

Challenges associated with developing XRF coating weight standards

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Abstract

The objective of this paper is to describe the challenges of creating accurate standards for calibration of online X-ray Fluorescence (XRF) based coating weight gauges. The lack of internationally recognized primary standards requires galvanizing lines to develop their own reference samples following the ASTM A754 / A754M standard test method. However, with an increase in the use of Advanced High Strength Steel (AHSS) and their unique chemistry in galvanizing lines, separate calibration samples may be needed to account for the different behavior of the substrate in the alloy layer growth.

The method used to demonstrate these challenges was to measure galvanized samples from different production lines on an XRF coating weight gauge and compare the predicted value with assigned coating weight based on destructive analysis of nearby samples.

A sample of results from the gauge readings will be presented demonstrating the influence of different substrate materials on XRF signals. The results will also include an overview of the sensor repeatability, statistical variation and long-term stability. Additional considerations are given with respect to typical variations that occur in the rolling environment. Related discussions on the range of calibration samples versus expected production range and potential errors from extrapolation are also presented.

The conclusions presented will include a modified technique for calibrating XRF based coating weight gauges that maximizes the sample data available. The benefits of increasing the number of samples on the overall gauge accuracy will also be presented.

Introduction

Galvanized steel sheet has literally thousands of applications in modern manufacturing. Metal fabricators, regardless of the end market, recognize the value in terms of extended functional life that a thin layer of zinc can provide to steel sheet. Designers specify the exact zinc coating weight required for optimum corrosion resistance required in their application. The expected environment, required lifetime, radius of bend in the sheet all influence the ideal value of the target coating thickness. In order to assure consistency across suppliers of zinc-coated sheet, internationally agreed product definitions, or coating designations were established. The ASTM standard A653 / A653M is one of a few international standards that list products and the coating weight that defines their designation¹. To assist with verifying the coating weight during production, ASTM also provides standard A754 / A754M, which describes the standard tests for coating weight measurement using X-ray Fluorescence². However, finding international standards that define coating weight reference material has been an ongoing challenge for galvanizers where quality / ISO regulations require traceability.

International reference standards

At the Bureau International des Poids et Mesures (BIPM) in Paris, France, you can find the original physical standards used to define length (meter) and mass (kilogram). Those standards, originally fabricated in 1799, have been retired and subsequent generations of the standards made of platinum-iridium served as the reference standard for international measurements for decades. The BIPM and other standards organizations have recently migrated to definitions of these basic units of measure that are based on physical constants, such as the speed of light in vacuum. However, with all the advances made to precisely define those quantities, there are no international permanent reference standards for galvanized steel sheet.

ASTM standard A90 / A90M provides a standardized test method for determining the coating weight of steel sheet coated with zinc and other metallic coatings, but there are three limitations with this approach³.

- The first is straightforward: the weigh-strip-weigh (WSW) test destroys the sample in the process of verifying the coating weight, thereby limiting the sample's effectiveness to just one point in time.
- The second is time itself. Even the most efficient line-to-lab transfers and testing process may take 5 – 15 minutes before a result is collected and communicated back to operations. During that time, an entire coil may have been rolled under similar line conditions, resulting in downgraded material if the test indicates any below tolerance coating values.
- The final limitation is subtle and revealed when analyzing the details of the procedure (section 7) of the standard. Specifically, section 7.3 indicates that the weight (mass) of the specimens be determined to the nearest 0.01g and section 7.4 indicates that the area of the sheet be determined to the nearest 0.01 in² (5 mm²). This section also refers back to note 2, which indicates a sample size of 3330 mm² or 65.1 mm ±0.1 mm in diameter. When the mass tolerances is divided by the sample area, the result produces an expected uncertainty of roughly 3 gsm (see Equation 1-3 and Figure 1).

$$(1) \quad CW = \frac{mass}{area} = \frac{mass}{\pi r^2}$$

$$(2) \quad \Delta CW = \sqrt{\left(\left(\frac{\Delta mass}{area}\right)^2 + \left(\frac{mass * 2\Delta r}{area * r}\right)^2\right)}$$

