

Generation of Hot Dip Galvanized Coated Sheet Certified Reference Materials Using X-Ray Fluorescence and Gravimetry

Larry F. Crawford, Theresa Simpson, and Fritz J. Friedersdorf

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A method for the generation of hot dip galvanized sheet steel Certified Reference Materials (CRMs) certified for coating mass is described. The method produces high quality coating mass CRMs with combined estimated uncertainties (95% confidence) of about 3% relative standard deviation (rsd). Initially, coating mass x-ray fluorescence (XRF) data are collected on multiple test specimens and used to sort the test specimens by observed coating mass. Several specimens near the mean of the sorted data are retained and the remaining specimens are analyzed for coating mass by a National Institute for Standards and Testing (NIST) traceable weigh-strip-weigh analytical method. The weigh-strip-weigh data are correlated to the initial XRF data using statistical techniques. The retained specimens' coating masses are calculated using this relationship and are used as the certified coating masses for the retained specimens. This correlation method is a more accurate and efficient technique relative to the traditional "perimeter" certification methods. The present method does not suffer from an increased estimated uncertainty due to the inherent hot dip Zn coating variability. Also, this method provides a simple means to generate NIST traceable high quality CRMs that can be tailored to meet individual users' requirements.

Keywords certified reference materials, coating mass, galvanized sheet, x-ray fluorescence

1. Introduction

The hot dip galvanized steel sheet (HDG) market is a multibillion-dollar industry. Zinc coated sheet produced by the hot dip process is used by the automotive industry, residential and commercial construction, and a myriad of additional applications. To ensure that coating mass control is appropriate to meet customer demands, high-quality, traceable coating mass Certified Reference Materials (CRMs) are needed. Currently, these types of CRMs are not commercially available from either the public or private sectors for coating mass calibration and/or verification of the online x-ray fluorescence (XRF) spectrometers commonly used by the HDG community.

The ASTM A754-96 Standard Test Method^[1] recommends that CRMs be generated by each individual production facility for use in that facility. It is necessary to calibrate the gauges used with high quality, traceable CRMs if their results are to be effectively used in calibrating quality assurance and on-line process control instruments. Zinc over-coating or under-coating is a significant quality and financial concern for HDG steel sheet producers and users. For example, at a business unit that produces 500 000 tons of 60 in. wide HDG material per year, the cost of just a 5 g/m² over-coating equals over \$550,000 USD based on the Zn price of \$800 per ton. The cost of under-coating is even higher, with repetitive customer

claims and eventual customer loss. The HDG community also needs high quality traceable CRMs as they become compliant with national and/or international quality system standards, such as ISO Guide 9001:2000, ISO/IEC 17025, QS9000, and the new ISO/TC 16949:2002.^[2-5] The certification protocol described here offers a reliable means to generate National Institute for Standards and Testing (NIST) traceable high quality CRMs for the HDG market. The presented protocol avoids many of the pitfalls associated with the traditional "perimeter" protocols prevalent in the current literature.

Traditional "perimeter" protocols for the generation of Zn coated sheet CRMs^[1,6] entail taking a series of samples around the periphery of a central sample that will be assigned a certified value based on the average of the periphery sample results. The periphery samples are analyzed by a weigh-strip-weigh technique, such as Ref. 7. This requires that a very uniform coated sheet of candidate material at the desired coating mass be identified and used. Current literature^[1,6] requires that the surrounding samples' average agree to within 3% of each other to assume the central sample is equivalent. This process requires that material be tested and discarded until a sample set with acceptable variation is obtained. This method is inherently unpredictable and potentially time consuming and labor intensive.

Typical coating mass variation across a HDG sheet is shown in Table 1 and was collected using XRF spectrometry on a full-width (edged) sheet. As shown in Table 1 the coating mass variation is very significant, varying from 83.8-126.5 g/m² in a sheet 51.75 in. wide × 18 in. long. Using the data from Table 1 that meets the literature acceptance criteria of 3% agreement of surrounding coupons, theoretical certified values based on the average of surrounding coupons and the associated standard deviations are presented in Table 2. An estimated uncertainty (95% confidence) was also calculated based on 2 times the

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Table 1 XRF Spectrometry Data on a Full Width Sheet Cut Into 2.25" Square Coupons Showing Typical Coating Mass Variation

