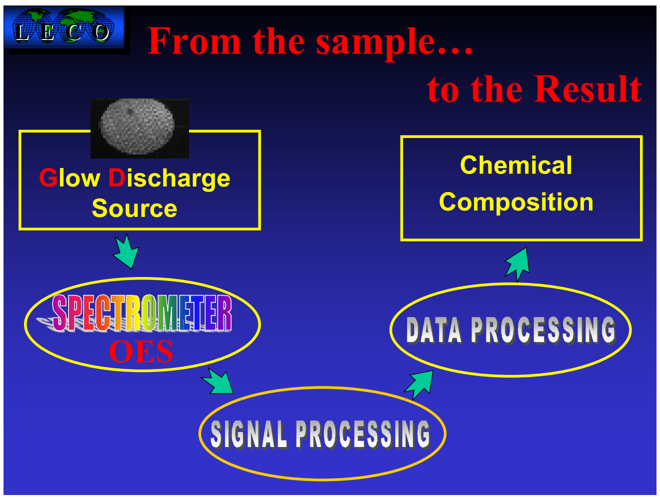
LECO® Glow Discharge Optical Emission Spectrometry (GD-OES): An Alternative Technique for Depth Profiling.

Investigation of Surface Properties from the Nanometer to the Micrometer Scale

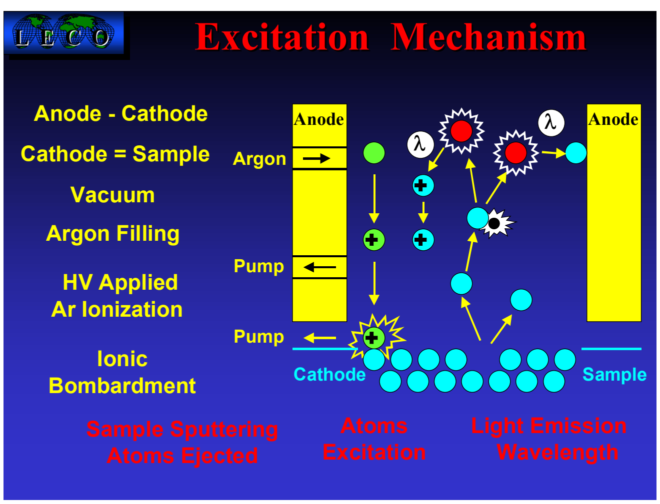
Glow Discharge Spectroscopy (GDS) is a direct analysis technique used to measure the elemental concentrations of solid materials. Glow Discharge offers an improved excitation source for fast, economical, and reliable sample turnaround (in as little as one minute) with excellent accuracy and precision. The source uniformly removes material from the sample surface, which reduces the effects of metallurgical and chemical history inherent in all samples. The large dynamic range allows the determination of major, minor, and trace elements.



Theory of the GD-OES Technique

First, the light emitted from the excitation of the sample by the Glow Discharge Source is analyzed in the spectrometer. Secondly, the signal and data are processed. Finally, the concentration of each element in the sample is obtained.

The figure to the left shows the different steps in a Glow Discharge Spectrometer.

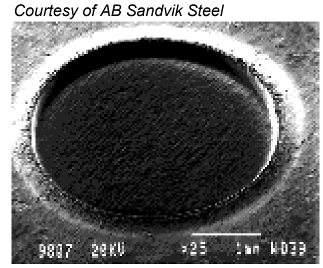


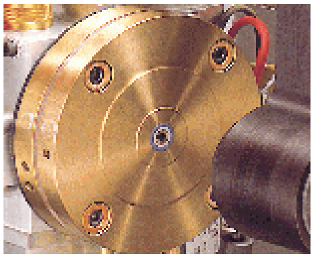
The figure above shows the different components in the Glow Discharge Source and the excitation mechanism.

- A vacuum is created in the chamber and then filled with Argon (Ar).
- By applying a controlled voltage (V) and current (I), the Ar is ionized and accelerated to create an ionic bombardment. This bombardment causes the ejection of the atoms from the sample (sputtering).
- The ejected atoms collide with electrons (or ions) creating mechanical energy which excites the atoms.
- When the excited atoms return to ground state, they emit their respective light (wavelength), which is known as the Optical Emission. This light is then analyzed in a spectrometer.

The result of the ionic bombardment is a sputter spot, as shown in the example to the right. When using a 4 mm diameter anode, this crater has a 4 mm diameter. For a smaller spot, a 2 mm diameter anode can also be used. A crater with a very flat bottom and vertical wall is needed for good in-depth resolution. This is accomplished by an optimization of the excitation parameters (V, I, Ar Pressure).

Courtesy of AB Sandvik Steel





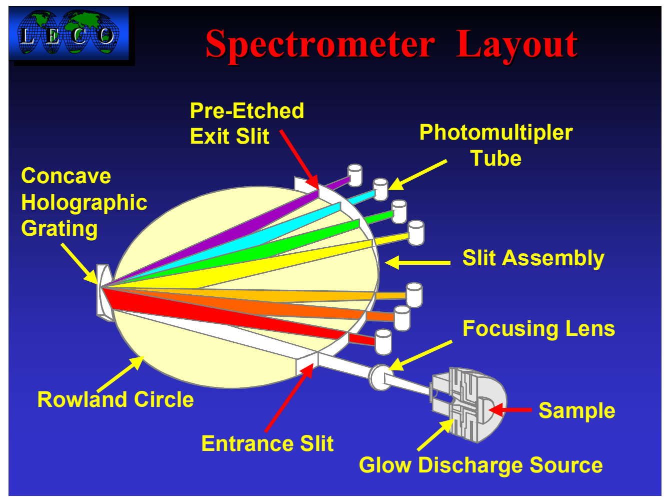
The picture to the left is of the Grimm-Type Glow Discharge Source.