For a 100 gsm sample, the uncertainty would be:

$$(3) \quad \Delta CW = \sqrt{\left(\left(\frac{0.01g}{0.003330m^2}\right)^2 + \left(\frac{0.333g * 2 * 0.0001m}{0.00333m^2 * 0.03255m}\right)^2\right)} = 3.067gsm$$

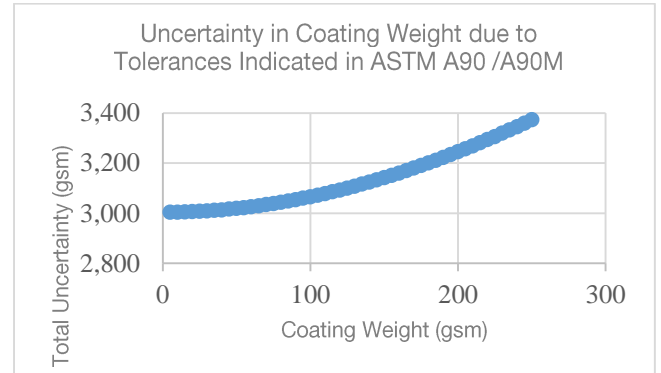


Figure 1. Uncertainty in coating weight due to tolerances in ASTM 90 / A90M

In an extreme worst case, the WSW process could have an error of +0.01 g on the weight of the coated samples, and a -0.01 g error on the weight of the stripped sample. This would result in an error on the order of 6 gsm in the final assigned value.

In an effort to produce permanent zinc coated samples traceable to basic metrology units, some have taken zinc foils of an area verified against certified length standards and then had the mass determined on a scale calibrated with certified mass standards. While the resulting sample has a “traceable” mass per unit area, there are several assumptions that prevent it from being a practical galvanized steel reference standard. Firstly, it cannot be assumed that the foil is the same thickness throughout the entire area. The purity of zinc may also be an issue, or most obviously, the act of gluing the foil to the steel base does not produce the same thin alloy layer generated in the hot dipped process. Each one of these factors limit the effectiveness of using zinc foils in calibrating on X-ray Fluorescence (XRF) based coating weight gauges.

Review of XRF coating weight gauges

Online coating weight measurement by XRF bring galvanizing lines the benefit of near real-time independent sensors that provide feedback on the product outcome. Process engineers can use the output of these instruments to tune process variables to optimize raw material, energy consumption and yield. One of the first practical considerations in selecting a sensor is that it must be non-contact. The coating applied has a primary job to inhibit corrosion, but in many cases, its secondary task, to look good, is equally important. If the sensor touches the strip at all, it would make marks, and lose much of its appeal to consumers. In the typical hot dip line (see Figure 2), the logical location for a coating sensor is directly above the air knife for minimum feedback time.

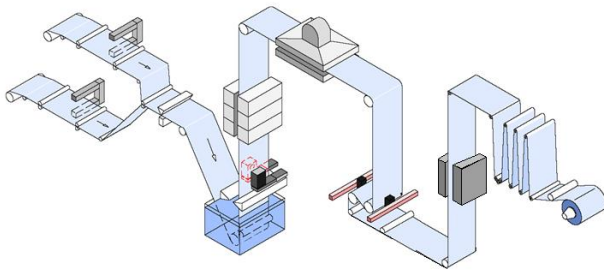


Figure 2. Hot dip galvanizing (HDG) line with cold gauge and hot gauge measurements

However, the heat from the pot and horizontal strip movement physically limit a cross-strip measurement sensor at this location. The more traditional sensor placement is well downstream from the cooling tower, where the environment is a bit friendlier to sensors scanning from edge-to-edge. A complete sensor solution that includes sensors in both locations provides maximum process optimization.

Measuring principle

The coating weight of pure metal coatings on steel is generally measured by excitation of the characteristic X-ray fluorescence radiation caused by the photoelectric effect (see Figure 3). This well-known state-of-the-art method is also used as the basis for various other types of measurement, such as evaluating the intensity of several material-characteristic fluorescence radiation energies.

