

Method of Determining Iron Content in Galvanized Coating of Zinc-Iron Alloy

Chun Fan[†], Jingjing Wang, and Ben Hua

Products & Technique Management Department, Baoshan Iron & Steel Co., Ltd., Shanghai 201900, China

(Received May 31, 2024; Revised July 30, 2024; Accepted July 31, 2024)

Iron content in a galvanized coating of zinc-iron alloys was determined using atomic absorption spectrometry and two X-ray fluorescence (XRF) methods (fundamental parameter and empirical coefficient methods). Results indicated that the chemical method provided the highest accuracy in measuring iron content. However, it suffered from a low detection efficiency, making it less suitable for use in production quality control. In contrast, the two XRF methods (fundamental parameter and empirical coefficient methods) offered viable alternatives for monitoring iron levels in galvanized coatings during manufacturing, with repeatability of 0.2% and 0.4%, respectively, superior to the 0.6% repeatability observed with the chemical method. However, it is important to note that the accuracy of these two XRF methods (fundamental parameter and empirical coefficient methods) could vary depending on the stability of processing units involved, potentially leading to less reliable results compared to the chemical method. Therefore, while the two XRF methods (fundamental parameter and empirical coefficient methods) are useful for rapid quality control, their applications should be carefully managed. They should be supplemented with more accurate techniques when necessary.

Keywords: Zinc-iron alloy, Iron content, X-ray

1. Introduction

Zinc-iron alloy steel plate is developed on the basis of hot-dip pure-zinc steel plate, which is mainly used in the automobile plate industry. This plate has been widely used because of its good corrosion resistance, heat resistance, paintability, weldability, anti-rust capability after painting, and good scratch resistance [1]. Zinc-iron alloy steel plate will form a zinc-iron alloy layer on coatings by alloying the hot-dip galvanized steel plate, and iron content in the whole coating is usually 8%–15% (see Q/BQB 420–2024 hot-dip galvanized/zinc-iron alloy/zinc magnesium alloy-coated steel plate and strip). The coating of zinc-iron alloy steel plate is not uniform. The surface layer is alloy in phase ζ , followed by phase δ_1 . The transition layer between the iron base and zinc coating, that is, phase Γ [2]. The iron content of the coating will affect the formation of the metallographic structure of each coating layer, cause pulverization and delamination defects, and affect the surface quality of stamped and formed parts [3]. Therefore, iron content in coatings is an important

control item for product quality.

The chemical method is the standard measurement method for iron content in zinc-iron alloy steel plate coatings (GB/T 24514–2009 Zinc and/or aluminum-based coatings on steel—Determination of coating mass per unit area and chemical composition—Gravimetry, inductively coupled plasma atomic emission spectrometry and flame atomic absorption spectrometry). After the coating is completely stripped with the stripping solution, flame atomic absorption spectrometry or inductively coupled plasma atomic emission spectrometry is used to determine the iron content in the stripping solution. The standard method has a long operation process and is unsuitable for production quality control. The X-ray fluorescence (XRF) method has been widely used in the detection of coated steel plates due to its advantages of accuracy, speed, and non-destructive testing [4–7]. XRF methods include different test principles and applications, which include empirical coefficient method [8,9] and fundamental parameters (FP) method [8,10–13]. Due to the presence of iron elements in both the substrate and coating of zinc-iron alloy steel plate, The commonly used K-line with strong penetration will excite the iron elements in both the substrate and coating. X-ray method

[†]Corresponding author: fanchun@baosteel.com

cannot distinguish whether the fluorescence intensity of the iron element to be measured comes from the coating or substrate. Therefore, the empirical coefficient method of X-ray cannot complete the determination of iron content in zinc-iron alloy coatings. To solve this problem, the author's laboratory attempted to conduct a large number of experiments using the FP method and the less commonly used L-line of empirical coefficient method. The application of XRF method on the iron content of zinc-iron alloy steel plate coating has been developed [14]. This article summarized the practical application advantages and disadvantages of these two X-ray fluorescence methods in the quality inspection of iron content in zinc-iron alloy coatings.