With GD-OES technology, sample material is uniformly sputtered from the surface. The non-thermal nature of the sampling process makes this an excellent technique for difficult applications, such as low melting point materials. Reduced line interference by Glow Discharge results in simple, linear calibration curves. An automated and efficient cleaning of the anode between each analysis minimizes the memory effects allowing quick matrix change. Each wavelength emitted in the Glow Discharge source is characteristic of the element from which it came. All the wavelengths, emitted by all the atoms of the sample, will give "white" light also named polychromatic light. This polychromatic light will then arrive in the spectrometer. A holographic grating (the main component of the spectrometer) will separate each wavelength, corresponding to one specific element, and will send this "monochromatic" light through an exit slit to be collected by a photomultiplier. Each photomultiplier is dedicated to one specific element. The detector then delivers an electronic signal proportional to the quantity of light received.

Components of the Spectrometer

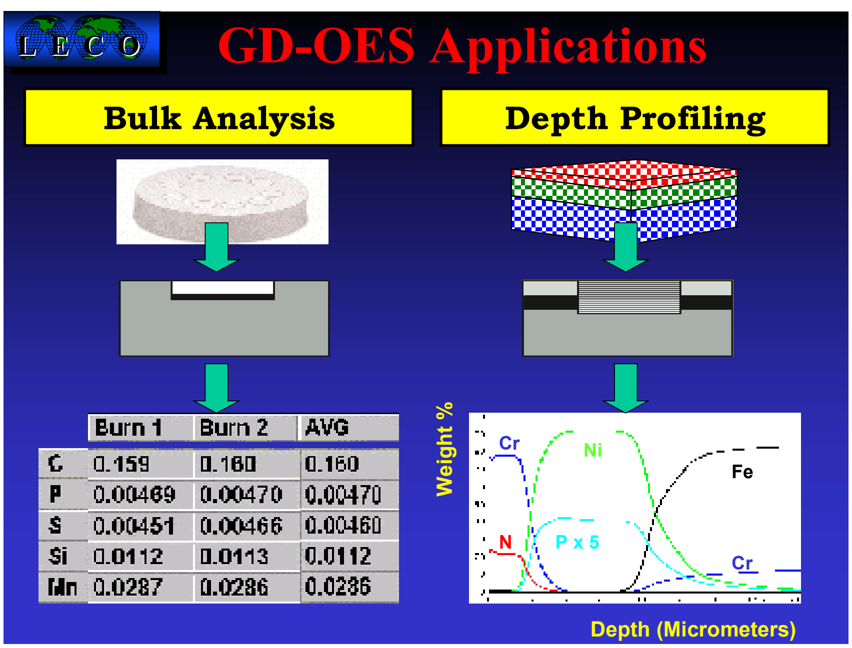
This spectrometer is simultaneous; meaning all available elements can be detected simultaneously. In this configuration, the three main optical components: the entrance slit, the grating, and the exit slits are located on a circle named the "Rowland Circle." Photomultipliers mounted on a mask behind the exit slits collect the light emitted for each element. For determining the elemental composition of unknown samples, the instrument is calibrated using Certified Reference Materials.

The figure to the right shows the layout of the spectrometer, known as a Paschen Runge mount.



GD-OES Applications

The purpose of this paper is to demonstrate the benefits of Depth Profile Analysis on specific applications. Although Depth Profile Analysis uses the same instrument and glow discharge source used for Bulk Analysis, it differs greatly in its philosophy of measurement**.**



Bulk analysis can provide the elemental composition of the sample in less than one minute.

Depth Profile analysis will sputter the sample from the surface and will pass continuously through all the layers until it reaches the substrate, giving the composition of each layer. The result will be a diagram showing the concentration of each element versus the depth.

As shown in the example on the left, the Glow Discharge technique can be used in two different ways: Bulk Analysis and Depth Profile Analysis (sometimes referred to as Quantitative Depth Profile Analysis or QDP).

Benefits of Depth Profile Analysis by GD-OES

Depth Profile Analysis is an ideal method for early identification of potential problems with materials, including coatings, layers, and thermochemical treatments. Depth Profile Analysis quickly identifies contamination and cleanliness at the surface and interfaces, migration and diffusion at interfaces, heterogeneity of coatings and substrates, adherence issues, problems of oxidation/ corrosion, inclusions/blisters, and characterization of coatings (thickness, composition and coating weight).

