The Grimm Source at Fifty: In Glow Discharge Spectroscopy, It Still Starts with the Lamp

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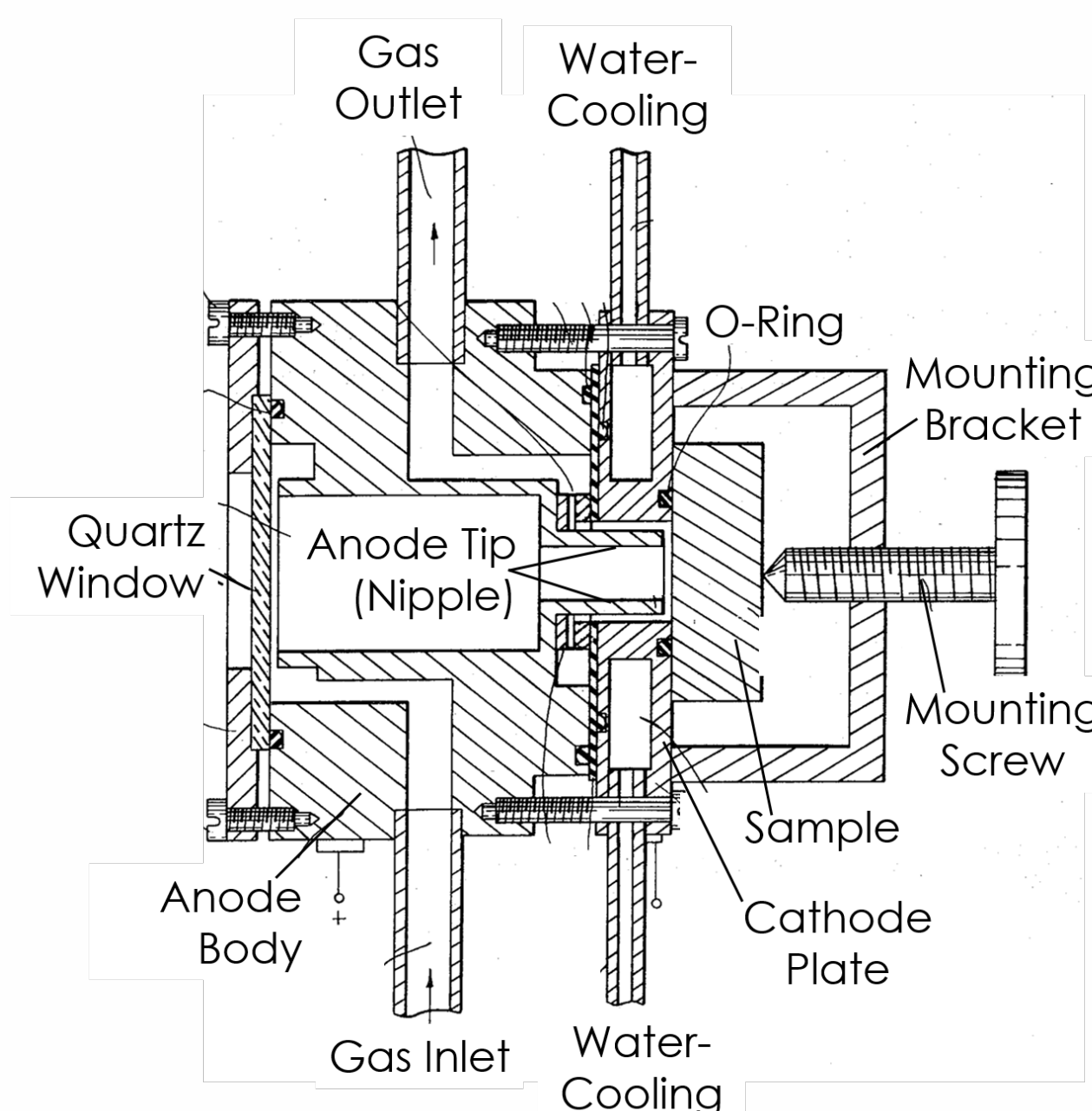
The Invention of the Grimm Lamp

The Grimm lamp is the geometry of choice for spectrochemical analysis of solid materials with a glow discharge. The basics of this design originated in the late 1960s when Werner Grimm of RSV Präzisionsmessgeräte GmbH in Hanau, Germany developed the lamp.[1] As this year is the 50th anniversary of the patent for this technology, it is useful to explore the insight that led to the invention and how it still applies today.

