Glow Discharge - A Modern Concept for Coatings Analysis

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Glow discharge – a modern concept for coatings analysis

Glow discharge-optical emission spectroscopy (GD-OES) is a fast, easy-to-use analytical procedure, which can produce detailed information on both conductive and non-conductive coatings quicker than wet chemical methods, and at a lower cost than other surface analysis. Bulk analysis can be performed in less than one minute and there is the added capability of direct depth profiling of the solid sample without the need for any prior preparation. Analytical data of this type is clearly of benefit in the control of the coating process and in the investigation and rectification of surface defects.

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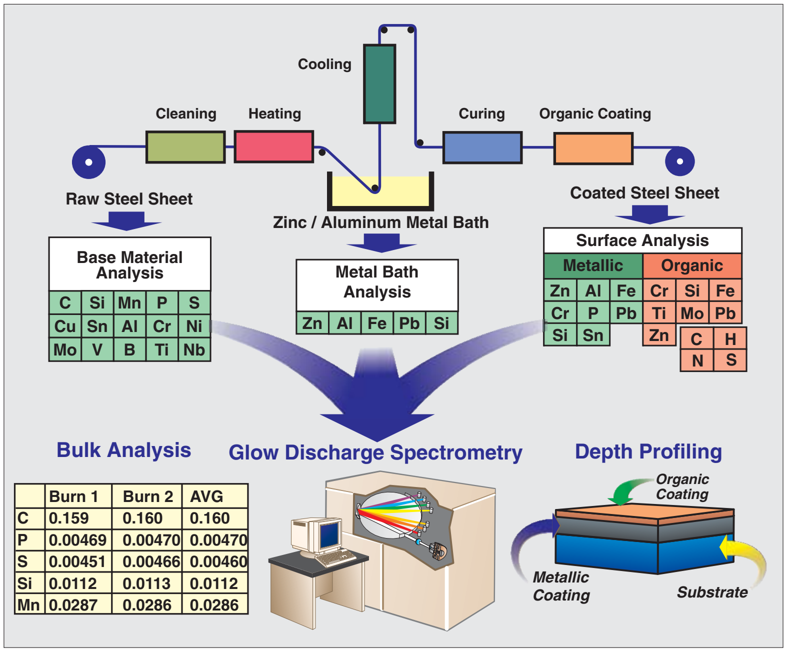


● **Figure 1** ***Schematic of a galvanizing line and analytical controls***

An uninterrupted quantitative depth profile analysis by GD-OES takes only minutes and provides a complete detailed sample-composition map at depths ranging from less than 10 nanometres to more than 100 micrometres. Depth resolution can be as good as several nanometres, depending on sample surface roughness. The detection limit of this technique is about 1–10 ppm depending on the elements determined and the material, and the capability to detect oxygen and hydrogen is particularly useful for surface treatment and corrosion investigations. A quantitative depth profile analysis delivers valuable information including:

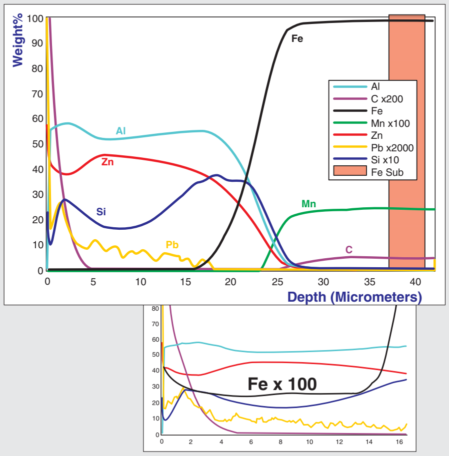
- Composition, concentration, coating weight, thickness and homogeneity of coatings
- Diffusion at interfaces and contamination at the surface and interface
- Substrate composition

This robust analytical technique can also be used for the quality checking of incoming materials and finished products, the control of industrial processes and R&D investigations.

The glow discharge process

Glow discharge utilizes a low-pressure, non-thermal process in which material is uniformly sputtered from the sample surface by a stream of argon ions. The sputtered material is then atomized and excited in a low-pressure plasma discharge, away from the sample surface. The cathodic sputtering of the sample surface removes material layer by layer, without any changes in sample chemistry caused by melting, selective volatilization, oxidation or re-solidification. The light emitted from this excitation is analysed using an optical emission spectrometer and the composition and intensity of the light allows quantification of the elemental components.