Typical depth profile analysis applications are:

- Galvanization (EG, Hot Dip, Galvalume, Galvanneal, Galfan, ZnNi, etc.)
- Plating (Ni, Sn, Cr, Cu, etc.)
- Thermochemical treatments (Carburizing, Nitriding, Carbonitriding)
- Hard coating (TiN, CrN, TiCN, etc.) made by PVD, CVD
- Clad material (Aluminum)
- Organic coatings, Glass, Ceramic

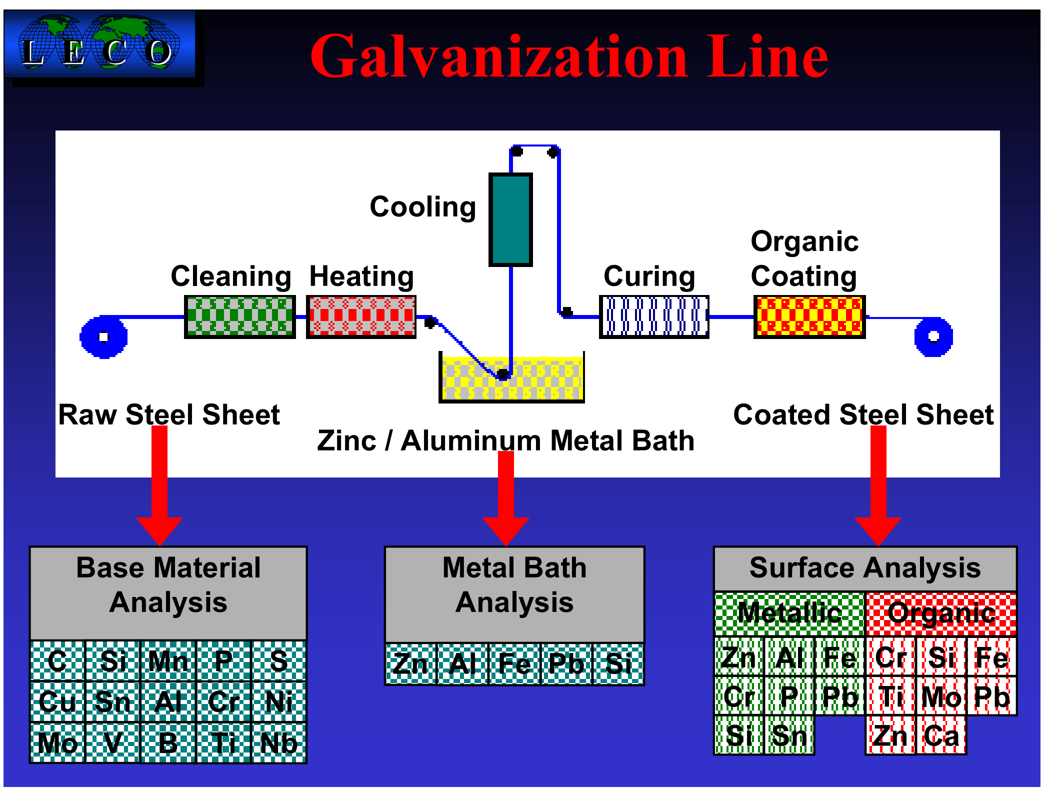
GD-OES can perform a depth profile analysis continuously from some tens of nanometers to more than one hundred micrometers. Combined with a fast sputtering rate (0.5 to 30 µm/min.), GD-OES can provide the complete chemical composition (ppm–100%) from the surface to the substrate in only a few minutes.

Depth Profile Analysis Applications

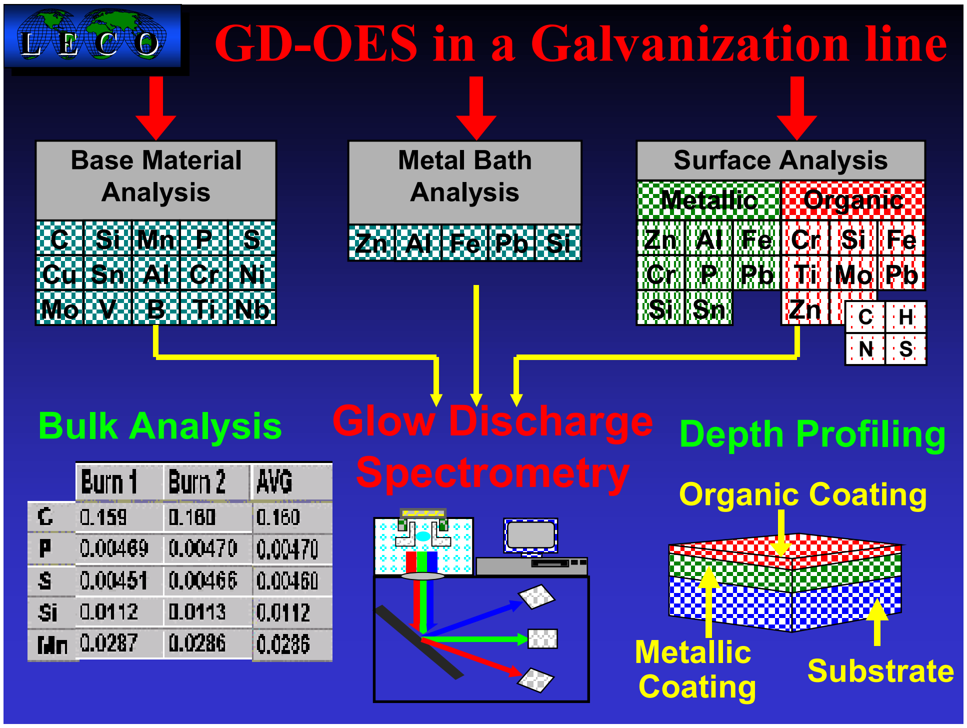
Specific, real applications encountered in the industrial field are described below. These examples demonstrate how the GD-OES technique has been useful for R&D investigations and process control—routine analysis to solve a process problem or explain the origin of an unexpected phenomenon on coatings.

