# **RF Glow Discharge Atomic Emission Spectroscopy of Non-Conducting Materials**

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## INTRODUCTION

In recent years the need for highly precise, quantitative methods for the analytical characterization of non-conducting bulk materials has increased significantly. Conventional methods such as sparks, ICP, and flames require the sample to be dissolved in liquid or mixed with a conducting matrix material for analysis. One method that is especially suited for analysis of non-conductors directly is Radio Frequency Glow Discharge Atomic Emission Spectroscopy (rf-GD-AES). The glow discharge is a plasma source, consisting of partially ionized gas (usually argon) and high energy electrons. The glow discharge is formed in a cell filled with a gas, either inert or molecular gas, at low pressure.

Discovered in the 1920-30's, Robertson and Clapp were the first to make the observation that material was removed from the walls of a glass tube when a high-frequency discharge was initiated between two external electrodes (1). This removal of material was attributed to a process called sputtering, removing miniscule amounts of sample into the vapor phase by atomic or molecular bombardment. The discharge served to clean the glass, and therefore, it was proposed that because of the high sputtering rates observed, the method could be used for relative yield measurements (2). By the 1970's a method of applying a radio frequency power source to a cell filled with low pressure inert gas could be used to quantitatively measure atomic emission lines from a sample, used as the cathode.

RF-glow discharge uses a radio frequency AC power source to generate a plasma within a glass or quartz cell. The cell is made up of a fixed anode and a sample cathode

enclosed and sealed within a glass casing. The cell is evacuated with a vacuum and then filled to low pressure, about 0.1-10 torr with an inert gas, usually argon (Fig. 1).



Figure 1: Standard configuration of a RF glow discharge power source.

When power is applied the argon fill gas is ionized, forming the plasma in which high energy ionized argon atoms accelerate towards the cathode, which is made up of the sample being studied. When the atoms of argon hit the cathode, minute amounts of cathode material are liberated. The material that has been vaporized traverses into the cell where it can collide with high energy electrons released during the ionization of argon. This process serves to excite the sample atoms where they can re-emit light that can be detected.

#### **OPERATIONAL PARAMETERS**

Three prominent regions are observed in most analytical glow discharge devices: the cathode dark space, the negative glow, and the Faraday dark space. While the two electrodes are specifically designed as the cathode and the anode, in order to simplify

instrumentation design the grounded source housing is employed as the anode in most devices. In the vicinity of the cathode, electrons are repelled, resulting in the creation of a positive space charge near the cathode. The majority of the potential difference between the two electrodes is dropped across a narrow region surrounding the cathode, known as the cathode dark space because of its low emission luminescence. Adjacent to the cathode dark space is the bright, collision-rich negative glow region. The visible emission is the result of gas-phase excitation and ionization collisions and is where most of the analytical information is collected (2). A glow discharge may exhibit a Faraday dark space, positive column, anode dark space, and anode glow region. In a DC glow discharge, the negative potential of the cathode creates fields that accelerate positively charged gas ions towards its surface. The positively charged gas ions liberate small amounts of sample material as they bombard the cathode as well as secondary electrons. Because the sputtering process is non-thermal and relatively low energy, the atoms that are released are mainly neutral atoms. Most of the sample atoms diffuse through the cathode dark space without any significant excitation, because the electrons released during the sputtering process are of low energy and do not cause collisional excitation efficiently. As the enters the negative glow region a large number of high energy electrons, generated from multiplication via ionization, collisionally excites the neutral sample atoms, which then radiatively decay to release characteristic photons. These photons can be detected with an optical emission spectrometer (3). The electrons in the Faraday dark space have undergone enough excitation/ionization collisions in the negative glow region to be of low enough energy to cause little further excitation.