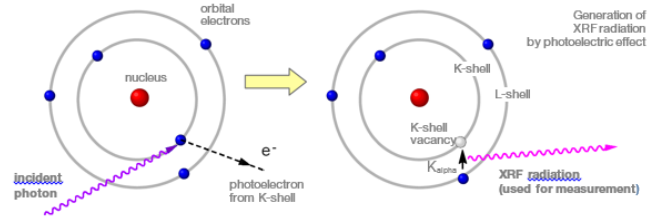


Figure 3. Generation of XRF radiation by photoelectric effect

Each element has characteristic fluorescence energies (K_{α} and L_{α}), and associated absorption-edges (K, L) at slightly higher energies. In practice, only the K series is normally used in coating weight gauges. The primary radiation beam must have some component energies higher than the K absorption-edge energy of the element required to fluoresce at its corresponding K_{α} energy.

For measurement of thin metallic coatings applied to steel strip, this XRF principle is used (see Figure 4). The coated steel strip is exposed to a primary beam of photon radiation. This photon radiation can be gamma rays or X-rays, having sufficiently high energy to stimulate excitation and emission (fluorescence) of X-rays. The excitation of iron atoms in a steel strip leads to emission of fluorescence radiation with an energy of 6.4 keV (1 kilo electronvolt = $1.6 \cdot 10^{-16}$ J).

If the steel strip is coated by zinc, the “iron fluorescence” radiation is attenuated while passing through the coating. It is also possible to use the fluorescence radiation of the coating material to calculate a coating weight measurement because the zinc fluorescence will increase with coating weight. In either case, ionization chambers measure the intensity of the fluorescence radiation⁴.

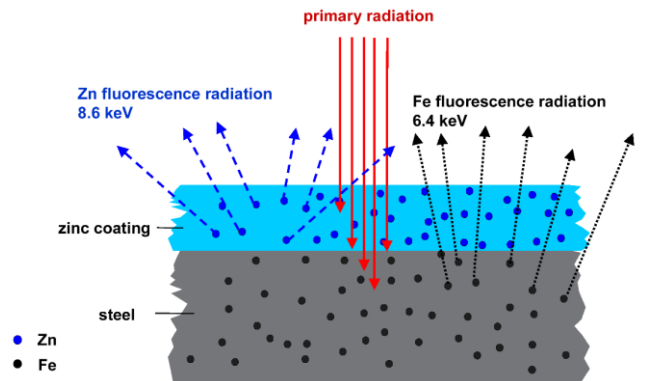


Figure 4. Zinc coating gauge, emission of fluorescence radiation

Calibration methods for XRF coating weight gauges

In order to establish a relationship or mathematical function that converts fluorescence signal to measured coating weight, coating weight standards are used. If traceable zinc foil samples are used for the base calibration, a well-behaved base calibration can be obtained (Figure 6a), but the absence of an alloy layer will cause an error when measuring actual galvanized samples (Figure 5b).

