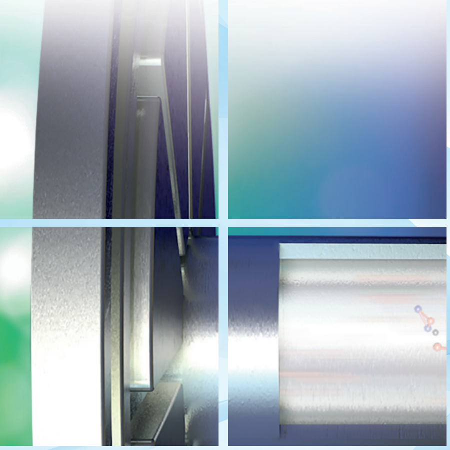
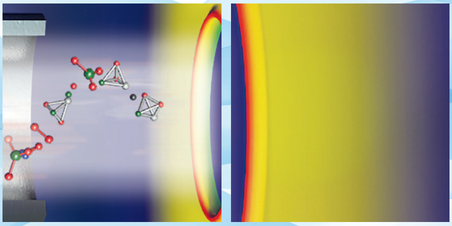
HORIBA
Scientific



Glow Discharge Optical Emission Spectrometry



Focus on: Instrumentation

From Bulk Analysis of Metals to Depth Profiling of Advanced Materials

Matthieu Chausseau, Patrick Chapon (HORIBA Scientifc)

Introduction

Materials characterization is key for the development, study and quality control of materials. Characterization can involve macroscopic level techniques, such as visual inspection, mechanical testing and thermal analysis. It can also involve microscopic level techniques to probe and map the surface and sub-surface structure of materials with instruments, such as an Optical Microscope, a Scanning Electron Microscope, a Transmission Electron Microscope, an Atomic Force Microscope, etc.

Spectroscopy is also widely used to reveal the chemical composition, composition variation, and structure of a material with techniques such as Ultraviolet-Visible spectroscopy, Raman spectroscopy, Photoluminescence, X-Ray Spectroscopy (Energy Dispersive, Wavelength Dispersive), X-Ray Photoelectron Spectroscopy (XPS) or Auger Electron Spectroscopy (AES) to name a few.

Materials developed for advanced applications involve more and more stacks of layers of different materials where the thickness of each layer, and also the presence or absence of elements, or their diffusion within the different layers, is of critical importance. The Glow Discharge Optical Emission Spectroscopy, also known as GD-OES, is an essential technique for elemental surface and depth profiling of thin films and industrial coatings[1]. Multiple developments made over the past years transformed Glow Discharge Optical Emission Spectrometry into a unique technique for elemental depth profiling of advanced materials.

GD-OES: Origins

Although the scientific examination of the glow discharge plasma happened during the latter half of the 19th century, the Glow Discharge Optical Emission Spectrometer in its closest form (compared to modern instruments), was invented in Europe by researchers from the metallurgical industry, mainly from Germany and France, in the late 60's – 80's, and was first used for bulk analysis. Soon people realized that the GD source could perform depth profiling of thin and thick films. However, both the economic situation of metallurgy in Europe at that time, and the lack of scientific papers published – or published in French or German only – contributed to keeping GD-OES as a "confidential" technique.

Since then, and despite the first depth profiles published being of GaAs thin films in 1970, the GD-OES technique developed in the metals industry and is now widely used for elemental bulk analysis and depth profiling for electrically conductive metallic coatings characterization. Over the past fifteen years however, multiple new instrumental developments have enlarged the field of applications of GD-OES to include the characterization of coatings and thin films for advanced materials, making it an essential tool for quality control and process optimization/monitoring. Glow Discharge is now able to characterize many different materials, electrically conductive and not, covering a wide range of applications from photovoltaic (CIGS, perovskites…) to packaging, from organic electronics to energy storage (lithium batteries, fuel cells…) and is the characterization companion tool to a variety of deposition techniques of thin and thick films (plasmas, electroplating, anodization, etc.). GD-OES also became a complementary technique to XPS and SEM.

Instrumentation

The Glow Discharge is a plasma created by an increase of voltage between two electrodes in a low-pressure environment. The electric field accelerates the electrons to sufficient energies to ionize gas molecules through collisions. When the excited species de-excite, there is emission of light. The observation of light with an Optical Emission Spectrometer permits the identification of the elements, thanks to their characteristic wavelengths emitted, and their quantification by means of a calibration curve.