Excitation of the atoms occurs in the glow discharge plasma discretely away from the sample surface, thus reducing the metallurgical and chemical history inherent in all samples. Calibration curves are essentially linear and permit a good estimation of concentrations by extrapolation beyond the calibration range.



Coating Composition for Majors ...

Depth (µm)	Zn (%)	Al (%)	Si (%)
1.00	39.9	56.3	1.92
4.00	42.2	54.3	2.27
7.00	46.6	50.7	1.61
10.00	44.6	52.6	1.72
13.00	42.8	53.6	2.40
16.00	38.4	56.3	3.37
18.00	35.7	54.9	3.67

... Minors and Traces

Depth (µm)	Fe (%)	Pb (ppm)
1.00	0.310	110
4.00	0.240	39
7.00	0.231	35
10.00	0.251	27
13.00	0.259	52
16.00	1.02	19
18.00	4.98	12

Thickness of Coating

Sample	Thickness (µm)
Galvalume	20.7

Substrate Composition (%)

Fe Sub	Mn Sub	C Sub
98.9	0.24	0.023

Coating Weight

Sample	Zn g/m²	Al g/m²	Si g/m²
Galvalume	36.6	48.5	2.74

● Figure 2 ***Quantitative depth profile analysis of a Galvalume sample***

This process characteristic makes glow discharge an ideal source for very precise bulk content analysis and an ideal analytical tool for depth concentration profile analysis. The design of the excitation source results in very little sample-to-sample carryover, allowing for quick matrix changes.

Control of a galvanizing line

Figure 1 shows a typical galvanizing line commencing with the raw steel coil. The different steps in obtaining a galvanized steel sheet are cleaning, heating, coating in the zinc bath, cooling and curing. Additionally, on some galvanizing lines, an organic coating is applied at the end of the process. Typically, in European plants, control measurements are made on the steel sheet before and after coating, and on the metal coating bath, using perhaps three or four different methods of analysis. The steel sheet is usually analysed using a conventional spark optical emission spectrometer (OES). The metal bath, where the control of impurities is extremely important, is analysed by atomic absorption spectrometry (AAS) or inductively coupled plasma (ICP-OES) and the finished product is analysed using X-ray fluorescence. The use of ICP-OES or AAS for the bulk analysis of the raw material or the metal bath, as well as for the analysis of the metallic zinc layer, is time-consuming and requires care because of the preparation of the samples by dissolution in acid.

In some European galvanizing lines, GD-OES has replaced all the above techniques. The GD-OES instrument, located near the galvanizing line is suitable for the precise and accurate bulk analysis of the raw steel as well as the metal bath, which usually has a very high concentration of aluminum and zinc.

To assist in control of the finished product, GD-OES can perform a depth profile analysis, which gives the composition of the different layers and substrate. The depth profile is a direct analysis of the solid sample without any sample preparation, as the time-consuming stripping process of the metal coating is no longer necessary. Additionally, light elements such as carbon, hydrogen, nitrogen and sulphur are determined simultaneously with all other elements.

Depth profiling provides the composition of the coating from the surface of the sheet to the steel substrate revealing any heterogeneity in the coating and migration of elements at the interface. This depth profile analysis also provides information about contamination at the surface, or at the interface, as shown later in this article. By using a radio frequency source, it is also possible to obtain a depth profile of the organic coating, as explained later.

In this article we shall show how GD-OES may be used to analyse Galvalume and paint coatings, and to identify the origins of surface defects in a hot-dipped galvanized product.

