Understanding Calibration for Glow Discharge Atomic Emission Spectrometry (GD-AES)

LECO Corporation; Saint Joseph, Michigan USA

Instrument: GDS850A

GD-AES Calibration: General Considerations

Spectrochemical analysis is a comparative technique; therefore, unknown samples are best analyzed against reference materials of similar composition. Certified Reference Materials (CRM) and Reference Materials (RM) are used to establish the relationship between concentration or mass ratio and light intensity or instrument response under precisely controlled lamp parameters.

LECO calibrations employ reference materials that are traceable to or certified by NIST or other internationally recognized Certifying Bodies (ISO Guide 31). Traceability in the hierarchy of certification is defined in ASTM E1724: "The property of a result of a measurement whereby it can be related, with stated uncertainty, to stated references, usually national or international standards, through an unbroken chain of camparisons (ISO Guide 30)".

GD-AES: Lamp Source

LECO Glow Discharge uses a Grimm-style lamp for Atomic Emission Spectrometry. It is a non-thermal, cathodic sputtering device that sputters material from the sample surface; available in 4mm anode diameter with 15 mm o-ring vacuum seal and 2 mm diameter (obtainable in two versions: large lamp, 15 mm o-ring, vacuum seal; and small lamp, 7 mm o-ring, vacuum seal). The sample is externally mounted on the vacuum seal o-ring. Sputtering is initiated when a high negative potential is applied under conditions of a partial pressure that includes a controlled supply of an easily ionized gas (argon). Argon ions impinge on the surface of the specimen removing atoms and small atomic clusters which may be dissociated into individual atoms. When excitation of the atoms or less frequently of ionic species occurs, a photon of light is emitted at a wavelength characteristic of the element from which the excited particle originated.

GD-AES Calibration: Considerations for Bulk Analysis

Choice of calibrants is crucial in forming robust working curves. Sufficient specimens must be chosen to reliably satisfy the entire concentration range for every element to be determined. The calibrants are measured at three locations around the piece, at minimum, to incorporate the uncertainty of the specimen on the working curves.

Figure 1 shows a normalized (concentration ratio) linear working curve from tenths of parts per million to over 16%. Most working curves are linear over a long dynamic range of concentration. Curve linearity allows accurate extrapolation even outside of the limits of the calibration range.

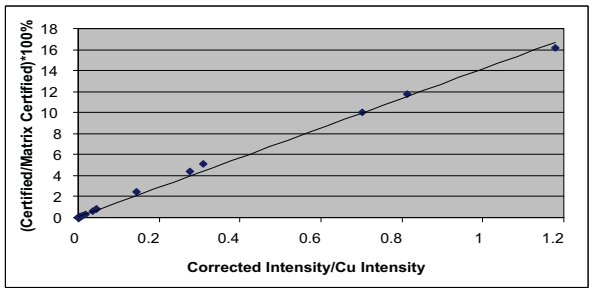

Figure 1. Pb Calibration in Copper (Bulk Calibration)

Instrument response can be accurately measured on array detectors or photomultiplier tubes (PMT).

Applicable ASTM Standards and Practices may include:

- E135 Terminology for Analytical Chemistry for Metals, Ores, and Related Materials
- E158 Fundamental Calculations to Convert Intensities into Concentrations in Optical Emission Spectrochemical Analysis
- E305 Establishing and Controlling Spectrochemical Analytical Curves
- E406 Using Controlled Atmospheres in Spectrochemical Analysis
- E415 Optical Emission Vacuum Spectrometric Analysis of Carbon and Low-Alloy Steel
- E520 Describing Photomultiplier Detectors in Emission and Absorption Spectrometry
- E1009 Evaluating an Optical Emission Vacuum Spectrometer to Analyze Carbon and Low-Alloy Steel
- E1507 Describing and Specifying the Spectrometer of an Optical Emission Direct Reading Instrument

Spectroscopy Performance Note

Delivering the Right Results

GD-AES Calibration: Considerations for Quantitative Depth Profile Analysis

Quantitative Depth Profile (QDP) is used to measure discreet layers or diffusion gradients from the surface into the substrate of a specimen. QDP employs a sputter rate corrected calibration using bulk reference materials. Strict control of voltage and current are required in order to maintain constant relationships between sputter rates of different materials. Data is collected simultaneously on all channels as intensity vs. time. Depth is calculated using material density and lamp geometry. There is no need for material specific thickness standards or expensive auxiliary equipment such as a profilometer in order to create a calibration.