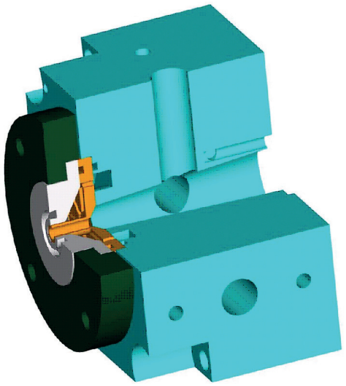


Figure 1: Cross-section of GD source

The HORIBA Scientific Glow Discharge Source

The plasma is confined in a small tube of a typical diameter of 4 mm.
The sample is mounted externally against a ceramic spacer (Figure 1).

The gas used to create the plasma is usually argon, but it can be other gases such as neon, or a mixture of gases such as Ar/O or Ne/O.

The tube is the positive electrode (anode) and the sample plays the role of the negative electrode (cathode), facing the tube and closing the plasma chamber. This design does not require an ultra-high vacuum, as only low pressure is used. The external vacuum and the close distance between the anode and the tube, approximately 150 µm, along with the double pumping of the source using two independent vacuum pumps, ensures confinement of the plasma within the tube, and constant pressure at the sample surface with depth.

Sputtering and Depth Profiling

The ions created in the Glow Discharge source accelerate toward the surface of the sample and sputter its surface. The erosion rate ranges typically from 10 to 150 nm/s, i.e. 30-500 atomic layers per second. The sputtered species are then excited into the gas phase, away from the surface of the sample. When de-exciting, atoms emit light at characteristic wavelengths with an intensity proportional to their concentration, as seen in the sample (Figure 2).

Under optimized operating conditions, the crater shape on the sample is flat, allowing for depth profiling analysis with high depth resolution. The conversion of sputtering time into depth is done by an online interferometric measurement, or by using the sputtering rate of the material studied, known either from tables, or after measurements from experiments.

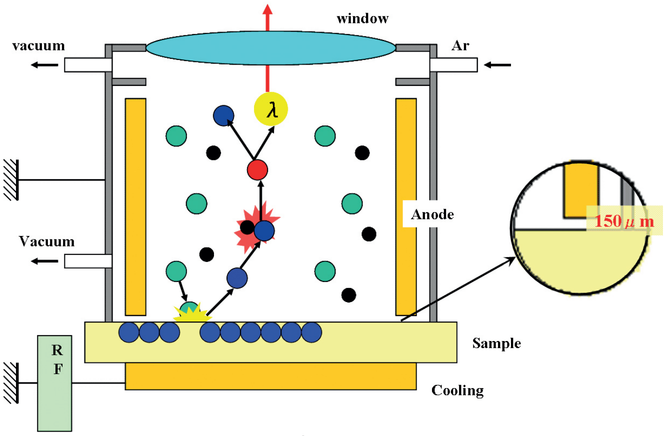


Figure 2: Principle of GD sputtering

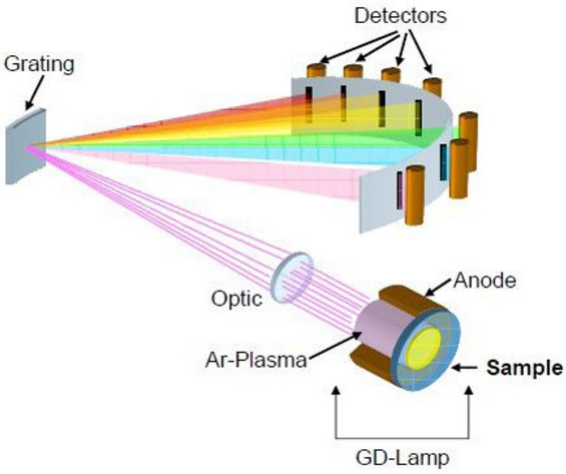


Figure 3: Paschen-Runge Polychromator

Elemental Analysis – Optical Emission Spectrometry

The light emitted from the plasma is collected through an optical interface and enters an optical emission spectrometer (Figure 3). Since depth profiling requires simultaneous measurements of all the elements, the GD instrument uses a Paschen-Runge mounted polychromator and a dedicated detector for each element of interest. For maximum light efficiency over the useful spectral range and for improved performance on key elements, the GD-Profiler 2 is equipped with a high-density blazed holographic grating working in the first and second order with enhanced efficiency in the VUV.