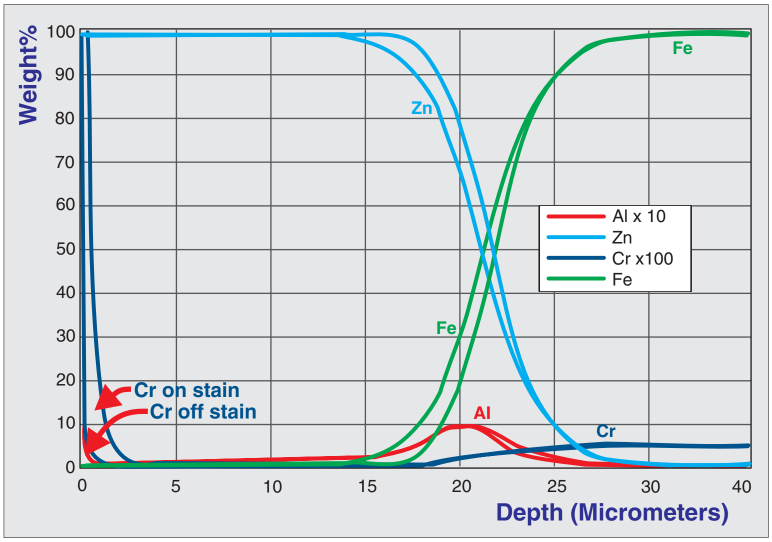
Analysis of Galvalume

The analytical data that can be provided by GD-OES may be illustrated by the depth profile of a Galvalume coating (50% Zn, 50% Al) shown in Figure 2.

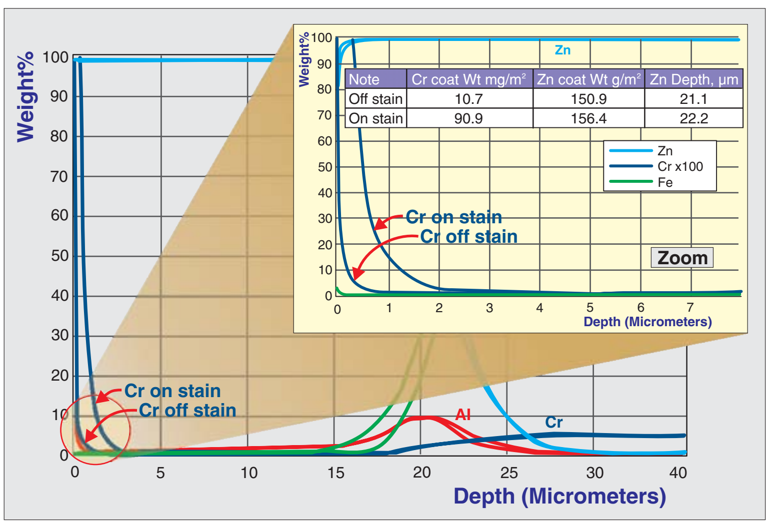
Only a few minutes are necessary to acquire the data and obtain the quantitative depth profile. From this it is possible to monitor each element from the surface through to the substrate. In this case, it is interesting to note that there is an increase in the silicon concentration at a point just above the zinc/ steel interface. This increase characterizes the silicon needle (where the size of the silicon grains is increasing) formed at the interface during cooling. An increase in aluminium content can be observed at the surface of the sheet due to the preferential oxidation of this element.

As soon as the depth profile analysis is completed, the following analytical information is available:

- Detection of major elements (Zn, Al, Si), minor elements (Fe) and trace elements (Pb)
- Calculation of coating weight (g/m2)
- Calculation of coating thickness (µm)
- Chemical composition of substrate and coating (weight % or atomic %)



● **Figure 3a** ***Depth profile analysis of stained and unstained hot-dipped galvanized sheets***



● **Figure 3b Detailed profile analysis near the surface of stained and unstained sheets**

- Detection of minor or trace elements in one layer and of major elements in another layer or substrate

This is exemplified in Figure 2 where the iron content of the coating is 0.3% compared with nearly 100% in the substrate, thus illustrating the wide dynamic range of measurement of this technique.

Analytical data of this type are also of value in controlling electrogalvanizing and hot-dip galvanizing, as well as processes involving the use of zinc alloys.

The origin of defects

In the steel industry, it is common to see defects appearing in the production line. These defects can be colour changes and stains or pinholes and blisters on the surface. They result from some deviation in the process, and, of course, they damage the quality of the products. Considerable resources may be needed to find the origin of the problem and solve it quickly.

GD-OES can often present a quick and easy method of identifying the origin of defects as illustrated in the following example.

On a hot-dip galvanizing line, some brown staining was observed on the finished chromated, galvanized product. Only a few minutes were needed to profile an unstained and a stained sample (see Figure 3a). Since this galvanized steel had been chromated, attention was focused on Cr and Zn coating weights and Zn thickness.