Sputter rate is a material constant. If Sample A has a sputter rate of 4 and Sample B sputters has a sputter rate of 1, Sample A would yield a signal four times higher than Sample B for the same concentration of a given analyte. Typical measured sputter rates for some typical pure materials are provided in Figure 2.

Sputter rate corrected calibration is required to create usable working curves. Signal intensity for an element is proportional to the concentration in the plasma rather than in the sample, Figure 3. The results of plotting intensity vs. concentration in a multi-matrix calibration are shown in Figure 4. Since the various alloys sputter at different rates, each family tends to group to itself. No single working curve can be made and quantification is not possible without correcting for the sputter rate differences. Figure 5 shows the result of applying sputter rate correction to the concentration axis of the calibration. The inclusion of the sputter rate allows all the families to fall on a linear working curve.

An example of a simple depth profile is a binary system such as zinc on steel, Figure 6. Data is collected starting at the surface of the specimen: Zn ≈ 100% and Fe ≈ 0%. As sputtering continues through the galvanized coating and into the steel substrate, the concentration of Zn decreases and the concentration of Fe increases. Both matrices must be calibrated so that the working curves span from traces to 100%. Additional elements should be calibrated to cover the range expected in either matrix.

Factory calibrations are possible for a wide range of materials including:

- Galvanizing – Hot Dipped, Electrogalvanized, Galvannealed, Zn-Ni, Zn-Al, etc.
- Aluminizing
- Aluminum Clad
- Electroplating – Au, Cu, Ni, Cr, etc.
- Tinplate
- PVD & CVD
- Heat treatments – Carburized, Nitrided, Carbonitrided, Nitrocarburized
- Thin oxide layers
- Painted metal

Element	Sputter Rate (μg/s)	Element	Sputter Rate (μg/s)
Aluminum	1.0	Chromium	4.3
Titanium	1.1	Copper	9.2
Iron	3.2	Zinc	15
Molybdenum	3.2	Tin	17
Zirconium	3.7	Silver	26
Nickel	4.2	Gold	38