GD-OES provides both qualitative and quantitative analysis. As with all comparative techniques, calibration is required to provide concentration vs. depth. Calibration for a dedicated application is usually straightforward. One of the characteristics of Glow Discharge is that the excitation of the species happens away from the surface of the sample. Thus, the composition of the sample has little effect on signals, and the calibration can involve materials of a different nature, thereby simplifying this step.

Advanced Features of HORIBA Scientific Glow Discharge Spectrometers

Elemental depth profile is very useful information for many materials and many different applications. Some earlier developments of the technique helped to improve its performance or to extend its use to a larger variety of samples. The HDD® mode extended the dynamic range of the technique and the Radio-Frequency generator paved the way for the analysis of non-conductive materials.

Some challenges remained for specific samples involving ultra-thin films, heat sensitive samples, organic layers, odd-shaped samples, new materials of unknown sputtering rate, etc. The most recent developments made by HORIBA Scientific now make it possible to readily address an even larger variety of materials and applications.

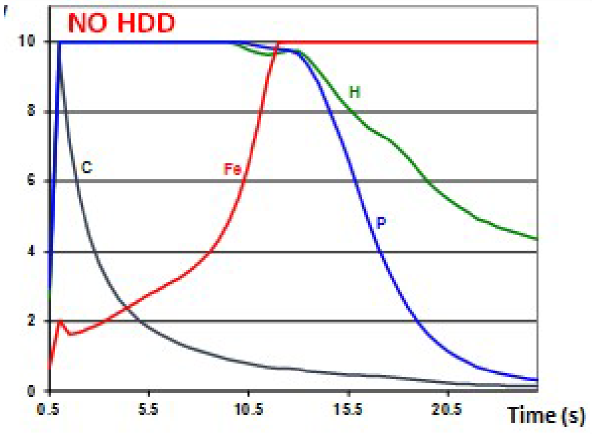


Figure 4: Coating on steel without HDD

HDD® Mode

HDD® stands for “High Dynamic Detection,” and refers to the possibility to have an extended dynamic range for the detection of both high and low concentrations. A patent was granted to HORIBA Jobin Yvon in 1998 for the HDD® mode.

In a depth profile analysis, an element of interest can be at the ppm level in some layers and 100% in the next. Due to the very rapid sputtering process, it is impossible to stop the measurement between the layers, and to adjust the gain of detectors to match the new level of signal. Preset gain values are then a considerable limitation to depth profiling operations, as a preset value may not offer the right sensitivity for low concentrations, or detector saturation may occur for high concentrations (Figure 4).

HDD® adjusts the applied voltage in real time to the output current of the detector, offering a true dynamic range of over 10^9 on all lines (Figure 5). There is no longer a need to pre-adjust the instrument and perform additional experiments to find the right setting, with a risk of experiencing lack of sensitivity or saturation, and there is no longer the need to use multiple wavelengths and multiple calibrations with different settings to cover the full concentration range.

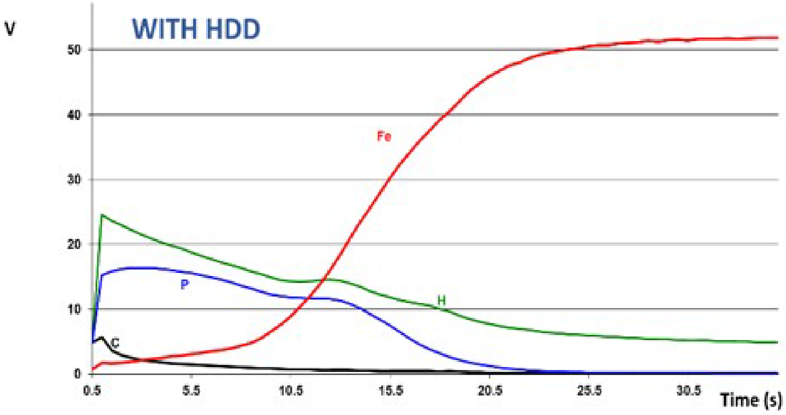


Figure 5: Coating on steel with HDD

Pulsed Radio Frequency Generator

Following the successful application of radio frequency on a Glow Discharge source achieved in 1987 by Richard Passetemps at Renault (a French car manufacturer), HORIBA introduced radio frequency sources on its systems in the mid-90’s.