Sample #	Location 1	Location 2	Location 3	Location 4	Location 5	Location 6	Location 7	Location 8
1	96.21	100.56	100.65	104.61	100.61	103.52	107.86	109.92
2	104.02	110.43	108.58	113.31	111.56	111.88	111.59	114.40
3	112.95	121.19	121.22	126.51	122.67	123.19	120.63	120.60
4	113.24	118.67	116.93	120.55	116.03	114.58	114.17	111.00
5	107.51	111.34	108.09	110.85	108.38	107.42	108.32	107.24
6	91.75	95.91	95.90	99.19	95.56	95.76	97.78	97.21
7	89.34	89.83	88.94	89.17	87.80	88.83	89.72	91.93
8	89.96	86.71	86.46	86.28	83.81	85.89	86.45	90.11
Sample #	Location 9	Location 10	Location 11	Location 12	Location 13	Location 14	Location 15	Location 16
1	113.50	117.90	120.62	122.71	124.48	119.19	113.20	108.28
2	114.53	117.42	117.19	118.57	118.23	111.18	102.71	98.67
3	119.39	119.95	117.15	118.92	115.46	110.57	102.04	97.42
4	108.92	109.89	109.36	116.14	117.52	116.35	113.75	109.66
5	103.99	106.63	104.35	109.12	111.36	114.29	113.72	112.91
6	94.64	95.11	96.37	98.95	100.64	100.68	99.85	100.22
7	92.27	92.59	92.50	95.27	96.62	96.03	95.21	94.98
8	91.87	95.55	96.04	97.96	96.30	94.76	93.56	95.84
Sample #	Location 17	Location 18	Location 19	Location 20	Location 21	Location 22	Location 23	
1	102.60	99.87	97.40	96.44	97.58	95.49	96.48	
2	94.60	93.21	91.95	91.46	91.43	91.16	91.78	
3	95.79	95.01	94.60	97.26	97.01	95.31	92.02	
4	105.06	103.38	101.01	100.31	101.11	99.18	96.69	
5	110.58	108.31	108.15	107.75	106.87	104.00	101.39	
6	102.05	101.39	100.34	100.07	98.83	95.71	94.51	
7	94.03	93.09	90.09	88.68	88.52	88.27	88.02	
8	95.34	95.62	93.47	92.07	90.87	88.55	88.71	

Note: Each "location" refers to 2.25 in. perpendicular to the rolling and each "sample" refers to 2.25 in. parallel to the rolling direction.

Table 2 Theoretical Calculation of Certified Coating Mass Using Perimeter Method

XRF Measured Coating Mass, g/m ²	Calculated Coating Mass From Surrounding Coupons, g/m ²	Standard Deviation of Surrounding Coupons, g/m ² (% relative)(a)	Estimated Uncertainty at 95% Confidence, g/m ² (% relative) (b)
114.5	116.2	2.7 (2.3%)	5.4 (4.6%)
117.2	118.4	1.6 (1.3%)	3.2 (2.6%)
118.9	116.8	1.4 (1.2%)	2.8 (2.4%)
116.4	114.0	2.8 (2.5%)	5.6 (5.0%)
92.5	95.1	1.7 (1.8%)	3.4 (3.6%)
95.3	96.5	2.8 (2.9%)	5.6 (5.8%)
94.9	96.3	2.7 (2.8%)	5.4 (5.6%)

(a) This value is directly comparable to the ASTM A754/A 754M-96 Standard Test Method acceptance criteria.

(b) This value is directly comparable to the estimated uncertainty reported for the materials certified by protocol.

standard deviation of the surrounding coupons. Surrounding coupons are defined as those above and below parallel to the rolling direction and those immediately beside the coupon in perpendicular to the rolling direction. Figure 1 shows the location of the ASTM periphery samples and the XRF spectrometer spot size/location for a 5.5 in. square sample. Table 2 clearly shows that the estimated uncertainty in the certified value can be high, approaching 6% in some cases.

Of the 126 potential CRM combinations (Table 1), only 17 (13%) meet the literature requirements for allowable variation of 3% in the surrounding coupons. The number of acceptable combinations decreases as the size of the coupons to be certified increases because the distance between the surrounding coupons increases. Such variability can make the perimeter

method costly and time consuming or potentially less accurate than required. In addition, the coating mass of the central sample cannot be verified using the weigh-strip-weigh technique because it is a destructive method. Literature^[1,6] also allows for XRF to be used in identifying a uniform area, although this can also be time consuming because multiple locations may need to be tested as indicated by the data in Table 1.