Standard conditions – 700V, 20mA

Figure 2: Sputter Rates for Pure Materials

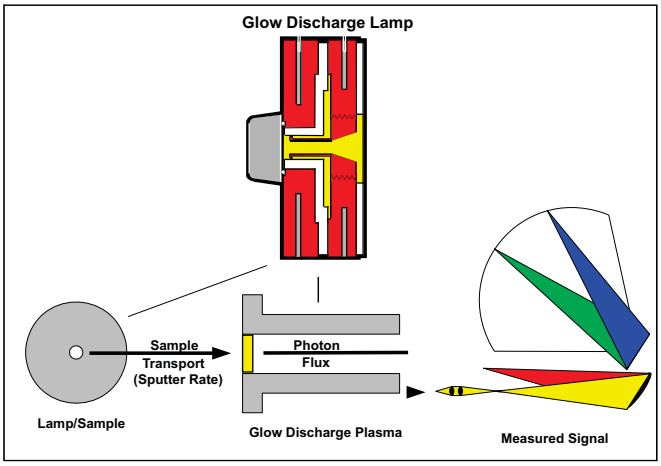

Figure 3: Sample Transport

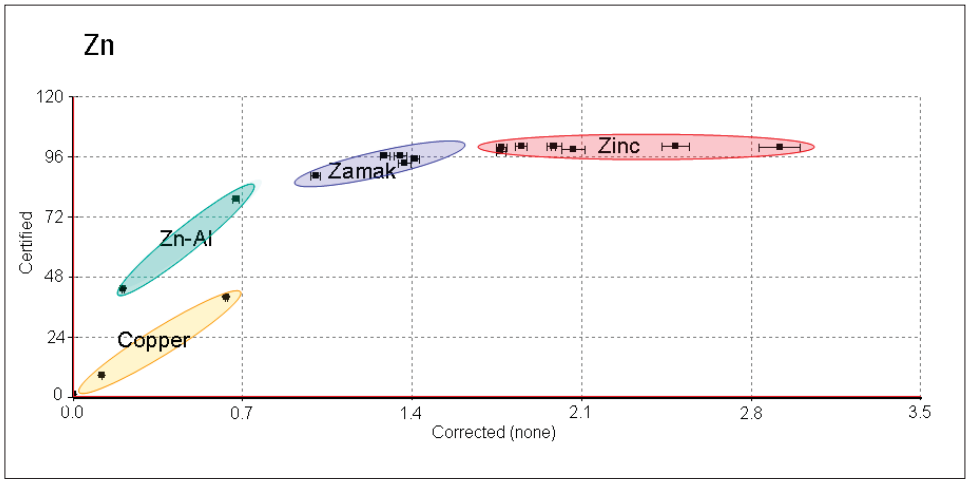

Figure 4: Zn Calibration – Intensity vs. Concentration

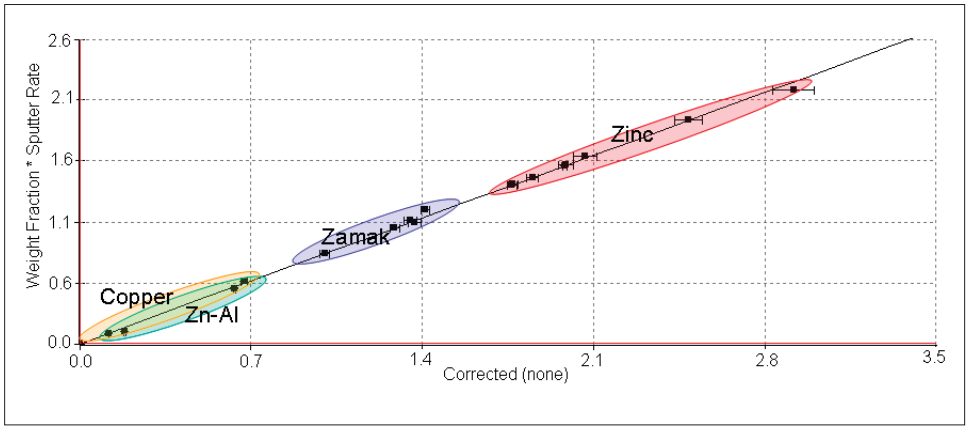

Figure 5: Zn Calibration – Sputter Rate Corrected

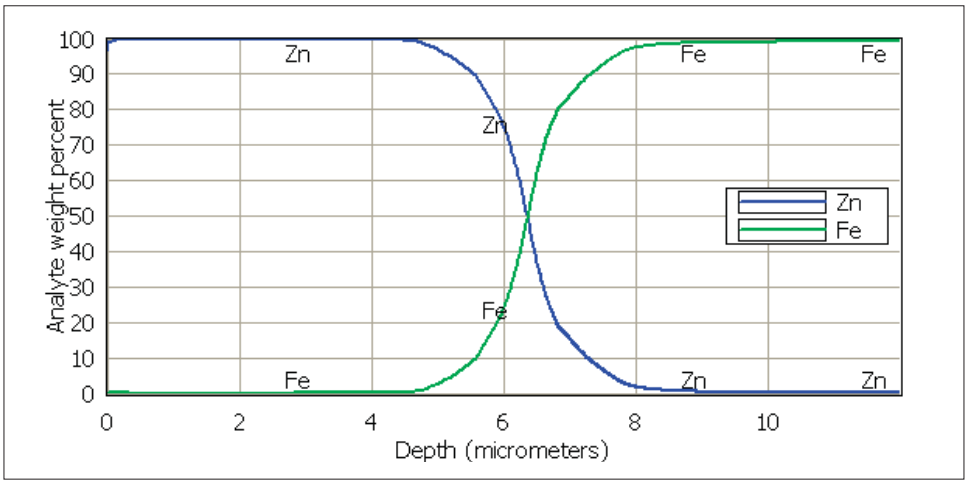

Figure 6: Zinc on Steel

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