GD-OES Role in a Galvanization Line

Presently, controls are made on the raw steel with a Spark Emission Spectrometer, on the coated product with an XRF, and a control of the metal bath is made with Atomic Absorption or ICP. The control of the raw material and the metal bath consists of a bulk analysis. The control of the finished product takes more time because of the chemical stripping of the coating with acid.



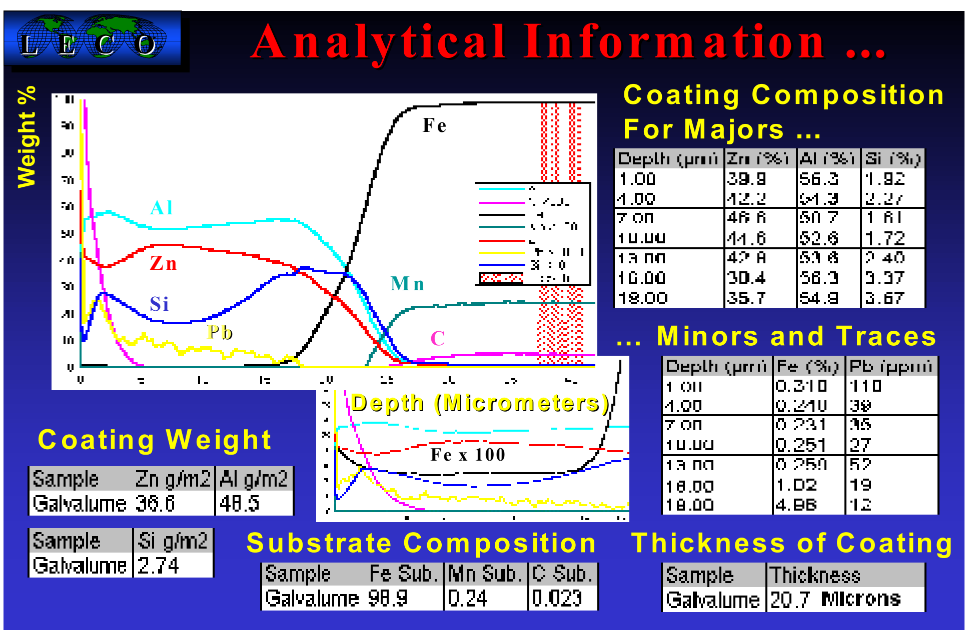
Schematic of a classic galvanization line with an organic coating at the end of the process.



The figure to the left shows where the Glow Discharge technique can be used in a Galvanization line.

GD-OES can perform precisely and accurately the bulk analysis of the raw steel, as well as the metal bath which usually consists of a very high concentration of Aluminum (Al) and Zinc (Zn). Due to the linearity of the calibration curve and its large dynamic range, GD-OES easily analyzes the metal bath. You can determine the composition of the coatings on the finished product directly without any preparation of the sample (the time consuming stripping process usually used is not necessary). Additionally, elements such as Carbon (C), Hydrogen (H), Nitrogen (N), and Sulfur (S) will be analyzed simultaneously with all other elements. Depth profile analysis will provide the continuous coating composition from the surface to the steel substrate, revealing any heterogeneity in the coatings and migration at the interface. These profiles will also inform about contamination at the surface, or at the interface, as we will see later in this document. Equipped with an RF source, the depth profile of the organic coating can also be obtained.

Analytical Information – Galvalume Application



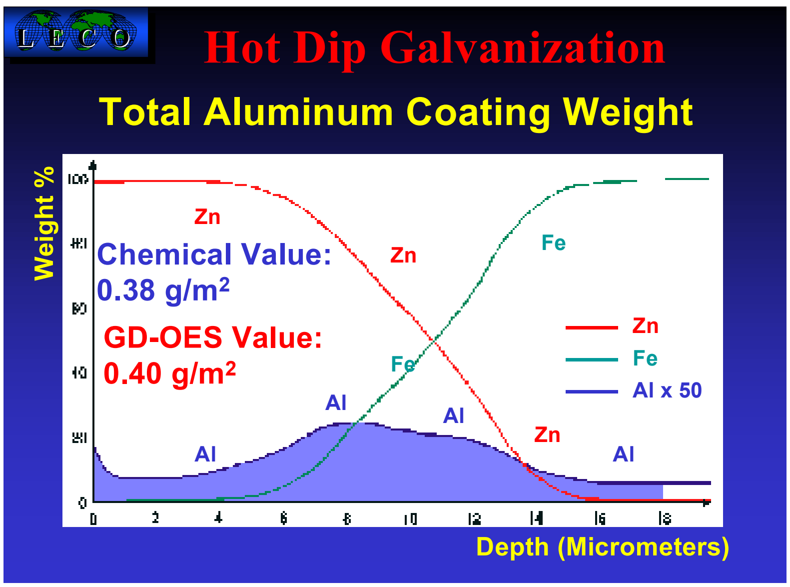
The figure at the left shows the depth profile analysis of a Galvalume sample (Zn 50%, Al 50%). The picture in the center of the figure is a zoom of the original profile, with a x100 scaler for the Fe.