The certification protocol presented here offers a simple means to generate NIST traceable Zn coated sheet CRMs in compliance with international standards for reference material production and certification, such as the ISO Guide 34:2000 and ISO Guide 35:1989^[8,9] while eliminating the problems associated with non-uniform coatings. It also offers a confir-

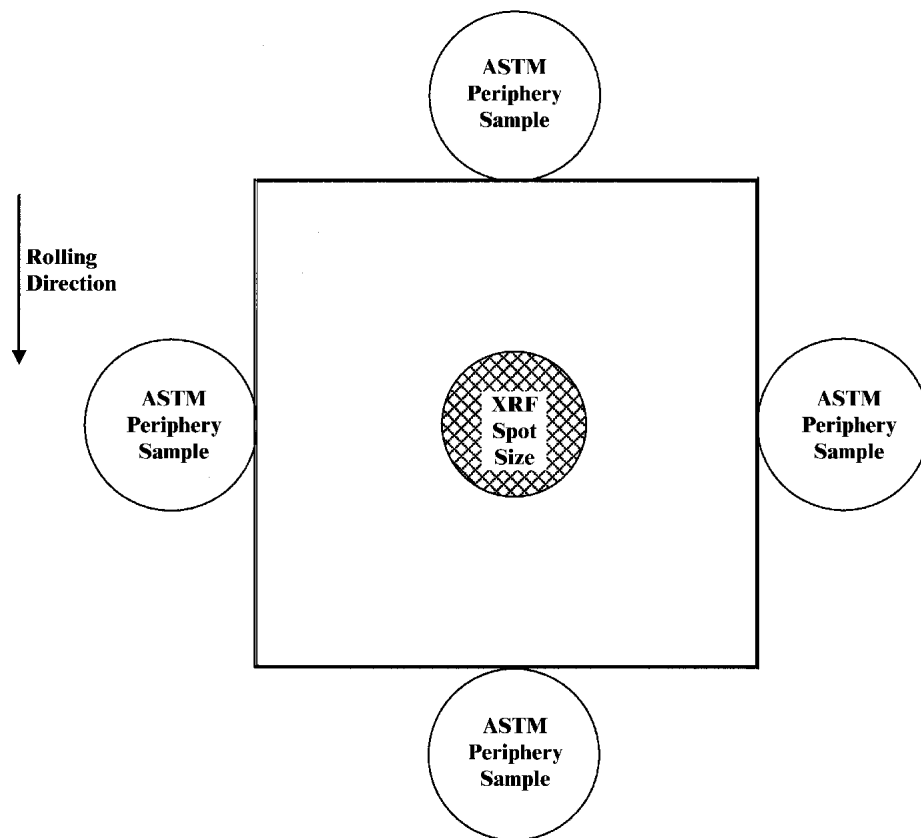


Fig. 1 Diagram showing typical periphery sampling required by ASTM A754, XRF spot size/location, and weigh-strip-weigh sample area

mation of the certified coating mass via the initial XRF spectrometry results. The protocol consists of collecting XRF spectrometry coating mass data on multiple test samples and using the data to sort the test samples by the observed coating mass. Several samples near the mean of the sorted data are retained and the remaining samples are analyzed for coating mass by a NIST traceable weigh-strip-weigh analytical method. The weigh-strip-weigh data is correlated to the initial XRF data by a least squares linear regression technique. The retained samples' coating masses are calculated using this relationship and are used as the certified coating masses for the retained samples. The regression analysis also yields prediction intervals for the calculated values that are used as the combined estimated uncertainties for the CRMs.

2. Experimental

2.1 Preliminary Sample Preparation

An appropriate length of HDG coated sheet at the desired coating mass was obtained. The length of coated sheet needed depends on the number and size of test pieces desired. For this certification work, 5.5 in. square samples were needed to fit into the XRF spectrometer and about 10-15 ft by production width of material was obtained. As described in ASTM A754-96,^[1] the edges of the candidate material were trimmed to remove the outer 2-3 in. of material parallel to the rolling direction and cut into 18 samples for further testing.

Traceability was maintained during cutting by labeling each sample individually with a permanent identification that would allow the original configuration of the coated sheet to be re-created, as required. The samples were free from obvious defects or physical damage, such as scratches, dents, entrapped dross, and coating "sag." All samples were flattened, deburred, and cleaned with acetone to remove any rolling oils, dirt, or fingerprints. A separate piece of material near the test sample area was also removed and analyzed by weigh-strip-weigh to confirm that the material was close to the desired target coating mass. If the weigh-strip-weigh data showed that the material was not near the desired target coating mass, new material was obtained.