Whereas the standard DC source only works on conductive materials, the radio frequency source makes it possible to characterize non-conductive materials. This major step for the Glow Discharge technique opened the door to the characterization of non-conductive materials and hybrid materials involving both conductive and non-conductive layers: Oxides, coatings on glass, painted car bodies, etc.

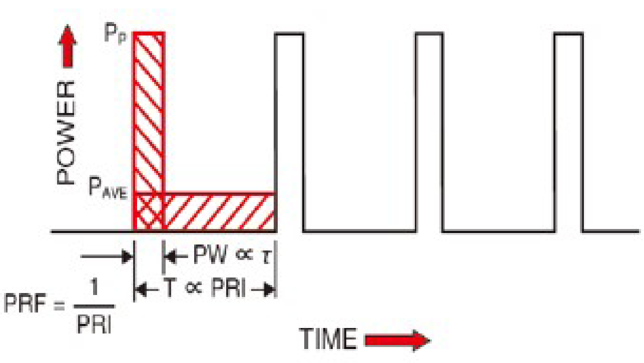


Figure 6: Pulsed operation

Despite its advantages, radio frequency was not enough to solve some of the challenges with thermally sensitive non-conductive samples. First described in 2009 [2], the analytical benefits of the pulsed mode are providing an additional way to control the plasma through the pulse parameters, i.e. pulse length and period (Figure 6), and reducing the thermal load on the sample without affecting the instantaneous power responsible for the sputtering and excitation by varying the duty cycle.

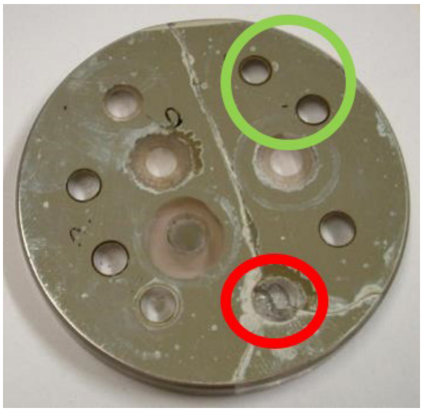


Figure 7: Glass sample - Pulsed RF mode (Green) vs. Standard RF mode (Red)

This was only in 2011 that it became possible to implement the pulsed mode routinely on commercial instruments, thanks to a patented development ensuring auto-matching of the radio frequency source in both pulsed and non-pulsed mode [3]. This development is a major breakthrough and opens the way to many new materials and applications.

Thanks to these two major advantages, the pulsed radio frequency source allows using higher instantaneous power, providing increased signal-to-noise ratio, and lowers average power, thanks to the duty cycle of the pulse, resulting in improved performance for fragile, thermally sensitive materials. Thus, the Glow Discharge becomes a more efficient tool for glass samples (Figure 7), polymers, and for the accurate determination of light elements, which may migrate under thermal load. It also helps to avoid surface damage on fragile samples. With the pulsed radio frequency generator, Glow Discharge is now a reliable technique for the characterization of Na in CIGS solar cells, lithium-ion battery cathodes and anodes, TiO_2 nanotubes, perovskite solar cells, and more.

Ultra-Fast Sputtering (UFS) Mode

The Ultra-Fast Sputtering mode [4] originates from the need to improve the performance of Glow Discharge for organic layers. In many cases, organic layers can be extremely thick, typically 10-100 µm, and the sputtering has to be done slowly, at low power, to minimize unwanted sample degradation. This leads to long analysis time and poor sensitivity.

In this mode, a combination of argon and oxygen replaces the argon plasma gas. The plasma becomes reactive, enhancing the erosion rate in some cases, and leads to faster analysis and much better signal-to-noise ratios. Since the materials requiring this mode are fragile, the Ultra-Fast Sputtering mode is often used along with the pulsed mode.

Since its introduction, this mode has been very useful for the characterization of materials, such as perovskites, that have a complex structure involving ITO glass substrates covered with hybrid organic/inorganic layers, and for lithium battery electrodes where it allows sputtering of the carbon layer and reaching the foil substrate (8-9).