It is interesting to notice the behavior of the Aluminum (Al) at the surface as well as the Silicon (Si) just before the interface. This application will illustrate all the analytical information which can be provided by GD-OES:

- Detection of Majors (Zn, Al, Si), Minors (Fe), and Traces (Pb ppm level)
- Calculation of coating weight
- Calculation of coating thickness
- Chemical composition of substrate and coatings
- Detection of an element present as minor or trace in a coating and present as a major element in another layer. See the Iron (Fe) in this example: Fe content in the coating is 0.3% - Fe content in Steel is near 100%. Both Fe in Zn and Fe in steel can be seen on the same depth profile analysis. This is possible due to the large dynamic range of the GD-OES technique and the associated electronics. Two or three minutes are necessary to get the complete depth profile analysis (depending on the thickness of the coating). As soon as the profiles are acquired, all the analytical information described above is available.

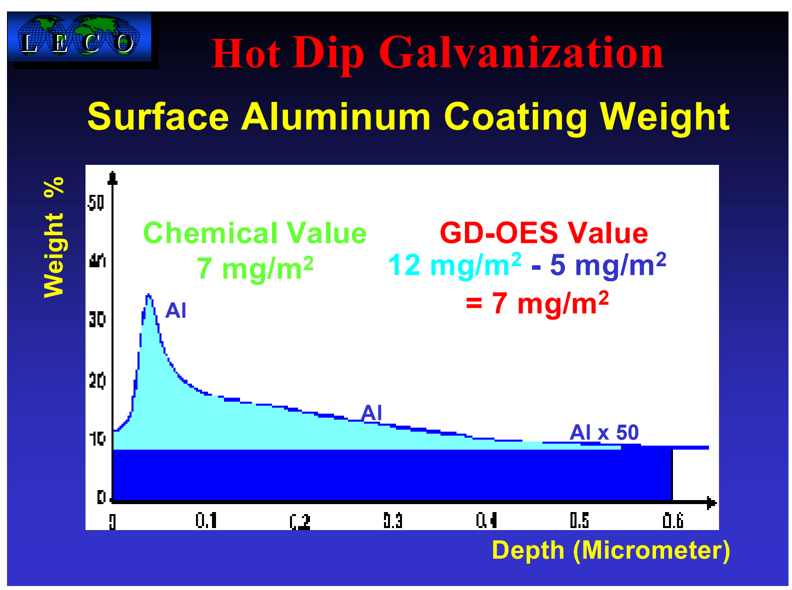
Hot Dip Galvanization

Hot Dip Galvanization is a hot process which involves chemical reactions at the Zinc/Steel interface. The presence of Aluminum (Al) in the Zinc (Zn) is characteristic of the Hot Dip Galvanization. Thickness, coating weight, and the total Al content in the Zn coating are the major tests made to check the quality of this product. These tests are presently made by chemical techniques which are time consuming. As seen in the previous example, thickness and coating weight can be obtained immediately after the acquisition of the profiles.



The top figure shows the typical profiles of a Hot Dip Galvanization, with a large Zn/Fe interface due to the hot process. This figure also explains the total aluminum coating weight calculation. The shaded area (from the surface to the substrate) has been defined for the calculation of the total Aluminum content. The total Aluminum determination, made by chemical method, was 0.38 g/m^2; the result obtained from the depth profile analysis was 0.40 g/m^2. The correlation between the two techniques is excellent (notice the increase in Aluminum at the surface). The bottom figure is a zoom of the above, showing the Aluminum peak at the surface.

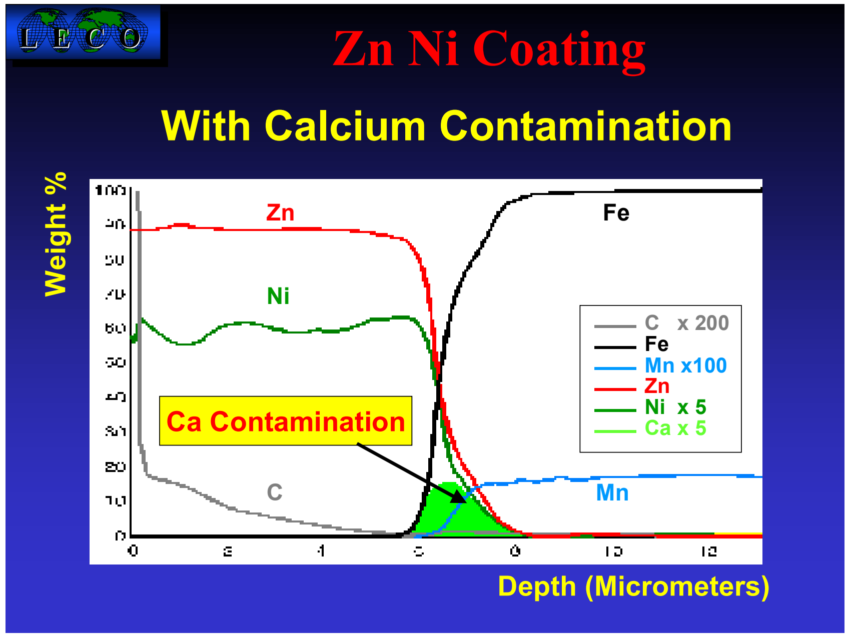
This phenomenon is critical, mainly when an additional coating (Organic) will be applied to the Hot Dip galvanized steel. Some investigations have shown there is a relationship between the amount of Aluminum at the surface of the galvanization and the strength of the epoxy-galvanized steel bond. Therefore, a systematic control of this Aluminum content at the surface becomes necessary before applying any additional coating. This Surface Aluminum content is presently made by time-consuming chemical techniques requiring experienced chemists. GD-OES will also provide the Surface Aluminum content with an excellent correlation, as explained in the bottom figure (A specific application note on Hot Dip Galvanization is available upon request, form number 203-821-071).