2.2 Data Collection by XRF Spectrometry

The XRF spectrometer used in this work was a Thermo Radiometrie Model 800 Zn/Fe Laboratory Coating Weight Gauge (Thermo Radiometrie, Gaithersburg, MD) and was set up to use a 30-s data acquisition time. All samples associated with the product of a single coating mass CRM are tested in a single continuous test session. Each sample is measured by XRF spectrometry three times and the run order is randomized using a random number generator for each set of materials. Three readings are averaged and used as a single XRF measurement result. The stability of the XRF spectrometer is verified by randomly selecting a quality assurance sample from the

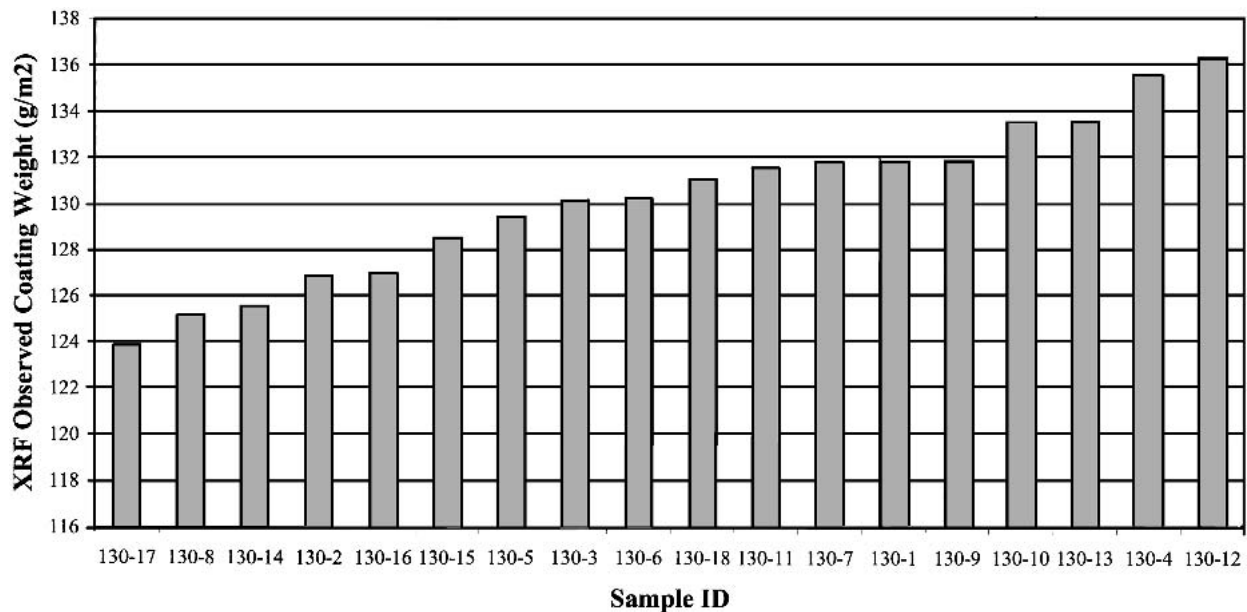


Fig. 2 XRF data sorted for a 130 g/m² aim composition

set for repetitive measurements throughout the test session. The repeat period for the quality assurance sample is every third or fourth sample. The quality assurance data was checked for normality, instrument drift and out of control conditions and instrument drift was found to be insignificant for all measurement sessions.

Samples were tested using a single orientation between the XRF spectrometer and the rolling direction of the HDG sheet samples. The CRMs associated samples were fabricated to assure proper, consistent positioning in the XRF spectrometer. Also, the location and size of the XRF focal spot must be known. This dictates the location that the weigh-strip-weigh samples are taken from after collecting the data on the XRF spectrometer. If the XRF spectrometer focal spot location and size are not known, the weigh-strip-weigh data will not correlate as well with the XRF data and will lead to higher estimated uncertainties for the CRMs being produced.

Table 1 shows data collected by XRF spectrometry on a full width sheet cut into 2.25 in. square coupons. The data in Table 1 clearly show that moving even 2.25 in. perpendicular or parallel to the rolling direction can yield very different coating masses, which can lead to erroneous use of the CRMs if the same spot that is tested is not used in the calibration and/or verification of the XRF spectrometer. Accordingly, only the location of the XRF spectrometer focal spot is certified in the final product. When multiple XRF spectrometers are to use the CRMs being produced, all the focal spot sizes must be approximately the same and must hit the sample at approximately the same location. The Thermo Radiometric Model 800 Zn/Fe Laboratory Coating Weight Gauge and the Radiometry top/bottom online gauges all had a spot size of approximately 2 in. in diameter and were aimed to hit the 5.5 in. square CRM in the center. This was confirmed photographically before data collection and again before using the CRMs to generate a calibration curve.