In his patent filing, Grimm cited several key drawbacks of the spark discharge and set out to design a source that would not suffer from self-reversal of spectral lines and not melt the surface of the sample resulting in segregation and evaporation of some components. Alternatively, he noted that many experiments with hollow cathode glow discharges offered the advantage of "cathodic evaporation" (typically referred to as sputtering today) in which layers of materials were removed slowly over time. However, these hollow cathode lamps (HCLs) did not have steady gas flow through the discharge lamp, and it was not easy to change between samples of interest. Accordingly, HCL emission measurements had minimal adoption beyond academic curiosity, despite improved quantitative results compared to spark discharges. Grimm's invention sought to merge the ease-of-use of a spark discharge with the analytical performance of an HCL.

As can be seen in **Figure 1**, Grimm's invention placed the tip of the anode very close to the sample cathode without touching it. In principle, this meant that the anode was closer than one mean free path from the sample at reduced pressure, limiting the possibility of an arc forming between the electrodes and permitting the principle drop in potential to occur over a very small distance.

Figure 1: Annotated image of Grimm lamp from original patent issued in 1968.[1] The anode body comprises most of the discharge cell and a water-cooled cathode plate contacts the sample. A mounting screw holds the sample in place before and after vacuum is initiated. This figure has been slightly modified from the original version.

In the years following his initial invention, Grimm would go on to work with glow discharges of several kinds, leading to several more patents. These included:

- Application of the Grimm lamp for bulk analysis of wire samples
- Use of a Grimm glow discharge for atomic absorption spectrometry
- Use of a glow discharge to polymerize organic compounds
- Analytical optimization for higher sample throughput, greater optical transmission, and more serviceable parts

The last set of studies ultimately influenced the commercialization of glow discharges for spectrochemical analysis. Grimm's ideas for wire analysis have also been commercially adopted and expanded upon. In 1979, Grimm's company (RSV Präzisionsmessgeräte, GmbH) released the first commercially available glow discharge spectrometer, the Analymat. LECO purchased the resulting product line in 1988 and has produced glow discharge spectrometers ever since. The similarities between the initial invention and LECO's modern Grimm lamp (**Figure 2**) are remarkable as LECO continues to make use of Grimm's inventive insights.

Why the Grimm Lamp Became the Standard Configuration

As many of the noted drawbacks of the spark discharge persist today, glow discharge instruments have continued to be used and further developed for spectrochemical analysis of solid materials. A key reason for the success of the Grimm geometry is the shape of the resulting crater formed by sputtering material from the surface of the sample and related characteristics. Optimally, these craters are flat-bottomed and result from the sequential removal of layers of material from the surface. This crater shape emerges from the very flat electric field with a sharp potential drop over only a few microns between an annular anode and the sample surface (which is the cathode). Argon ions and atoms are directed toward the surface, resulting in even bombardment and sputtering of the sampled area. The short distance between the sample cathode and the anode is too short for an arc to form and obviates other luminous areas of the discharge other than the analytically useful negative glow.