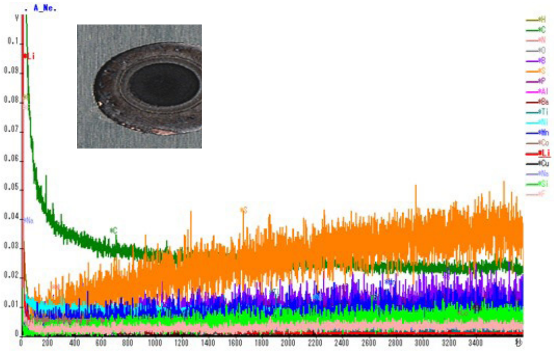


Figure 8: Depth Profile of lithium battery anode without UFS. Slow sputtering rate observed and only 11 µm sputtered after 60 minutes

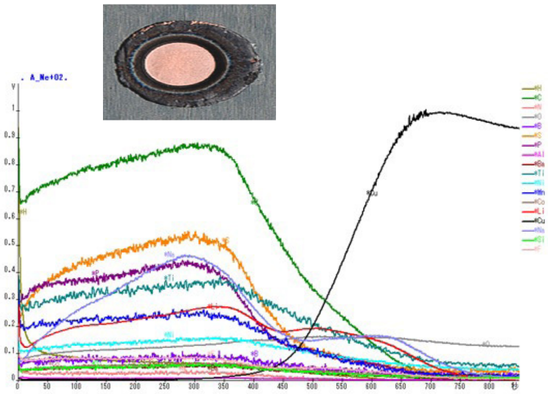


Figure 9: Depth Profile of lithium battery anode with UFS. 70 µm sputtered in 10 minutes, from surface to the Copper foil

Differential Interferometry Profiling

Differential Interferometry Profiling (DiP), is a patented setup recently introduced in GD [5, 6] that allows direct measurement of the crater depth.

The main principle is the measurement of the variation of the distance between the bottom of the GD crater, and a reference point at the surface of the sample. To achieve this, a Class 1, eye safe, red laser diode is split into two beams of orthogonal polarization. One of the beams is focused onto the reference zone at the sample surface, and the second beam is focused on the center of the crater (Figure 10).