2.3 Weigh-Strip-Weigh Sample Preparation and Data Collection

After XRF spectrometry data collection, the observed coating mass data were sorted and graphed to determine which samples were best suited for certification. Figure 2 gives an example of the sorted data for a 130 g/m² aim coating mass. The 5.5 in. square samples are numbered corresponding to the location from the candidate material with 6 samples being taken perpendicular to the rolling direction (130-1 through 130-6) and 3 sets (of the six samples) being taken parallel to the rolling direction for a total of 18 samples. The spread of the observed XRF spectrometry coating mass data is over 11 g/m². Clearly attempting to use the “perimeter” protocol with this data would induce higher errors in the certified coating mass than is obtained with the presented protocol. Based on Fig. 2, samples 130-11 and 130-18 were retained and the center of the other samples was removed either by shearing or punching ensuring that the sample identification was not lost during processing. The accuracy of the observed coating mass measurement is not important, although it is critical that the instrument is stable and capable of a precise measurement to determine the relative differences between the samples.

The two samples with coating mass near the population mean were retained as CRMs and the rest of the sample set was destructively tested by the weigh-strip-weigh ASTM Standard Test Method A90/A90M-01 for Weight (Mass) of Coating on Iron and Steel Articles with Zinc or Zinc-Alloy Coatings.^[7] NIST traceability of the weigh-strip-weigh of this data was maintained by using calipers that are verified monthly using a NIST traceable 50 mm Gage block. In addition, the analytical balances are calibrated with 10 mg, 100 mg, 1 g, 20 g, and 100 g NIST traceable weights annually and verifying them daily with 20 g and 100 g NIST traceable weights. The NIST traceable weigh-strip-weigh data is correlated via least squares lin-

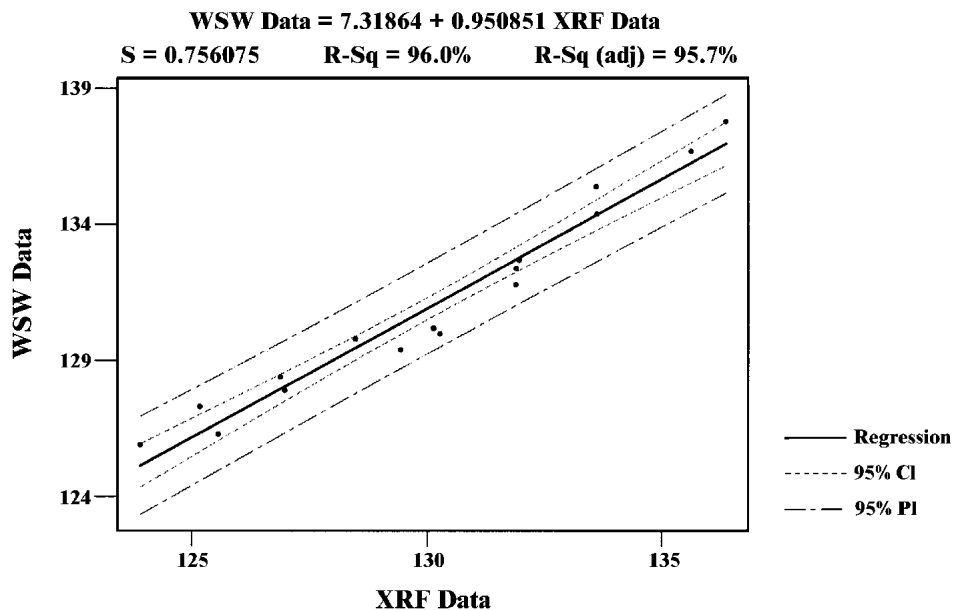


Fig. 3 Example WSW versus XRF data for 130 g/m² CRM

ear regression analysis to the original XRF spectrometry data. This linear relationship is then used to calculate the coating mass of the retained samples.

3. Results and Discussion

3.1 Regression Analysis

Linear regression analysis of initial XRF spectrometry data and the NIST traceable weigh-strip-weigh data are used to develop a relationship between these data. Minitab (version 13.3) was used in this work. Any unusual observations reported by Minitab were removed from the original data set and the regression was repeated. This was done only once based on the initial set of data. Unusual observations are defined as data with large residual values or those exhibiting a large influence on the regression equation. Typically, no data had to be removed, although in certain data sets a maximum of two data points were removed. Figure 3 shows a graph of the weigh-strip-weigh (g/m²) data versus the XRF spectrometry (g/m²) data for the 130 g/m² example and is typical of the relationship obtained.