2. Experimental Procedures

2.1 Experimental instruments

Simultix 14 XRF spectrometer (Rigaku Corporation, Japan), ZSX Primus XRF (Rigaku Corporation, Japan), and Magix Pro XRF spectrometer (Malvern Panalytical, Netherlands) were used in this research.

2.2 Experimental condition

Measurement conditions of XRF spectrometers are presented in Table 1.

2.3 Experimental method

At least six groups of zinc-iron alloy samples were prepared with different coating amounts and iron content in coatings. Every sample group should not be less than 4–5 pieces. Each sample was continuously punched along the rolling direction in disc specimen with a diameter of 50 mm. The XRF intensity of characteristic elements of each sample plate was measured under

experimental conditions of the XRF instrument. The two samples with the closest XRF intensities were selected (the deviation of the XRF intensity of the two samples should be less than 1%). One was retained as a standard sample, and the other was used to determine the coating mass and iron content in coatings by the chemical method. Under experimental conditions of the XRF instrument, the X-ray intensity of Zn and Fe was measured using zinc-iron alloy standard samples. On Simultix 14 XRF spectrometer X-ray intensity of Zn- $k_{\alpha}(20^{\circ})$, Fe- $K_{\alpha}(20^{\circ})$, Zn- $k_{\beta 1}(40^{\circ})$ and Fe- $K_{\alpha}(40^{\circ})$ were tested. On ZSX Primus XRF and Magix Pro XRF spectrometer X-ray intensity of Fe- L_{β} were tested. Then A linear or quadratic linear relation of iron in coatings was determined on the three type of X-ray spectrometers. The iron content of coatings can be calculated on the linear or quadratic linear relation by measuring the X-ray intensity of characteristic elements of the samples.

3. Results and Discussion

3.1 Influencing factors of the fundamental parameter method

The irradiation depth of the K-line of metal elements detected by the XRF instrument is approximately 200 g/m². Since steel is the base material of zinc-iron alloy steel plates, the determination of iron content in coatings via the K-line of Fe is inevitably disturbed by Fe in the substrate. The detection principle of the Simultix 14 XRF spectrometer is to detect Fe- K_{α} at different angles. High-energy spectral lines were used to measure the deeper position of the zinc-iron alloy layer as much as possible. In order to distinguish the thickness of the coating and the signal of iron content in the coating,

Table 1. Measurement conditions of XRF spectrometers

Instrument	Method	Element	Spectral line	Integration time /s	PHA	Detector
Simultix 14	FP method	Zn/Fe	Zn- K_{β} Zn- K_{α} Fe- K_{α} Fe- K_{α}	20	100–300	PC/SC
ZSX Primus	Empirical coefficient method	Fe	$K_{\beta 1}$	20	100–300	SC
Magix Pro	Empirical coefficient method	Fe	$K_{\beta 1}$	20	100–300	SC

different fluorescence intensities of zinc and iron were collected at high and low angles. The fluorescence signals were calculated by the ratio processing method using the FP method [15]. Strength ratios of $Zn-K_{\alpha}(20^{\circ})/Fe-K_{\alpha}(20^{\circ})$ and $Zn-K_{\beta}(40^{\circ})/Fe-K_{\alpha}(40^{\circ})$ were calculated and corrected by the FP method. The iron content of the coating was obtained by establishing a mathematical model (Fig. 1).