Detection and Identification of Contamination at Interface–Zinc Nickel (ZnNi) Coating Application

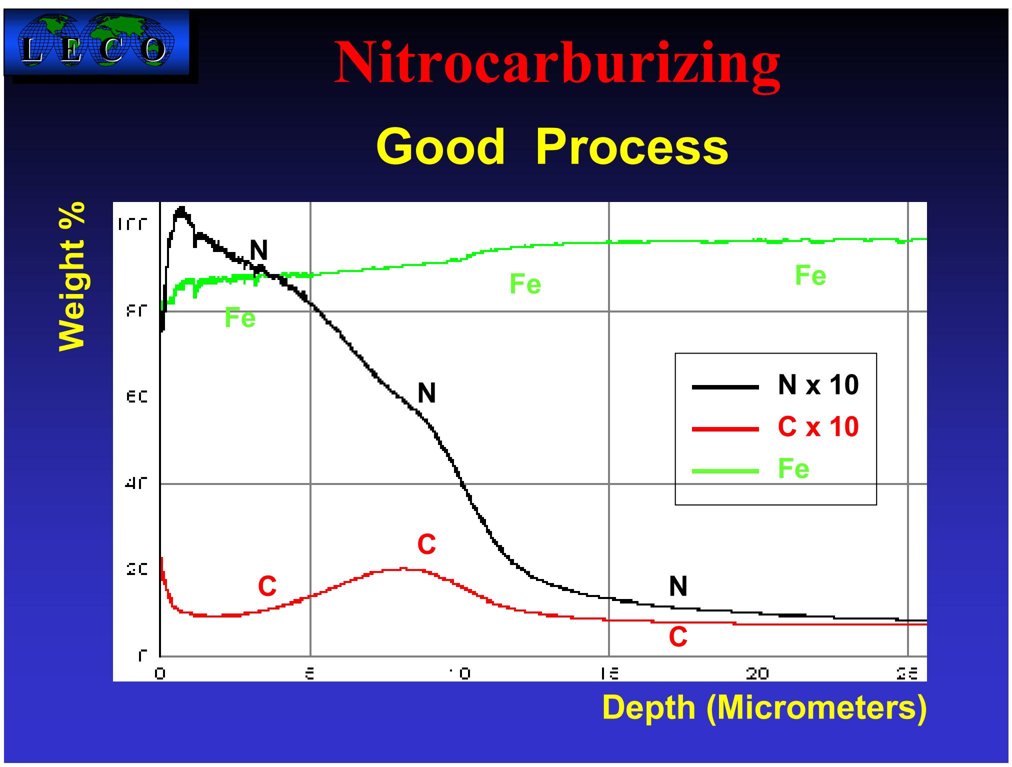
The figure on the right is an example of ZnNi coating on a steel sheet, showing a Calcium contamination at the interface.

The control of this contamination is critical. Its presence can reveal a bad rinsing of the steel sheet during the cleaning process. This contamination, which can be a residue from the cleaning baths, can have a damaging effect on the adherence of the ZnNi Coating on the steel sheet. This type of contamination is usually located at the interface and the concentration level is low. Other types of contamination can be observed at the interface. For example, a peak of Carbon could reveal an oil contamination.