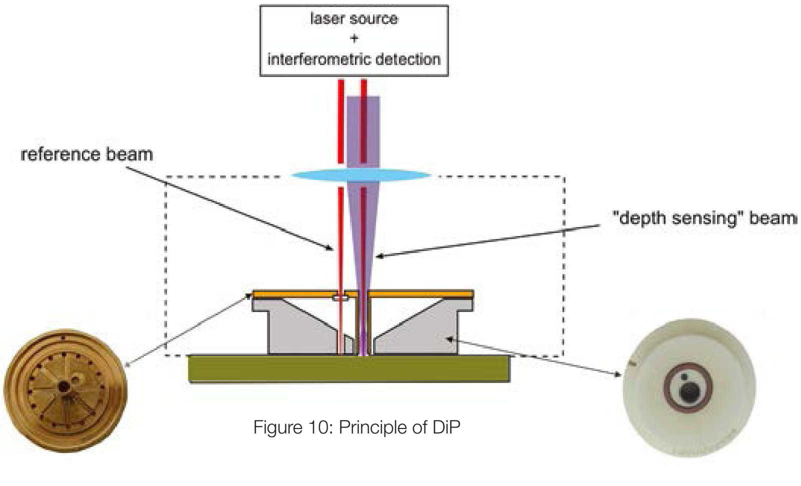


Figure 10: Principle of DiP

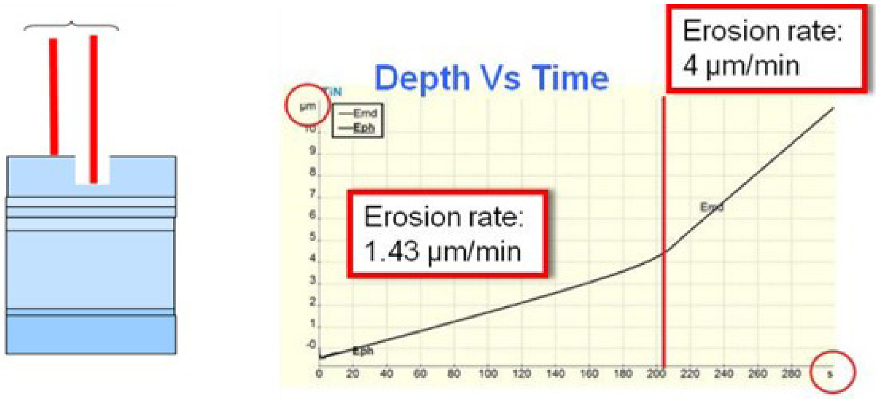


Figure 11: Erosion rate and depth vs. time using DiP

For non-transparent samples, the crater depth is directly linked to the phase and thus, DiP is measuring the depth of the crater, as a function of time (Figure 11). This information, combined with the signals measured as a function of time, gives access to the total depth, the thickness of each layer and the erosion rates for each layer in a material. For transparent materials, the calculation is also simple, but requires information on the optical index of the layer sputtered.

Since its introduction, DiP has been successfully used to determine the depth of many different materials of various structures: TiN/WC, DLC, CIGS, NiP/Ni/Cu, Ag/Pd/Ni/CuFe.

Special Accessories

Since its discovery and the first instruments developed, the Glow Discharge technique had major developments over the past years. It is now capable of addressing a much wider span of applications and new developments to keep increasing its capabilities.

In parallel to the major hardware developments, multiple accessories were developed to facilitate sample handling, or to make possible the characterization of materials without altering their structure or composition. The most popular special accessories for GD-OES applications are:

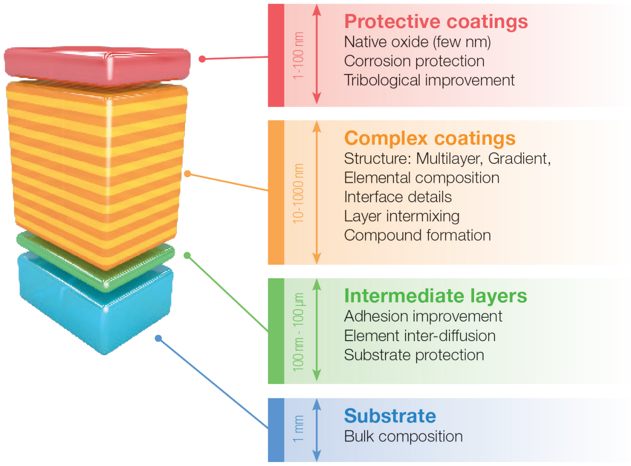
- Small sample holder for samples that are too small to cover the o-ring of the anode
- Lithium bell for transfer of air sensitive samples from glove box to instrument, or for characterization of very rough samples with overpressure of Argon
- Special anodes for specific shapes (concave samples…)
- Indium kit for very small samples, or samples that need to be cut (drill bits)
- Sample holder for SEM cross-sectioned samples

Conclusion

Glow Discharge Optical Emission Spectroscopy is a technique invented to provide specific answers to scientists. Researchers who developed the technique were looking for a solution to their application. It continues to evolve.

As of today, Glow Discharge Optical Emission Spectroscopy is able to provide qualitative and quantitative elemental depth profiling, measure elements from hydrogen to uranium, and characterize layers from the first nanometer down to 150 µm into the sample, within minutes.

Glow Discharge Optical Emission Spectroscopy is now widely used in both industry and academia for the characterization of materials and for process optimization, for metals and coated metals, of course, but also for photovoltaic materials, LEDs, hard disks, aluminum packaging and lithium-ion battery materials.
It is also widely used as a complementary technique of X-ray Photoelectron Spectroscopy (XPS) or Scanning Electron Microscopy (SEM).



Bibliography

[1] T. Nelis & R. Payling, Practical Guide to Glow Discharge Optical Emission Spectroscopy, RSC 2003
[2] P. Belenguer, M. Ganciu, P. Guillot and T. Nelis, Spectrochimica Acta Part B 2009, 64, 623-641
[3] US Patent 8,581,180 - Method and device for measuring glow discharge spectrometry in pulsed mode
[4] US Patent 10,361,075 – Process and apparatus for measuring an organic solid sample by glow discharge spectrometry
[5] US Patent 10,073,038 B2 - Glow discharge spectroscopy method and system for measuring in situ the etch depth of a sample
[6] S. Gaiaschi, S. Richard, P. Chapon and O. Acher, J. Anal. At. Spectrom. 2017, 32, 1798-1804