Irradiation through this method can reach the coating depth of 200 g/m^2 , and the coating thickness of zinc-iron alloy steel plate is generally 30–70 g/m^2 . Therefore,

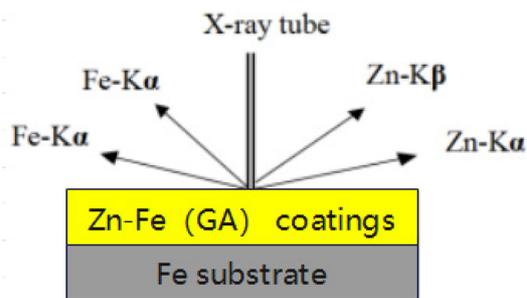


Fig. 1. Principle diagram of Simultix 14 X-ray fluorescence spectrometer of Rigaku

in principle, this method can detect iron content in the coating of all zinc-iron alloys. This method has been practically applied in the author’s laboratory for ten years. However, this method was unsuitable for two types of samples: low-coating and ultra-high-strength steel substrates. Low-coating zinc-iron alloy samples of 30–40 g/m^2 or lower cannot be tested by this method, mainly due to the insufficient detection resolution in the low coating caused by the detection principle of the equipment [4]. For zinc-iron alloys with ultra-high-strength steel substrate, equipment test results are occasionally completely consistent with those of the chemical method. However, abnormally high test results are also possible.

Table 2 shows the results of iron content measurement in the coating via the FP and chemical methods for a zinc-iron alloy sample of a certain steel-grade substrate with ultra-high strength.

As shown in Table 2, for zinc-iron alloy samples with a substrate of the same steel grade, two different determination results were obtained by the FP method. Some findings were consistent with those of the

Table 2. Test results between XRF fundamental parameter and chemical methods

Sample	Iron content in the coating/%			Substrate state after coating stripping	Remark
	FP method	Chemical method	Deviation		
1	12.1	8.4	3.7		With stripe defects
2	13.8	8.5	5.3		With stripe defects
3	12.6	12.8	-0.2		No stripe defects
4	10.6	10.1	0.5		No stripe defects

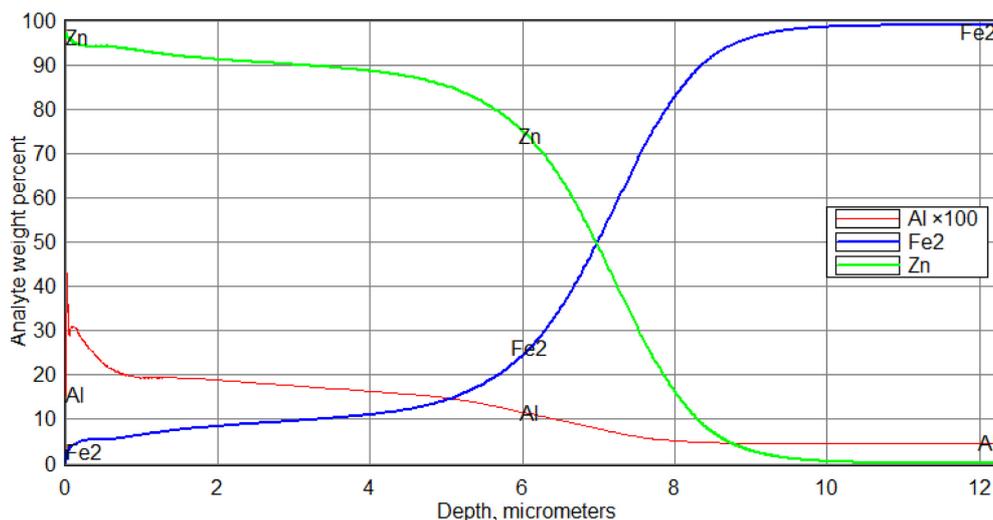


Fig. 2. GDS analysis chart of the Zn–Fe alloy sample plate

chemical method, and others were abnormally high. Abnormally high results occurred for samples with black stripe defects on the substrate after coating stripping due to the transformation of black stripe defects on the substrate to an abnormal bulge after high-temperature treatment, which shortened the optical path of X-ray of Fe and led to high values. However, whether such black stripe defects will appear on the zinc–iron alloy substrate of the same steel grade could not be observed from the surface. These defects can only be detected after the coatings are stripped by the chemical method, and whether these substrate stripes would appear on the zinc–iron alloy sample could not be predicted in advance. Therefore, there are high risks of result deviation for such samples measured by the FP method.