Deviation of a Process–Nitrocarburization Application

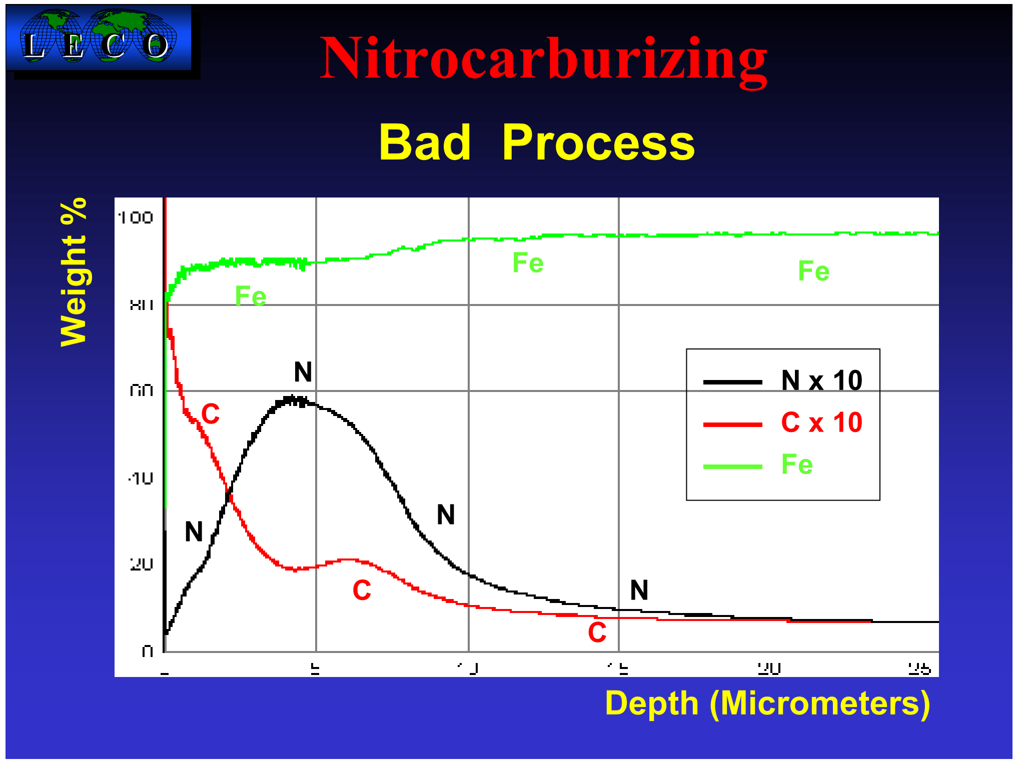
Through this application, we will see that GD-OES is useful for the control of surface treatments and the control of the process. First we can see the Nitrogen enrichment at the surface, then the decrease in Nitrogen until it reaches its nominal value in the steel. Nitrocarburizing processes involve a lot of parameters such as temperature of the oven, gas-blowing, etc. If for any reason some parameters of the process change, these deviations can have a critical influence on the quality of the treatment.



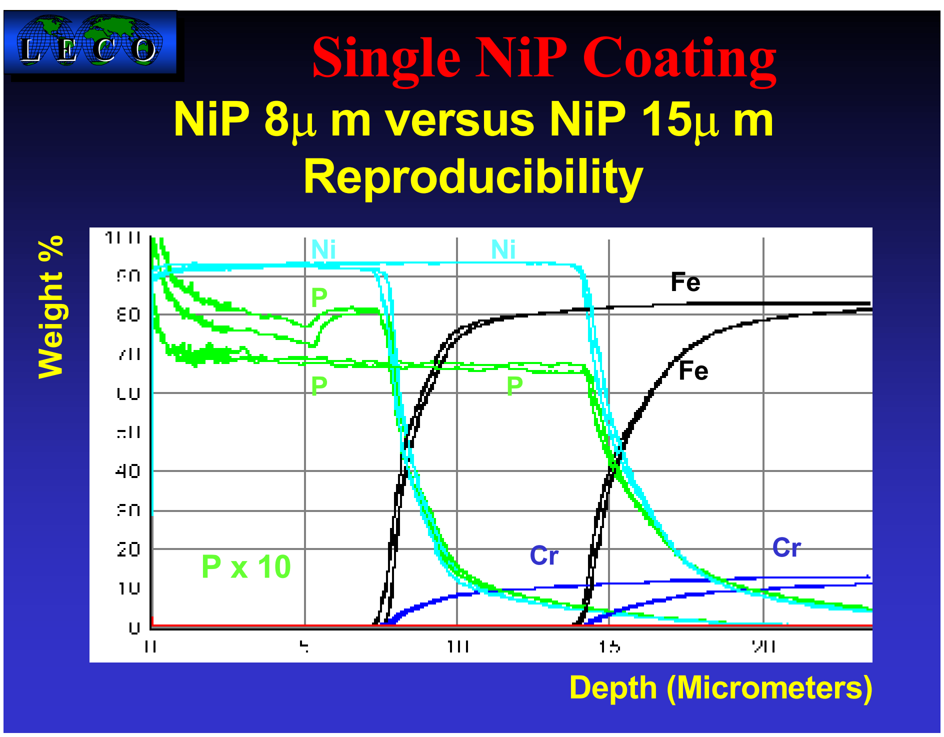
The "Good Process" shows an example of Nitrocarburizing: Nitrogen and Carbon are the two main elements of interest in this type of treatment.

The "Bad Process" shows how the Carbon and Nitrogen profiles can be affected due to some deviation of the process.

The purpose of this document is not to discuss about the origin of these deviations, but to show that the GD-OES technique can identify problems occurring in the process. The "Bad Process" shows a completely different behavior for the Nitrogen and the Carbon that was observed in the "Good Process." We observe a lack of Nitrogen at the surface, which is compensated by an increase in Carbon. Nitrocarburizing treatment gives pieces specific mechanical properties. The change in Carbon and Nitrogen concentration, due to a deviation of the process, will change the mechanical properties of these pieces.



Optimization of a Process – Electroless Nickel-Phosphorus (NiP) Coating
In this example, two different thickness of Electroless Nickel-Phosphorus coating were evaluated. Processes A and B were respectively set to provide an 8 and 15 micron thickness coating.



