

Depth Profile Analysis of Organic Coatings: A Novel Approach Using Glow Discharge Optical Emission Spectroscopy

Application Note

Coating GD42



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Abstract: In this application note, we present a novel methodology for depth profiling of organic layers using **GD-OES**. By introducing oxygen (O_2) into argon (Ar) plasma, a patented technique developed by HORIBA France SAS, sputtering efficiency has been significantly enhanced, particularly for carbon-containing materials. This enables uniform and stable erosion, providing clear distinction between layers in complex coatings. This method offers improved analytical capabilities for multilayer analysis containing both organic and inorganic layers for industries including automotive, aerospace, electronics, and photovoltaics.

Keywords: Glow Discharge Optical Emission Spectrometry (GD-OES), Organic coatings, Depth profile, Multilayer analysis, Automotive coatings

Introduction

Modern automotive coatings consist of complex, multi-layer structures, combining both inorganic layers (e.g., zinc phosphate or chromate coatings) and organic materials (e.g., primers, pigments, and varnishes) as illustrated in Figure 1. These layers serve protective and aesthetic purposes; however, they also present analytical challenges.

For inorganic layers, GD-OES is a well-established analytical methodology that enables rapid erosion with high depth resolution.

However, analyzing carbon based or organic layers is generally more challenging. RF (Radio Frequency) operation is of course required, possibly pulsed, but in all cases the operation using pure Ar plasma gas leads to slow erosion (hence lower sensitivity) and is often accompanied by issues such as non-uniform sputtering, poor resolution at the interfaces and possibly thermal degradation of the organic layers.

In this application note, we propose an innovative methodology to measure such materials that involves introducing O_2 into the Ar gas. This gas mixture promotes

chemical reactions in the plasma between O_2 and carbon (C) of the material, enabling ultra-fast and very uniform erosion. This methodology, patented by HORIBA France SAS [1], offers an effective solution for analyzing samples containing both organic and inorganic layers.

Application

This measurement solution is applicable to any material containing carbon-based layers (such as DLC) or organic layers, as in automotive, aerospace, encapsulated electronics or perovskite solar cells. It enables more comprehensive quality control, defect analysis, and product development – particularly for applications where coating integrity and layer interfaces are critical.

Depth profile of organic layers

We applied this method to probe specimen test samples provided by Renault Group, a leading global automotive manufacturer. These samples consist of various inorganic and organic multilayer coatings on metallic substrates. An example is presented here.

[1] Patent EP-2434275-A1. HORIBA Jobin Yvon SAS (2012). Method of Measuring a Solid Organic or Polymer Sample by Luminescent Discharge Spectrometry.

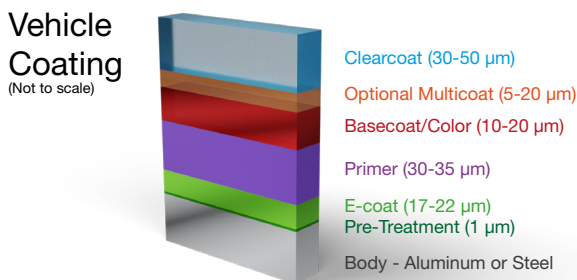


Figure 1. Schematic illustration of a coating for automotive applications

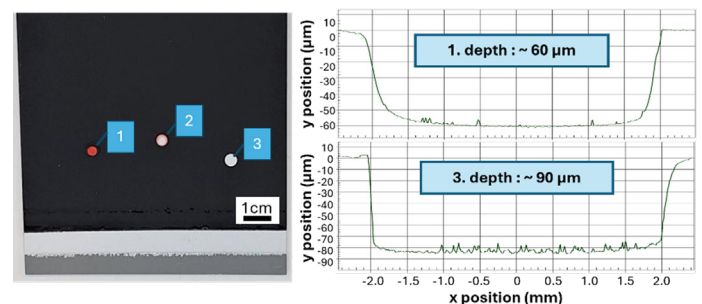


Figure 2. (left) Image of the test sample provided by Renault Group; (right) crater profile corresponding to different depths.

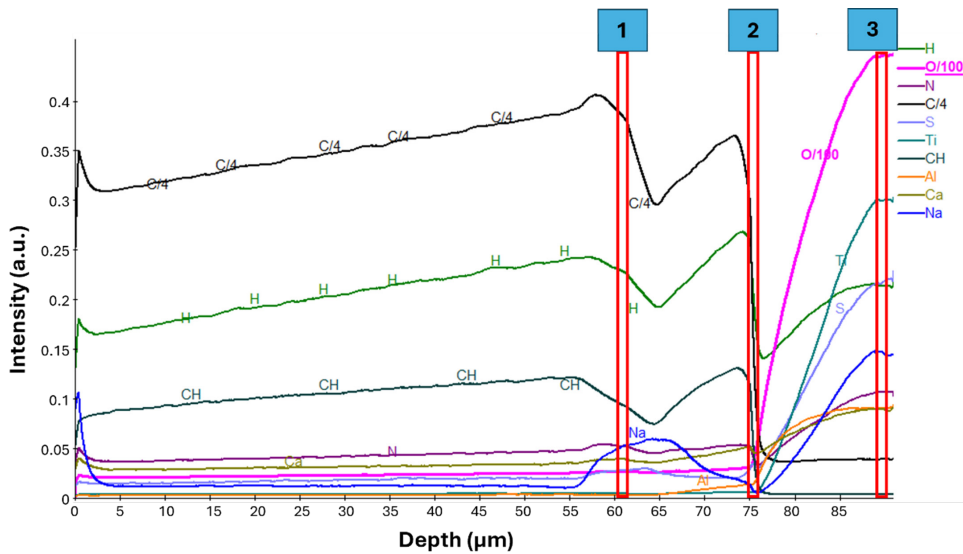


Figure 3. GD-OES qualitative depth profile over time, showing different trends in each layer.

The measurement was performed using pulsed RF plasma at 800 Pa, 30 W with a pulse frequency of 3000 Hz and a duty cycle of 0.25.

With the Ar + O₂ plasma, erosion is stable and uniform, enabling controlled access to an intermediate organic layer of red color in one crater in Figure 2 (upper right) at around 50 60 µm or to the white primer layer at approximately 80 µm. Layer transitions illustrated in Figure 3 can be identified by:

- Steady changes in the C, H signals or the CH molecular band emission,
- An increase in titanium (Ti) signal after between 500 seconds, indicating the transition to the titanium dioxide (TiO₂) containing primer,
- A sharp increase in the O₂ signal, marking the end of the reactive layers (in which O₂ specifically reacts with C).

Additionally, depth measurements of the resulting craters, performed via profilometry, showed flat bottoms with no significant redeposition near the edges. This indicates that further in-depth investigation can be carried out reliably. (This will be the topic of an upcoming application note).

Summary

The integration of O₂ into the GD-OES plasma offers a consistent and reproducible solution for depth profiling of organic coatings.

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This methodology enables:

- Accurate investigation of intermediate and buried layers
- Characterization of multi-material stacks, including polymers and inorganics
- Application to paints, protective coatings, adhesives, and photovoltaic materials
- Deep depths profiles (record obtained was 850 µm), depending on the material and application requirements

Acknowledgement

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Figure 4. GD Profiler 2: 4th generation of GD-OES

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