtering rate is made in figure 8, but it is included in figure 9. Hydrogen CT excitation has also been observed in Ti II and Cr II spectra.

![Figure 8](image-url)

**Figure 8.** (a) Ratio of intensity using Ar + 0.3% v/v H$_2$ to intensity with pure Ar, plotted against TEE. (b) As (a), but using Ar + 0.08% H$_2$, for TEE close to the hydrogen ionisation energy. Iron sample, 700 V, 40 mA, 8 mm diameter anode tube. Reproduced from [23] with acknowledgements to Elsevier.
3.5 Effects on the atomic spectra of the sample.

In all cases, data has been obtained on the atomic spectra of the samples as well as on the ionised spectra, but until recently there was very little information on the excitation mechanisms involved. Added hydrogen increases the intensity of Fe I lines by a growing amount up to energy levels ~ 5 eV, with a marked peak or resonance effect at about 5.5 eV (figure 10). There is no similar effect when the added gas is nitrogen (figure 11). These data were obtained by FT spectrometry using two spectral regions "uv" (200-300 nm) and "visible" (300-600 nm); it is worth noting that if spectra from the "uv" region had not been recorded, then the sharp resonance would have been less obvious. This emphasises the need to investigate the effect of the added gas on as many levels as possible – to do this it is usually necessary to cover a very wide wavelength region.

A similar, but more marked general trend is observed in the spectrum of Ti I (Fig 12), although the sharp resonant effect is not observed. For both Fe I and Ti I, the effects of the added hydrogen are greater at lower currents (and powers) (figure 13); this is a very important result analytically. For the measurement of thin layers a low sputtering rate is helpful; under these conditions, the time taken to remove any hydrogen surface contamination will be longer, and also this hydrogen will have a greater effect on the measured intensities.
We have suggested [21] that the increase for both Fe I and Ti I lines may be due to the process:

\[ \text{M}_0 + \text{H}_2^+ \rightarrow \text{M}^* + \text{H} + \text{H}^+ \]

where \( \text{M}_0 \) is the ground state sample atom and \( \text{M}^* \) the excited sample atom. The total \( \text{H}_2^+ \) dissociation energy is ~18.6 eV; allowing for the hydrogen ionisation energy of 13.6 eV, the process could provide up to ~5 eV for the excitation of the sample atom \( \text{M} \); an additional particle is available to satisfy conservation criteria for various amounts of surplus kinetic energy, so the process is feasible up to energies of about 5 eV. We have as yet no suggestions on the origin of the resonant process observed with Fe I. Investigations on the behaviour of the atomic spectra of other elements are continuing.

### 3.6 Effects on the spectra of the plasma gases

Hodoroaba [12] reported the effect of hydrogen on about 30 lines in the ArI and ArII spectra and Šmid [24] reported the effect of nitrogen on about 12 argon lines, but there has been no detailed study on the possible underlying discharge processes. In general, the effects produced by nitrogen are smaller; hydrogen increases the intensity of ArII lines whilst nitrogen causes a fall; on the other hand, for ArI lines, a fall occurs in all cases with hydrogen; for some lines nitrogen causes increased intensity. High resolution measurements show that hydrogen greatly reduced the self absorption of ArI transitions (e.g.811.531 nm) to the metastable argon levels, whilst nitrogen has a smaller, but still very significant effect.

Šmid [24] measured the intensities of some N I lines in the vacuum uv region and showed that there is a good linearity between the intensities and the nitrogen content up to concentrations of about 0.2 %v/v but that the rate of increase then declines greatly; the lines studied are transitions to metastable levels but profile changes corresponding to reduction of self absorption could not be detected. The intensity of bands in the 2\textsuperscript{nd} positive system of nitrogen also showed marked non-linearity with increasing hydrogen concentration. Hodoroaba [12] and Steers [23] both reported very non-linear behaviour for the intensity of the H\( \alpha \) and H\( \beta \) lines (656.2 nm and 486.1 nm, respectively); these lines should not be subject to self absorption. It is clear that for both hydrogen and nitrogen, the degree of dissociation is highly dependent on the discharge conditions.
4. Conclusions
After a brief account of the use of glow discharges for analytical purposes, the complex spectral and other changes produced by the presence of molecular gases in the discharge gas are reviewed. The concentration ranges which have been studied are those which can occur in analytical applications. Some of the effects observed can be explained in terms of the excitation processes involved, but a large amount of further work using other sample materials and noble gases is required before a comprehensive picture can be obtained. At present, corrections can be made empirically in analytical work but a greater understanding of the processes involved will enable such corrections to be made on a more systematic basis. In addition, these results provide experimental data for comparison with modelling predictions.

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