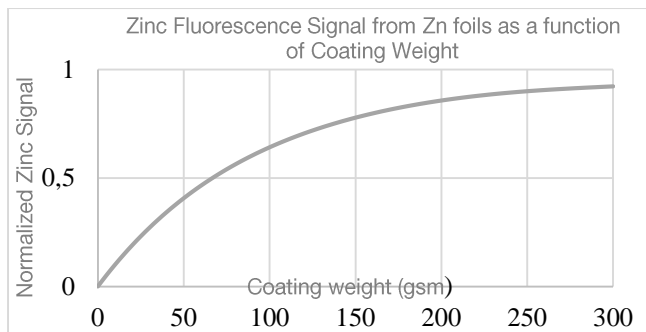


Figure 5a. Zinc foil curve

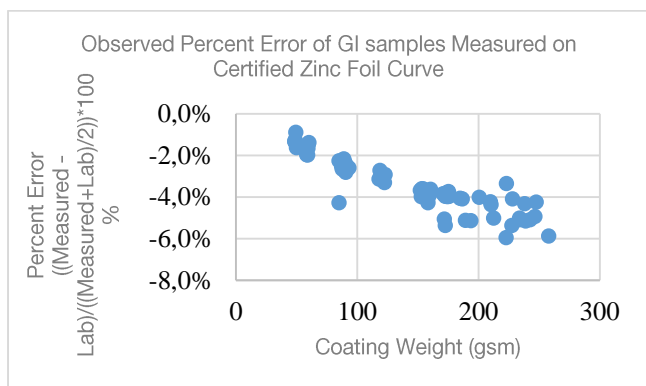


Figure 5b. GI sample measurement errors on zinc foil curve

The linear behavior of the residual errors can be corrected by applying a gain and offset to the uncorrected measurement. The increase in percent observed by the GI sample weight increases may be related to some metallurgical effect of the alloy layer associated with thicker samples. It is not clear if it is impacting the WSW value or the XRF reading, but it is quite apparent. Additionally, it has been found that for optimum measurement accuracy, different gain and offset terms are needed for dramatically different substrate types. This is assumed to be related to the different alloy layer growth at the coating/substrate interface.

An alternative method for collecting calibration samples for XRF coating gauges is defined in ASTM A 754 / A754M, section 6.2. While this process does not produce a directly traceable sample (only analyzing nearby samples), it has proven effective and is used

throughout the industry. The key text of the standard follows:

Standards – Recommended sampling is to choose a uniform area approximately 9 by 9 in (239 by 230 mm). This can be measured by using an XRF instrument to find areas of uniform signal, from which five WSW samples are cut in a cross-like pattern, wherein the center sample is in line with two other samples in the longitudinal direction and with two other samples in the cross-sheet direction. If chemical determinations of the coating weights (masses) of the four “satellite” samples agree to within 3%, the center sample can be assumed to have a coating weight equal to the average of the four samples and can be considered a good calibration standard. If standards representing a particular type of coating and substrate are not available from any reliable source, their preparation may be undertaken, but only if trained personnel are available².

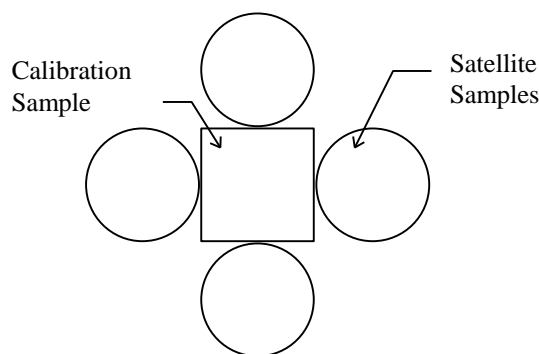


Figure 6. Ideal calibration sample map

As instructed above in A754, calibration samples should be discarded when the difference between the values of their satellite samples significantly exceeds 3%, however as pointed out in the details of A90, the acceptable tolerance of 0.01 g in the sample weight can result in an error of 3 gsm (or more). Strictly adhering to these standards can result in a large number of discarded samples and a corresponding increase in lab time costs. The success rate can be increased when following the suggestion of “using an XRF instrument to find areas of uniform signal”. The benefits of following this recommendation were the basis for the 2003 paper from L. Crawford et al. where certified reference samples were collected for samples ranging from 40 to 250 gsm⁵. The data provided in the Crawford report has been plotted below to show the uncertainty in the lab measurement as a function of coating weight (Figure 7).

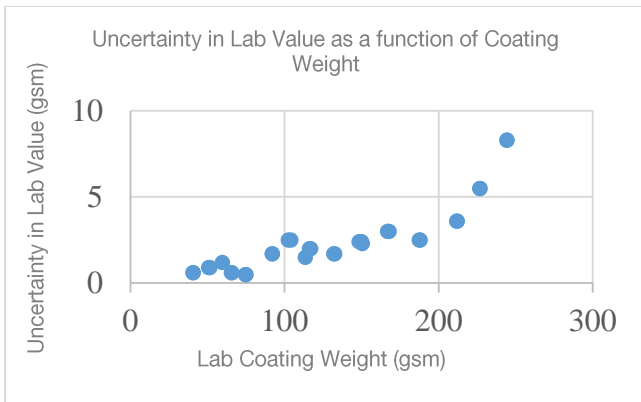


Figure 7: Uncertainty in lab value for CRM samples in L. Crawford et al. report

However, due to the inherent errors with ASTM A90 / A90M pointed out above, the calibration of the coating weight gauge must be based on a statistical mean (least-squares curve-fit) through the readings obtained from a large number of samples. Consequently, while the WSW costs increase with each additional sample, the final measurement precision of a coating weight gauge can be better than the known precision of individual samples used for its calibration.