For bulk analysis (like the work carried out by Grimm), step-by-step removal results in the independent analysis of virgin material for each subsequent period of integration while sputtering in the same location on the sample. Because the previously sputtered material is evacuated from the cell, these separate integrations are free of metallurgical history from layers nearer to the surface. This mechanism also results in data that separate the surface layers from the bulk for more accurate characterization. Additionally, as-cast materials can be analyzed because graphitic materials are not selectively sublimed in the glow discharge. Glow discharge craters are more shallow and cover less surface area than spark spots, resulting in less required grinding for sample preparation and less reference material consumption.
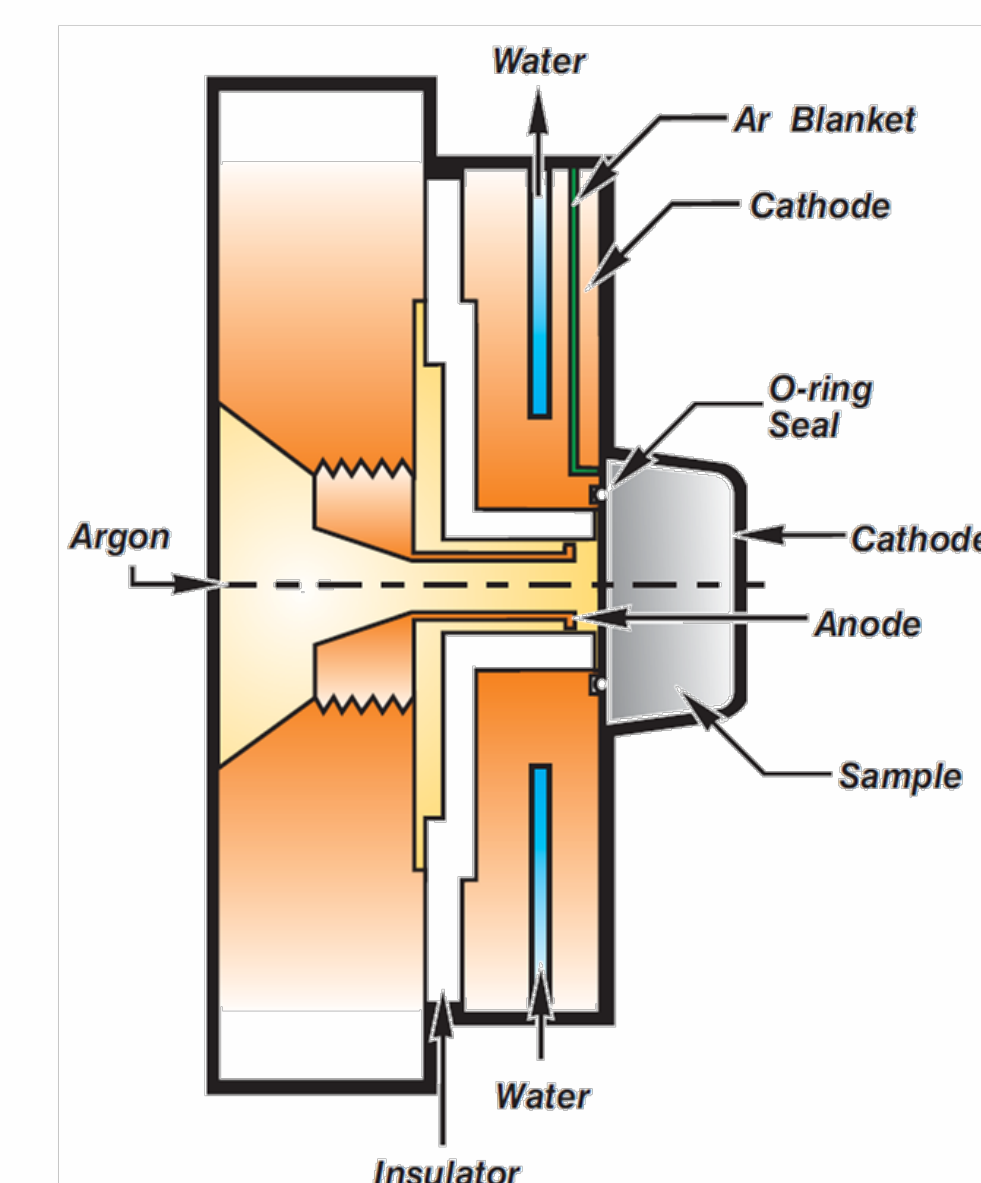
Figure 2: Annotated schematic diagram of LECO's modern glow discharge lamp, with many similarities to the original design by Grimm, including water cooling in the cathode plate, front coupling of the cathode plate to the sample, small distances between the end of the anode and the sample cathode, and the same direction of Ar flow.

Additional benefits exist in terms of the depth-profiling capabilities of these instruments. Within a few years of Grimm's invention, this potential was demonstrated by several researchers including Boumans[2] and Laqua[3]. These initial experiments highlighted the importance of precisely knowing the power parameters used in the discharge and accounting for variations in sputtering rates of materials.

Compared to conventional high-vacuum surface analysis techniques, the glow discharge offers several critical advantages for compositional depth profiling:

- Larger areas that are simultaneously sampled with competitive depth resolution and superior quantitation
  - More sampled area results in greater signal
- Faster depth profiling analyses
- More simplicity for non-expert users
- Lower vacuum requirements (no turbo-molecular or diffusion pumps needed for the lamp)

How the Grimm Lamp Has Changed

Although the general geometry has remained similar over the last half-century, many adjustments have been made to meet performance and practical sampling goals for users.

One of the most obvious differences between the lamp built by Grimm and those used in modern instruments are the reamer and facer assembly that automatically cleans the source between analyses. This instrument feature nearly eliminates sample carryover and removes the need to manually clean the electrodes as commonly done with other plasma sources. The reamer is also used to hold samples in place, removing the need to manually use the mounting screw and bracket shown in **Figure 1**. To reduce the amount of atmospheric gas that enters the discharge chamber, an argon blanket has been introduced to create an argon-rich environment around samples when they are initially mounted.[4]