The figure above shows an overlap of profiles made:

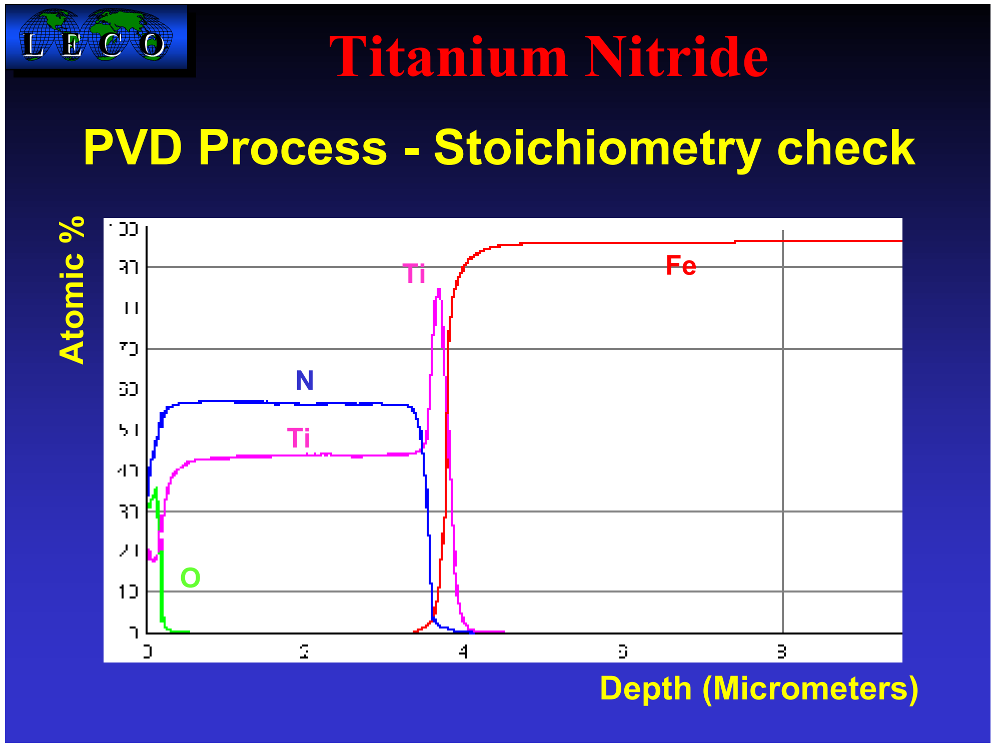
- ***on two pieces treated by process A***
- ***on two pieces treated by process B***

These profiles confirm the expected thickness of the NiP coatings (8 and 15 micrometers). The 15 micron NiP coating shows a perfect reproducibility in terms of thickness and composition. The 8 micron NiP coating shows a perfect reproducibility in terms of thickness and composition for the Ni, but we can note that the phosphorus concentrations are not the same. Additionally, the P profile is not constant and shows a non-homogeneity.

Conclusions: Process B produces a homogeneous coating, while Process A produces a coating with variations of Phosphorus. Process A and B do not produce the same Phosphorus concentrations.

Titanium Nitride (TiN) by PVD Process

The rapid depth profile analysis shown here identifies the Stoichiometry of the coating. Presence of Oxygen can be observed at the surface. The Titanium peak at the interface illustrates the Titanium bombardment made on the substrate to clean it before the TiN coating is applied. GD-OES is able to analyze all the coatings made by PVD or CVD, including non-conductive materials as Al_2O_3. Additionally, thin layers obtained by the pulsed process can also be seen.



The figure on the right shows a Titanium Nitride coating on steel with Atomic % Y-scale.

Conclusions

As a conclusion, we can summarize the benefits of the GD-OES technique:

- Bulk Analysis / Depth Profiling
- Continuous Profile of Concentration
- Large Dynamic Range With Concentrations From ppm to 100% by Weight
- Large Dynamic of Thickness (tens nm to 100 μm)
- High Sputtering Rate (1 to 30 μ/mn)
- Short Analysis Time (some minutes)
- Reasonable Cost Compared With Other Surface Techniques
- Production/Routine Control
- R&D for Investigations
-

And to summarize the analytical information provided as well as all the issues resolved:

- Chemical Composition
- Thickness of Coatings
- Coating Weight
- Homogeneity of Coatings
- Element Migration at Surface and Interface
- Penetration of Surface Treatment
- Surface and Interface Contamination
- Adherence Problems
- Correction of the Process Parameters

Advantages of GDS Over Other Analytical Techniques

- Separation of sputtering and excitation
- Linear calibration curves with wide dynamic range
- Lowered self-absorption and material re-deposition
- Excitation of almost exclusively atom lines
- Fewer and narrower emission lines reduce interferences
- Freedom from metallurgical history
- Fewer standards required for calibration
- Minimal memory effects from a quick matrix changes
- Low Argon (Ar) gas consumption (less than 1 liter per analysis)
- Automatic cleaning between samples

LECO GDS850A

Specifications

Optics:	0.75 meter simultaneous vacuum spectrometer; DC/RF source compatible
Spectral Range:	120 to 800 nm
Resolution:	<0.025 nm over spectral range
Channels:	58 maximum with background and multiscan capabilities
Source:	4 mm DC standard (2, 7 optional); 2 and 4 mm RF optional
Grating:	2400 groove/mm holographic standard (3600 groove/mm and 1800 groove/mm optional)

LECO Corporation
3000 Lakeview Avenue
St. Joseph, MI 49085-2396 U.S.A.
Phone: 800-292-6141 • Fax: 269-982-8977
info@leco.com • www.leco.com

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