Minitab is used to calculate the coating masses of the retained CRM samples and also calculate a prediction interval for the coating mass. Residuals were checked for normality on an Individuals and Moving Range (IMR) chart. This allows the tracking of both the process level and process variation at the same time, as well as detecting the presence of special causes. All residuals were in control on the IMR chart and the residual data was absent of any significant shapes or trends for all CRMs generated. For the 130 g/m² example, the calculated coating masses were 132.5 ± 1.7 g/m² (95% confidence) and 131.9 ± 1.7 g/m² (95% confidence) for samples 130-11 and 130-18, respectively. The prediction interval indicates that a 95% probability that the true coating mass of the sample is

within the interval range and is equivalent to the estimated uncertainty of the coating mass in this case.

3.2 Homogeneity Testing

Homogeneity testing of the CRMs generated is not necessary with this certification protocol. Typically, homogeneity problems are in the form of between-sample and within-sample heterogeneity. The between-sample heterogeneity is not significant as each specimen was certified separately. Within-sample heterogeneity is also insignificant because the analysis area on the XRF spectrometer and the weigh-strip-weigh method analyze approximately the same spot (both size and location) on the CRM. This allows the reported estimated uncertainty to be minimized and be solely a function of the relationship developed between the XRF spectrometer and the weigh-strip weigh data. If the spot locations or the spot sizes are not the same, the homogeneity relating to any differences in analysis location and/or size will need to be quantified and incorporated into the reported estimated uncertainty.

3.3 Certificate of Analysis

A certificate of analysis was generated for each CRM produced. An example certificate of analysis for a 130 g/m² CRM is shown in Fig. 4. Each certificate of analysis was compliant with ISO Guide 31:2002.^[10] These certificates of analysis provide the users detailed information regarding the CRM and its use. They also satisfy the requirements commonly looked for by auditors during registration or accreditation audits.

3.4 Final Results

Multiple CRMs were generated with coating masses ranging from 40-245 g/m². Table 3 shows the identifications, certified coating masses, estimated uncertainties, and relative percentage error of the estimated uncertainties of the CRMs



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Certificate of Analysis

Ferrous Chemical Committee Certified Reference Material

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Hot Dip Galvanized Zinc Coated Sheet (Ref. 1)
Certified Values

Table 1

CRM Identification	Analyte	Compositional Analysis ¹ g/m ²	Combined Estimated Uncertainty ² g/m ²	Laboratory ³	Method of Analysis ⁴	Date of Certification
CCCGI020	Coating Mass	131.9	1.7	a, b	A, B	January 2003

¹ The meaning of the Compositional Analysis is given in Section 9.

² The meaning of the Combined Estimated Uncertainty is given in Section 12.

³ Laboratories are shown in Section 10.

⁴ Methods of Analysis are shown in Section 11.

1. **SOURCE:** Material produced by Bethlehem Steel Corp. at Columbus Coatings Corp, Columbus, Oh.

2. **PREPARER:** Bethlehem Steel Corp, Bethlehem PA, 18016.

3. **DESCRIPTION:** This CRM is Zn coated Hot Dip Galvanized sheet with the coating mass listed in Table 1. Coating mass was determined as described in Section 9. The CRM is in the form of 5.5"x5.5" squares.

4. **INTENDED USE:** For calibration and control of X-Ray Fluorescence Spectrometers used to determine the coating mass on Zn coated sheet.

5. **STABILITY, TRANSPORTATION, AND STORAGE:** Transport and store under normal atmospheric conditions.

6. **INSTRUCTIONS FOR CORRECT USE:** Material should be clean, free of dirt, fingerprints, etc. Only one side of each material is certified and that side must be used. The uncertified side is identified as such.

7. **METHOD OF PREPARATION:** Hot Dip Galvanized Zn Coated Sheets were received and tested. Test specimens were taken, labeled, and used to certify coating mass by the methods described in section 9 and discussed in detail in Reference 1. Homogeneity of the CRM is described in section 8 (Ref.1).

8. **STATE OF HOMOGENEITY:** Homogeneity Testing was not carried out on this CRMs. Homogeneity is typically in the form of between-sample and within-sample sample heterogeneity. The between-sample heterogeneity is not significant as only one specimen of this CRM exists. Within-sample heterogeneity is also insignificant because the analysis area on the Columbus Coatings XRF and the weigh-strip-weigh method analyze approximately the same spot on the CRM.