3.2 Influencing factors of the empirical coefficient method

The empirical coefficient method selected the characteristic spectral lines of Fe- L_{α} through experiments. The XRF irradiation depth of Fe- L_{α} was generally 10 g/m^2 . Thus, the influence of iron on the substrate can be completely avoided. A 10 g/m^2 detection depth was observed for the Fe- L_{α} spectrum line, and such a value was needed by the 10 g/m^2 coating to represent all coatings. Glow Discharge Optical Emission Spectrometry (GDS) is a spectral analysis technique developed based on the principle of inert gas discharge at low pressure. The quantitative layer by layer analysis of GDS results in a graph with the analysis depth (m) of the tested sample

as the x-axis and the mass fraction (%) of the elements as the y-axis [15]. Fig. 2 shows the GDS analysis diagram of the zinc–iron alloy sample plate.

As presented in Fig. 2, iron content in the whole zinc–iron alloy coating was uneven and gradually increased with the increase in coating depth. The theoretical basis for the accurate determination of this method was based on the results presented in Fig. 3. The change trends of iron in the coating of standard samples used to establish the calibration curve of the XRF empirical coefficient method and samples to be tested were similar. Therefore, this method can be used to determine iron content in coatings when standard samples and samples to be tested match.

The control test between the empirical coefficient and chemical methods was carried out on zinc–iron alloy samples of various steel grades using the same process in the same production unit. The results are shown in Table 3.

As presented in Table 3, the results of the empirical coefficient method were in agreement with those of the chemical method in the same production process. Whether iron content distribution in the zinc–iron alloy coating is consistent for different production processes and areas needs to be tested and confirmed before this method is practically applied. If iron content distribution in the coating is inconsistent, specific XRF calibration curves must be established to ensure the accuracy of measurement results.

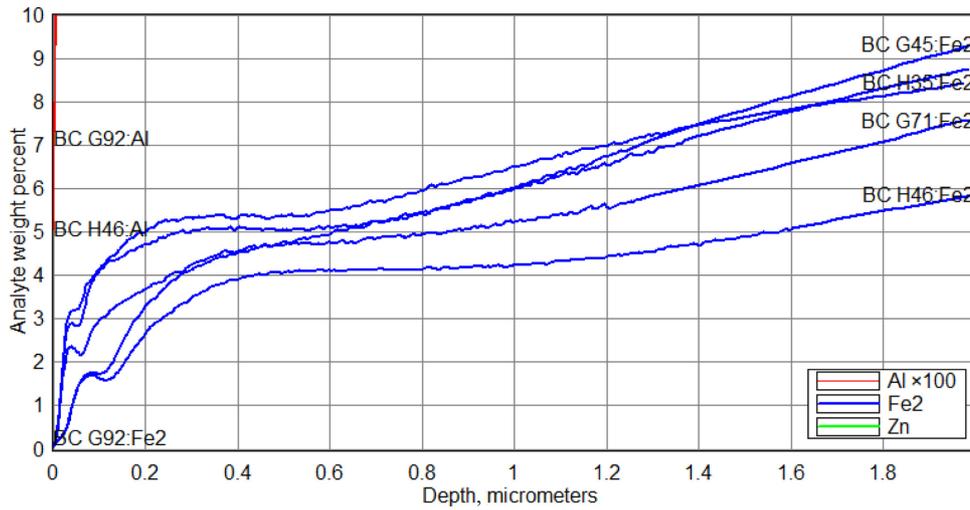


Fig. 3. Distribution of Fe content in the Zn–Fe alloy sample plate

Table 3. Test results between empirical coefficient and chemical methods (%)

Samples	Iron content in the coating		
	Empirical coefficient method	Chemical method	Deviation
1	10.37	10.15	-0.22
2	10.19	9.60	-0.59
3	10.86	10.37	-0.49
4	10.98	11.35	0.37
5	10.05	10.51	0.46
6	10.18	9.76	-0.42
7	9.55	9.22	-0.33
8	9.42	9.53	0.11
9	9.45	8.29	-1.16
10	9.05	9.41	0.36
11	9.22	9.00	-0.22