A major advance in glow discharges that has led to some of the most dramatic changes in lamp architecture has been the introduction of radio-frequency power for the analysis of non-conductive samples. Lamps for these samples needed to be modified to have smaller powered areas. LECO's RF lamp design includes only a small ring electrode around the O-ring to power samples as shown in **Figure 3**.[5] This design most closely mimics the Grimm source and minimizes the required capacitive coupling to bias the surface of a nonconductive sample. Other approaches have retained some elements of the Grimm lamp, such as the close placement of an annular anode, but differ in how they apply power to the opposite side of the sample.
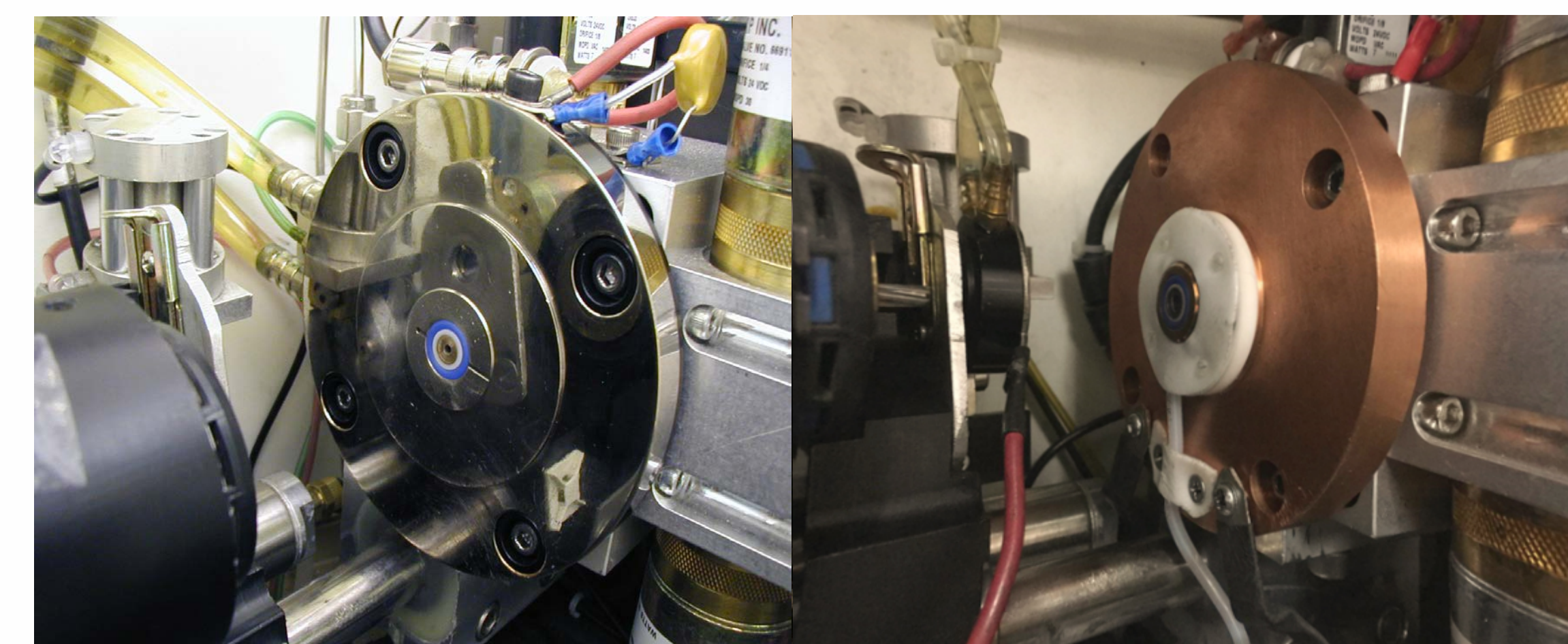
Figure 3: Photographs of LECO's DC (left) and RF (right) discharge lamps. The DC lamp still has many similar features of the original Grimm design while the ring electrode on the RF lamp is used to power nonconductive samples for analysis.

Additional changes in lamp design were practical for users of the instruments. For instance, it is important for users to have more easily replaceable anodes, which wear over time. The anodes on LECO lamps are easily unscrewed for replacement. Grimm's original design depended on very close spacing between the outer diameter of the anode tip and the cathode block, with minimal physical insulation. For more robust operation, commercial instruments include replaceable ceramic sleeves to separate the electrodes.

Certain fine adjustments have also been made. Anode depths were noted by Grimm to be optimal at 0.2 mm, but modern instruments are optimized to run with depths nearer to 0.12 mm to minimize arcing. Grimm suggested analysis parameters up to 500 mA, 3000 V, and 20 Torr. Today the maximum power parameters are typically around 50 mA and 1200 V with pressures in the range of 5 to 15 Torr.