L. F Crawford, Research Engineer

Date

* This Certified Reference Material was produced following the principles of ISO Guide 34 (Ref. 2). This Certified Reference Material was produced in accordance with the ISO 30 Series Guides (Ref. 3-5).

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Fig. 4 Certificate of analysis (continued on next page)

generated. The increase in relative percentage error as the coating masses of the CRMs approach 250 g/m² is because the amount is approaching the upper limit of the XRF spectrom-

eter's capability. The laboratory and the online XRF spectrometry gauges have been successfully calibrated using these CRMs.

9. COMPOSITIONAL ANALYSIS:

FIGURE 4, Page 2 of 2

Coating Mass - Method of Analysis A: The concentration value given in Table 1 is the predicted value (of the CRM sample retained from the original 18 specimens sampled for certification) from the correlation of method of analysis A and method of Analysis B (Ref. 1). No drift correction was applied to this data.

10. LABORATORY:

a: Analytical Chemistry Group, Bethlehem Steel Corporation, Homer Research Laboratories, Bethlehem, Pennsylvania, 18016 L. M. Matyas, W. Ace (An ISO 17025 Accredited Laboratory).

b: Columbus Coatings Corporation , (a wholly owned subsidiary of Bethlehem Steel Corporation), 1800 Watkins Rd, Columbus, Oh, 43207 L. F. Crawford

11. METHOD OF ANALYSIS:

A: CO-055 - Analytical Method - Determination of Coating Weight on Galvanized, Galvanneal, and Galvalume Coated Sheet Steel by Gravimetric Analysis, Bethlehem Steel Corporation, Homer Research Laboratories (see Ref 1 for exceptions). Traceable to CRMs (Ref. 1): 1g, 10g, 20g, and 100g NIST traceable CRMs (balances) and NIST traceable 50mm Gage block (vernier calipers). Laboratory a.

B: Columbus Coatings Corporation (a wholly owned subsidiary of Bethlehem Steel) laboratory's in-house method for operating the DMC XRF Coating Thickness Gauge – Model 800 Zn/Fe Coating Weight Gauge, based on a 30s acquisition time. Laboratory b.

12. CALCULATION OF COMBINED ESTIMATED UNCERTAINTY

The estimated uncertainty in the certified value due to compositional certification, $u_{Compositional}$, was calculated as prediction interval for the coating mass values predicted from the correlation of Test Methods A and B. For the certified value, the prediction interval is the range in which the new response value (certified value) is expected to fall based on the correlation of the Comparative and Definitive Test Methods. That is, the prediction interval provides an interval of possible response values given a combination of predictor levels.

$$u_{Compositional} (95\%confidence) = PI(95\%confidence)$$

Where:

PI: Prediction interval from correlation of the Comparative and Definitive Test Methods Data.

The certified coating mass value and its combined estimated uncertainty is presented in Table 1 as the predicted value for the CRM test specimen (x) \pm the combined estimated uncertainty ($u_{combined}$) (2-sigma):

$$u_{Combined} = u_{Compositional}$$

$$= u_{combined} (95\% confidence) = 2 * u_{combined}$$

Where:

$u_{Compositional}$: The estimated uncertainty due to the compositional analysis (section 9).

13. REFERENCES:

1. Crawford L. F., Bethlehem Steel Corporation Ferrous Chemical Committee Certified Reference Material CCCGI001-CCCGI033 Report Compositional Certification by Gravimetry, Dated January 20, 2003, Bethlehem Steel Corporation, Homer Research Laboratories, Bethlehem, Pennsylvania, 18016.
2. ISO Guide 34 - 2000 Quality System Guidelines for the Production of Reference Materials.
3. ISO Guide 30 - 1992 Terms and Definitions used in Connection with Reference Materials.
4. ISO Guide 31 - 2000 Contents of Labels and Certificates of Reference Materials.
5. ISO Guide 35 - 1989 Certification of Reference Materials - General and Statistical Principles.