3.3 Precision test

Different methods were used to repeatedly determine the iron content of coatings on 11 zinc–iron alloy samples, which were continuously punched along the

rolling direction on the same steel coil. Relative standard deviations of the results were calculated, and findings are listed in Table 4. The results show that the repeatability of FP and empirical coefficient methods reaches 0.2% and

Table 4. Precision test (n = 11) (%)

Method	Result	Average	Standard deviation
Fundamental parameter method	10.51, 10.72, 10.70, 10.86, 10.37, 10.84, 10.37, 10.88, 10.50, 10.45, 10.82	10.64	0.2
Empirical coefficient method	10.42, 10.70, 11.35, 10.63, 10.98, 10.27, 10.65, 10.25, 10.15, 10.82, 10.35	10.60	0.4
Chemical method	10.42, 9.52, 9.97, 10.63, 11.21, 9.68, 10.27, 11.18, 9.57, 10.07, 11.04	10.32	0.6

0.4%, respectively, which are better than that of the chemical method (0.6%).

4. Conclusions

Although the iron element substrate can cause serious interference in the X-ray fluorescence detection of iron content in the galvanized coating of zinc-iron alloy, X-ray fluorescence can still reduce this interference through methods such as FP method or selecting L_{β} spectral line with shallow excitation depth. In this paper, the application of XRF methods to determine the iron content in zinc-iron alloy steel plate coating has been established and well applied in quality control of zinc-iron alloy. According to the discussion and analysis above, several conclusions can be summarized as follows.

(1) FP and empirical coefficient XRF methods can be applied in the production quality control of zinc-iron alloy coatings, and the detection repeatability of XRF methods was better than that of the chemical method.

(2) For zinc-iron alloy coatings with 30–40 g/m² or lower and ultra-high-strength steel as substrate, accuracy was poor due to the defect of detection sensitivity of the FP method and limitation of the XRF optical path. The application of this method in these kinds of samples should be studied more carefully.

(3) Application of the empirical coefficient method in the detection of iron content in zinc-iron alloy steel plate coating was closely related to the distribution characteristics of iron content in the coating caused by the production process and process stability of the unit. The detection accuracy of zinc-iron alloy coatings produced by different units was poorer than that of the chemical method if the same XRF linear relation was used, and thus, such a procedure should be carefully applied.