Grimm's original lamp had a sampled area with a diameter of 6 mm and modern lamps have been optimized to have a 4 mm diameter area following the introduction of depth-profiling analyses when such a diameter was shown to generate a more optimal flat-bottomed crater (see **Figure 4**).

Controlling the Lamp is Critical

Over the past three decades, increasing attention has been paid to control and monitoring of the discharge parameters in the Grimm lamp. Early studies by Boumans[2] indicated that current and voltage are key parameters for Boumans' calculation of sputter rate and quantitation of emission. **Equation 1** shows the calculation for sputter rate (Q), where C_Q is a material-dependent sputtering constant, V_0 is a threshold potential for sputtering to occur, and i_g and V_g are the discharge current and voltage, respectively.

$$Q = CQ \cdot ig \cdot (Vg - V_0) \qquad \text{Equation 1}$$

One should be mindful that two samples with the same concentration of a given element will have emission proportional to their sputter rate. Without accurate characterization of power and sputter rate, quantitation is not possible. When layered materials of disparate composition are analyzed (**Figure 4, left**), appropriate quantitation can only be achieved with sputter-rate corrected calibration curves. Such calibrations rely on the maintenance of similar power conditions throughout analysis to sputter as expected, leading to flat-bottomed craters (**Figure 4, right**). For bulk analyses, consistent power is needed for samples to fit on a calibration curve.
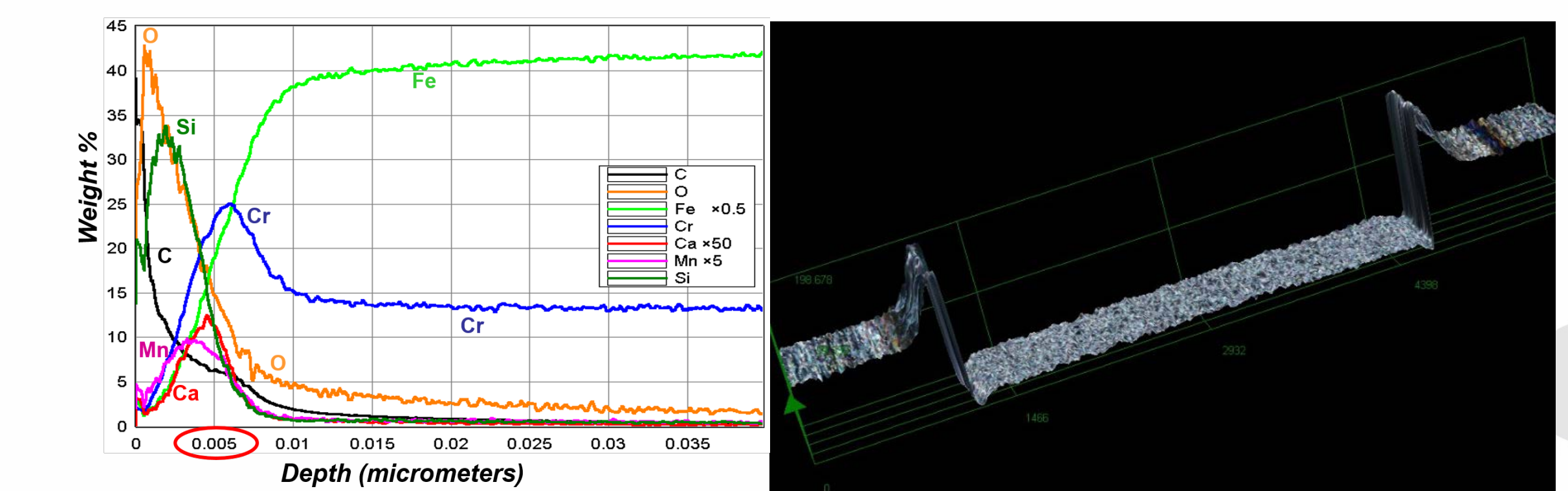

Figure 4: Depth profiling can deliver high precision measurements of both depth and elemental composition (left), but requires fine control of the discharge parameters to obtain flat bottomed craters (right, cross-section imaged by DSX Digital 3D Microscope).

Lamp control and monitoring become more critically important when RF power is used due to many sources of power loss between the power supply and the lamp. LECO's glow discharge team has spent a great deal of effort to characterize these losses and develop mechanisms for calculating these losses in real time during analyses to measure and stabilize the discharge parameters.[6] This method, known as True Plasma Power® is the critical step in LECO's accurate application of RF power, and is what allows for accurate characterization of both depth and composition of nonconductive materials. For some thin layers, knowledge of the initial powering parameters can be used to correct the data obtained prior to complete stabilization in accordance with **Equation 1**.

References

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