Ideal GI sample collection process

When planning to build a set of certified GI reference samples, it is critical to consider the product mix of the production line. In order to prevent production measurements that are extrapolated from the base calibration curve, candidate samples should be collected at least 10% above and below the typical production range. Candidate samples should be collected following the ASTM A754 / A754M procedure, where full 9 in x 9 in panels are taken from the line. However, instead of immediately destroying the four satellite samples with WSW analysis, each of the five individual candidate samples (central sample and 4 satellite samples) should be measured on the XRF gauge, as suggested in the L. Crawford et al. paper. As the samples are measured, the fluorescence signals should be stored in a data file. With this approach, it is possible to establish a calibration curve, post XRF-measurement that is based on all five samples, four of which will have traceable values determined via destructive ASTM A90 process. This method was proposed in the 1995 paper by M. DeKa⁶. Including all the samples in the development of the calibration curve will increase the statistics of any least squares regression, because as pointed out above, there is some uncertainty in both the WSW process and the XRF measurement. For some coating weight gauges, the reproducibility of the XRF measurement, as defined by IEC 1336, is stated as $\pm 0.15\%$ of the nominal

coating weight or ± 0.1 gsm, whichever is higher. When the human element is added, errors in sample placement can occur leading to a larger value, as much as 3.8% as indicated in the 1992 paper from J. Leeker et al⁷. Additionally, there may also be a benefit of extending the calibration range with samples above and below the production range with the outlying satellite samples.

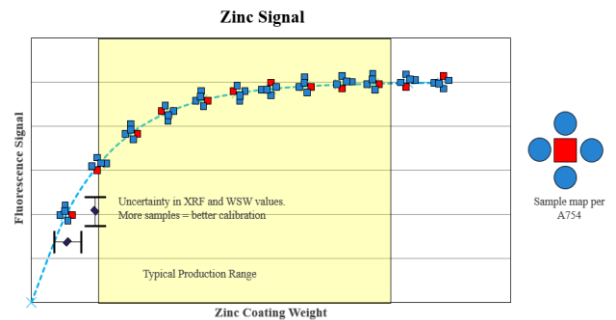


Figure 8: Ideal calibration curve using and developing traceable GI reference samples

Summary

The ability of an online XRF based coating weight gauge to save time and raw zinc is well known in the galvanizing industry. The lack of an internationally recognized physical reference standard for coating weight has resulted in the development of well-meaning standards and procedures that, despite certain limitations, are widely followed in the industry in an effort to comply with ISO traceability requirements. Taking full advantage of the ability to store XRF voltages from GI samples, a method of developing GI reference samples has been proposed that minimizes the observed error in online coating weight calibration curves. Further understanding of the impact of different substrates and bath chemistries on the growth of the alloy layer encourages the collection of additional check samples of different galvanized products, which are used to adjust the well-characterized base calibration for the various products. This results in improved measurement accuracy, which provides galvanize operators the ability to produce more uniform coatings while minimizing zinc consumption.

References

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² ASTM designation A754 / A754M – 18, Standard Test Method for Coating Weight (Mass) of Metallic Coatings on Steel by X-ray Fluorescence, West Conshohocken, PA

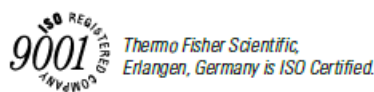
³ ASTM designation A90 / A90M – Standard Test Method for Weight (Mass) of Coating on Iron and Steel Articles with Zinc or Zinc-Alloy Coatings, West Conshohocken, PA.

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⁷ J W Leeker, D Kleimeyer, G S Burgess, “Calibration Program – Coating Weight Standards for Online Gauges”, Proceedings of the Galvanizers Association, 1992.



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