References

1. J. S. Liu, F. Li, R. D. Liu, Influence factors on properties and research progress of galvannealed technology, *Hot Working Technology*, **39**, 155 (2010). https://caod.orioprobe.com/articles/26518108/Influence_Factors_on_Properties_and_Research_Progr.htm
2. J. X. Wang, B. F. Huang, Discussion on the influence of iron content in hot galvanizing alloyed layer on coating mass by X-ray fluorescence spectrometry, *Metallurgical Analysis*, **38**, 41 (2018). https://caod.orioprobe.com/articles/54209087/Discussion_on_the_influence_of_iron_content_in_hot.htm
3. D. C. Lou, J. J. Qiao, D. Wen, J. G. Diao, Y. Li, S. G. Yu, Study on process control for iron content of coating of GA, *Steel Rolling*, **31**, 12 (2014). Doi: <https://doi.org/10.13228/j.boyuan.issn1003-9996.20140055>
4. Christian Petrilli, The basics of coating thickness measurement, *Metal Finishing*, **99**, 10-13 (2001). Doi: [https://doi.org/10.1016/S0026-0576\(01\)81189-2](https://doi.org/10.1016/S0026-0576(01)81189-2)
5. ISO 3497:2000, Non-destructive determination of the coating film thickness by X-ray powder diffractometry and correlation with the dissolution behavior of film-coated tablets (2000). <https://www.iso.org/standard/20319.html>
6. ASTM B568-98, Standard Test Method for Measurement of Coating Thickness by X-Ray Spectrometry (2021). <https://www.astm.org/b0568-98r21.html>
7. GB/T 16921-2005, Metallic coatings-Measurement of coating thickness X-ray spectrometric methods (2005). <https://std.samr.gov.cn/gb/search/gbDetailed?id=71F772D7C7DD D3A7E05397BE0A0AB82A>
8. A. G. Revenko, A. L. Tsvetyansky, A. N. Eritenko, X-ray fluorescence analysis of solid-state films, layers, and coatings, *Radiation Physics and Chemistry*, **197**, 110157 (2022). Doi: <https://doi.org/10.1016/j.radphyschem.2022.110157>
9. Stefano Martinuzzi, Claudia Giovani, Walter Giurlani, Emanuele Galvanetto, Nicola Calisi, Michael Casale, A robust and cost-effective protocol to fabricate calibration standards for the thickness determination of metal coatings by XRF, *Spectrochimica Acta Part B: Atomic Spectroscopy*, **182**, 106255 (2021). Doi: <https://doi.org/10.1016/j.sab.2021.106255>
10. Kataoka Yuyuki, Kono Hisashi, Kawara Naoki, Koshi Tomotomoyou, Nishiye, Makoto Nakamura Hideki, Development and Application of Basic Parameter Method in XRF Analysis, *The japan society for analysis chemistry*, **69**, 363 (2020). Doi: <https://doi.org/10.2116/bunsekikagaku.69.363>
11. D. K. G. de Boer, Fundamental parameters for X-ray fluorescence analysis, *Spectrochimica Acta Part B: Atomic Spectroscopy*, **44**, 1176 (1989). Doi: [https://doi.org/10.1016/0584-8547\(89\)80114-4](https://doi.org/10.1016/0584-8547(89)80114-4)
12. M. Bos, J. A. M. Vrielink, Constraints, iteration schemes and convergence criteria for concentration calculations in X-ray fluorescence spectrometry with the use of fundamental parameter methods, *Analytica Chimica*

- Acta*, **373**, 291-302 (1998). Doi: [https://doi.org/10.1016/S0003-2670\(98\)00412-7](https://doi.org/10.1016/S0003-2670(98)00412-7)
13. X. Y. Hana, S. J. Zhuo, R. X. Shen, P. L. Wang, A. Jia, Comparison of the quantitative results corrected by fundamental parameter method and difference calibration specimens in X-ray fluorescence spectrometry, *Journal of Quantitative Spectroscopy & Radiative Transfer*, **97**, 68 (2006). Doi: <https://doi.org/10.1016/j.jqsrt.2004.12.018>
 14. J. J. Wang, C. Fan, Discussion on influencing factors during the determination of iron content in galvanized coating of zinc-iron alloy by X-ray fluorescence spectrometry, *Metallurgical Analysis*, **39**, 49 (2019). https://caod.oriprobe.com/articles/57598581/Discussion_on_influencing_factors_during_the_deter.htm
 15. Takao Moriyama, Kenji Kodama, X-ray fluorescence analysis of zinc and zinc-iron alloy coated steel sheet, *Rigaku journal*, **38**(2), 25-29 (2018). [https://resources.rigaku.com/hubfs/2024%20Rigaku%20Global%20Site/Resource%20Hub/Knowledge%20Library/Rigaku%20Journals/Volume%2034\(2\)%20-%20Summer%202018/RigakuJournal34-2_25-29.pdf](https://resources.rigaku.com/hubfs/2024%20Rigaku%20Global%20Site/Resource%20Hub/Knowledge%20Library/Rigaku%20Journals/Volume%2034(2)%20-%20Summer%202018/RigakuJournal34-2_25-29.pdf)
 16. Y. Zhang, Y. Y. Chen, Z. Y. Zhang, Analysis of Galvanized Steel Sheets by Glow Discharged AES, *Physical Testing and Chemical Analysis Part B Chemical Analysis*, **40**, 191 (2004). https://caod.oriprobe.com/articles/7607419/ANALYSIS_OF_GALVANIZED_STEEL_SHEETS_BY_GLOW_D ISCHA.htm