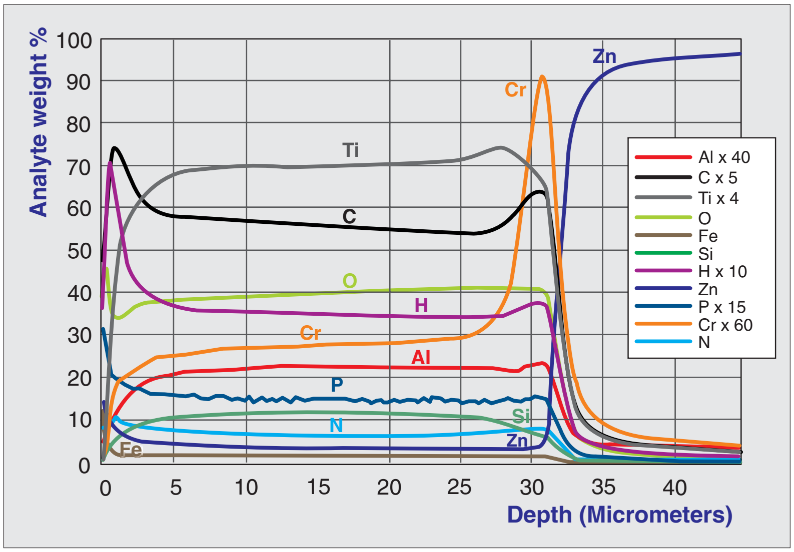
Figure 3b shows the first 8 μm of the depth profiles. From this data, it was possible to observe that while the Zn thickness and coating weight were not modified in the stained area, the Cr coating weight was much higher and present only at the surface and without any damage to the Zn coating or the Zn/steel interface. Following investigations, the problem was identified as Cr contamination from a leak in the chromate supply pipe feeding the chromate bath.

This example provided a convincing demonstration of the benefits of GD-OES and the ability to identify and rectify operational problems quickly.

Other important parameters such as the total and surface weights of aluminium coatings may also be calculated for hot-dip galvanizing. These are available in minutes from the depth profile analysis. The presence of aluminum at the surface of the galvanized sheet has a very important influence on the subsequent adherence of the epoxy layer. These two parameters are usually measured by time- consuming chemical methods.

Analysis of painted sheet

As previously mentioned galvanized steel sheets are quite often coated with organic coatings such as primer, sealer, paint, varnish and anti-finger print compound. When equipped with a radio frequency (RF) powered source, the technique is known as RF



● Figure 4 **Quantitative depth profile analysis of a yellow paint coating on galvanized sheet**

glow discharge, optical emission spectroscopy (RF GD-OES), and can perform the depth profile analysis of these non-conductive organic coatings. With this technique it is important to control several excitation parameters such as incident power, reflective power, DC bias, current, voltage, phase and load. The behaviour of these parameters in the excitation process is very complex and varies from one type of coating material to another. The ability to control the RF power incident on the plasma, called True Plasma PowerTM (TPP), is the result of a long investigation into these plasma parameters and opens up an opportunity for accurate quantitative depth profile analysis of non-conductive materials.

This new tool for investigations of organic coatings reveals, more accurately, the composition and coating weight, and the quantitative depth profile analysis can also explain the origin of some defects found on paint such as stains, corrosion or change in colour. This is also valuable in the study of the behaviour of paints when exposed to ultraviolet radiation.