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Fig. 4 cont. Certificate of analysis

Table 3 Listing of CRMs Produced With Estimated Uncertainties

Aim	CRM Identification, g/m ²	Certified Coating Mass, g/m ²	Estimated Uncertainty, g/m ²	Relative Percent Error
40	GI001	40.77	0.6	1.3
	GI002	40.60	0.6	1.3
50	GI003	51.53	0.9	1.7
	GI004	50.65	0.9	1.7
60	GI005	59.7	1.2	2.1
70	GI006	65.76	0.6	1.0
	GI007	65.46	0.6	1.0
80	GI008	74.94	0.5	0.8
	GI009	74.52	0.5	0.8
90	GI010	92.1	1.7	1.8
	GI011	92.0	1.7	1.8
98	GI012	104.0	2.5	2.4
	GI013	102.5	2.5	2.5
110	GI016	116.1	2.0	1.7
	GI017	117.0	2.0	1.7
120	GI018	113.5	1.5	1.3
130	GI019	132.5	1.7	1.3
	GI020	131.9	1.7	1.3
140	GI021	150.4	2.3	1.5
150	GI022	149.9	2.4	1.6
	GI023	148.4	2.4	1.6
170	GI024	166.8	3.0	1.8
	GI025	167.8	3.0	1.8
190	GI026	187.3	2.5	1.3
	GI027	188.0	2.5	1.3
210	GI028	212.0	3.6	1.7
	GI029	211.7	3.6	1.7
230	GI030	226.8	5.5	2.4
	GI031	226.7	5.5	2.4
250	GI032	244.2	8.3	3.4
	GI033	244.2	8.3	3.4

3.5 Applicability to Galvannealed Materials

This certification protocol is not directly applicable to the certification of galvannealed materials, particularly for the certification of %Fe composition. For coating mass certification in galvannealed material, the protocol is applicable. The correlation between the %Fe data generated by the XRF spectrometer and by the weigh-strip-weigh data is inadequate to certify reference materials. This is due to the difference in how the XRF spectrometer used in this study measures %Fe in galvannealed coatings. For galvanized and coating mass in galvanneal, the x-ray beam is perpendicular to the sample and penetrates to or near to the substrate layer, which is comparable with the weigh-strip-weigh method. For galvanneal %Fe analysis, the x-ray beam is angled and does not penetrate to the substrate layer. This makes the analysis highly dependent on the top layers of the Zn coating, namely the delta, zeta, and eta layers, whereas the weigh-strip-weigh method strips all layers: gamma, delta, zeta, and eta. We believe this is what causes the

poor correlation between the two methods for %Fe inducing unacceptable errors. Currently, the traditional perimeter methods are recommended for the certification of %Fe in galvannealed coated sheet.

4. Summary

This paper presented a simple protocol to generate reliable, NIST traceable HDG CRMs using a correlation technique between XRF spectrometry and weigh-strip-weigh data. The CRMs produced by the protocol are of high quality with estimated uncertainties typically less than 2% relative error and can be tailored to meet a business unit's individual requirements. The protocol presented avoids many of the problems associated with the traditional methods of CRM production and is less time consuming.

Acknowledgments

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References

1. Anon: ASTM Designation A754/A 754M-96 (Reapproved 2000)—Standard Test Method for Coating Weight (Mass) of Metallic Coatings by X-Ray Fluorescence, ASTM, West Conshohocken, PA.
2. Anon: ISO 9001:2000—Quality Management Systems—Requirements, ISO, International Organization for Standardization (ISO), Geneva, Switzerland.
3. Anon: ISO/IEC 17025:1999—General Requirements for the Competence of Testing and Calibration Laboratories, ISO, International Organization for Standardization (ISO), Geneva, Switzerland.
4. Anon: QS9000 Quality System Requirements, 3rd Edition, 1998, Chrysler Corporation, Ford Motor Company, General Motors Corporation.
5. Anon: ISO/TC 16949:2002—Quality Management Systems—Particular Requirements for the Application of ISO 9001:2000 for Automotive Production and Relevant Service Part Organizations, ISO, International Organization for Standardization (ISO), Geneva, Switzerland.
6. Anon: Procedure and Criteria for Obtaining Calibration Samples for Thermo Radiometric Coating Weight Gauges, Thermo Radiometric.
7. Anon: ASTM Designation A90/A 90M-01—Standard Test Method for Weight (Mass) of Coating on Iron and Steel Articles With Zinc or Zinc-Alloy Coatings, ASTM—Vol 01.06 Feb 2002, West Conshohocken, PA.
8. Anon: ISO Guide 34:2000—General Requirements for the Competence of Reference Material Producers, ISO, International Organization for Standardization (ISO), Geneva, Switzerland.
9. Anon: ISO Guide 35:1989—Certification of Reference Materials—General and Statistical Principles, ISO, International Organization for Standardization (ISO), Geneva, Switzerland.
10. ISO Guide 31:2000 Reference Materials—Contents of Certificates and Labels, ISO, International Organization for Standardization (ISO), Geneva, Switzerland.