Why use a radio frequency power source? In a normal DC glow discharge, both the cathode and the anode must be made of conducting material. To analyze nonconducting materials, they must be ground up, mixed with high purity conducting powders and pressed into a disk, which will make up the cathode (4). This can introduce contamination of sample, trapping of gases, and loss of spatial information of elements in the original sample. With radio frequency power sources electrical conductivity of the sample is no longer required. The placement of a high voltage on the surface of a nonconductor induces a capacitor-like response where the surface acquires the applied potential only to be neutralized by charge compensation by ions or electrons. Rapid reversing the polarity of the voltage pulse allows for rapid charge compensation and reapplication of the desired high voltage, overcoming the inherent decay time constant. To achieve a "continuous" discharge, pulse frequencies on the order of 1 MHz are required. Typically a frequency of 13.56 MHz is used simply because that is the frequency the FCC has deemed an available frequency.

### ANALYSIS OF NON-CONDUCTING MATERIALS

Analytical applications of rf-powered glow discharge are only beginning to attract the interest of optical spectroscopists. Therefore publications of analytical applications of rf glow discharge as a source for atomic emission spectroscopy have been limited. The largest interest for rf glow discharge has been in the semiconductor industry, although this is more for thin film deposition and depth profiling, not atomic emission. The analysis of composition of polymers, such as plastics, and ceramics and glass are the primary uses for atomic emission spectroscopy. There has also been a small interest in the analyzation of paints and coatings.

In the analysis of painted surfaces one of the considerations is the shape of the crater formed during the sputtering process. This will provide an accurate depth profile as to the composition of the layers of the coated surface. Early studies by Payling (5) suggested that rf glow discharge OES could be a very powerful method for the depth-resolved analysis of polymer pigments. The ability to form flat craters was critical to this process. This was accomplished through observation of the transition zones in depth profiles or by use of a secondary evaluation of the product crater (Fig. 2). The actual depth profiles of polymer coating show the increase in emission intensity for both metals and nonmetals after ~5000s of sputtering. The majority of the sputtering time is due to the removal of the clear-coat.

Note the difference in temporal response, this is due to the heterogeneity of the sample. While the Co (I) and Ca (I) responses mirror eachother well, they are different from the Ti and Cr. The response of the C (I) seems to reflect that of the first set of metals, where the response of S is like the latter (6).



Figure 2: Crater profile analysis of the sputtering of a painted automotive component.

This is due to the presence of C in most samples, where S is unique to certain coatings. At about 6500s the appearance of Fe (I) identifies the first layer of the steel body surface. In 1997, Sanz-Medel (7) used a similar configuration that cooled the painted sample to minimize melting of the coating to measure crater profile analysis and also used a CCD detector to achieve the true benefits of rf glow discharge, including low noise and high stability.





The analysis of glass and ceramics has been extensively studied in the 1990's, especially due to the boom in the computer industry and the search for superconductors. In 1996, Saprykin et al were able to optimize a rf glow discharge with the use of a magnetron for the trace analysis of glasses and ceramics (8). In the presence of an externally applied magnetic field charged particles in the plasma process around the magnetic field lines. If the magnetic field strength of a few hundred Gauss are used, only plasma electrons are significantly affected by the field. The electric and magnetic field gradients cause electrons trapped in a circular orbit near the cathode surface. This results in a increase in the effective electron path length and a corresponding increase in the efficiency of plasma gas formation by collisions with high kinetic energy electrons. This configuration allows for very high sputter rates and ionization yields. The increase in sputter and collisional excitation also serves to increase the signal of the analyte while at the same time reducing the background caused by the emission of argon and molecular carbon dioxide. It is possible to achieve a 10 fold decrease in background with a concurrent 4 fold increase in trace element signal. Using this method it is possible to get detection limits in the low ppb range (9).

#### CONCLUSIONS

The use of radio frequency power sources in glow discharge spectroscopy has been in the development stages for decades. Yet only in the last few years has this source been taken advantage of as a low background, high stability, narrow line width source. Because the emission from the sample is primarily from neutral atoms, the line intensities will be high, and identification fairly easy. One of the more recent innovations in rf glow discharge is its use as an atomization source for insertion into a mass spectrometer. This method serves to increase sensitivities by direct introduction of nonconducting samples into a MS, as well as maintaining molecular species for analysis via MS characterization. With the onslaught of the ICP method for atomic emission spectroscopy the niche in which glow discharge, and in particular rf glow discharge, once reign unique is shrinking. It still remains one of the under exploited methods for atomic characterization of non-conducting materials.

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