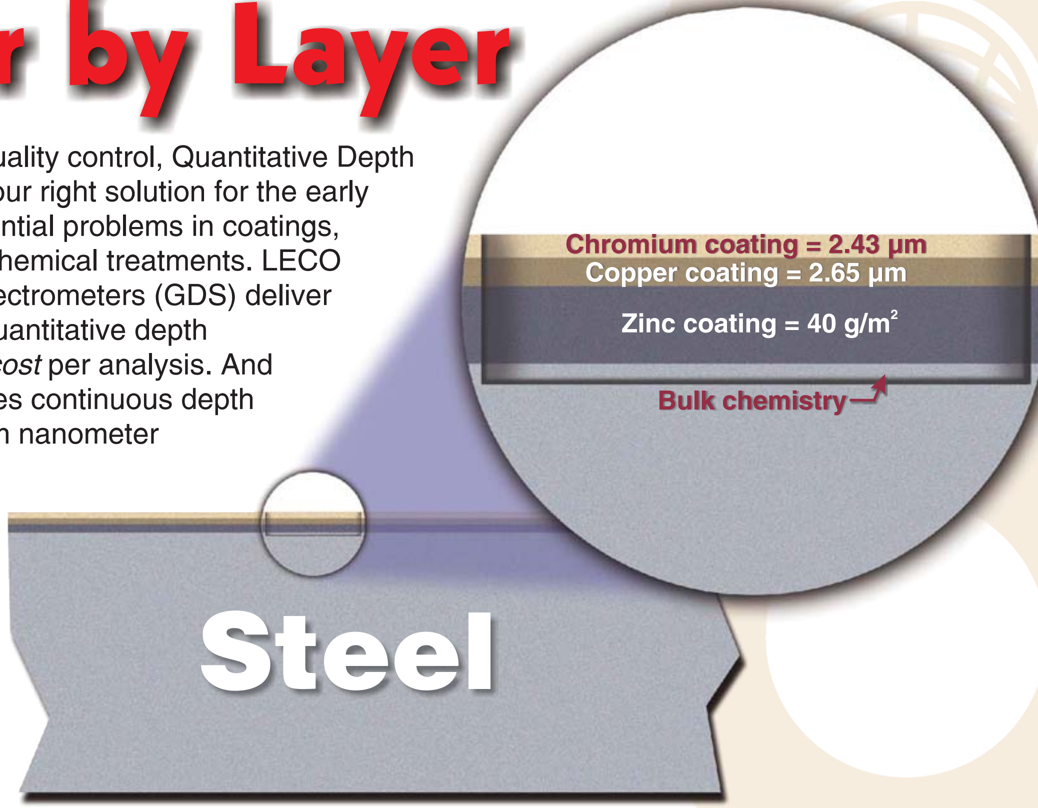
Figure 4 is an example of a yellow paint coating on a galvanized steel sheet. This figure has been cropped at the zinc layer to emphasise the paint coating and the interface. The high chromium content at the interface between the paint and the zinc coating is known to improve the adherence of the paint to the galvanized sheet.

Conclusions

The applications described in this article are focused on the steel industry and, more specifically, on galvanizing. Other definitive applications dealing with coatings in other industries demonstrate how GD-OES can be used to identify problems associated with thermo-chemical treatments, annealing, physical vapour deposition, chemical vapour deposition, cladding, ion implanta-tion, plating and electroplating processes. Recent developments allow the investigation of very thin layers at the nanometre scale and this new capability opens up applications, which until now were only available through the use of other surface analysis techniques such as ESCA (electron spectroscopy for chemical analysis), XPS (X-ray photoelectron spectroscopy), AES (Auger electron spectroscopy) or SIMS (secondary ion mass spectroscopy). Investigations using these techniques are time-consuming and expensive, and require highly skilled operators. GD-OES is complementary to other surface analysis techniques. Therefore for laboratories that are already equipped with surface analysis techniques, GD-OES can be an efficient tool in primary and rapid investigations of coatings more than 0.1 μm thick. The ability to obtain a continuous profile and the capability of detecting oxygen and hydrogen, are also advantageous. For laboratories not yet equipped with surface analysis equipment, GD-OES is an excellent technique to start surface analysis investigations with minimum investment in terms of capital, running costs and operator training.

Quality Control...® Layer by Layer

When it comes to quality control, Quantitative Depth Profiling (QDP) is your right solution for the early identification of potential problems in coatings, layers, and thermochemical treatments. LECO Glow Discharge Spectrometers (GDS) deliver *high performance* quantitative depth profiling at a *lower cost* per analysis. And it's fast! GDS ensures continuous depth profile analysis (from nanometer to more than one hundred micrometers), to provide you with the complete chemical composition (ppm to 100%) from the surface to the substrate, in a matter of minutes. Find out today how LECO can provide the right solutions to all of your quality control needs.



QDP Quickly Identifies:

- Contamination and cleanliness at the surface and interfaces
- Migration and diffusion at interfaces
- Heterogeneity of coating/substrate
- Oxidation/corrosion
- Chemical composition
- Layer thickness/coating weight

QDP Applications

- Galvanizing (Electro Galvanizing, Hot Dip, Galvalume, Galvanneal, Galfan, Zinc Nickel, etc.)
- Plating (Sn, Cr, Cd, Ni, Cu, etc.)
- Thermochemical Treatments (Carburizing, Nitriding, Carbonitriding, etc.)
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