Chemical Analysis of Zinc Electroplating Solutions by X-ray Fluorescence Spectrometry

Sung-Mo JUNG,1) Young-Mo CHO2) and Han-Gil NA2)

1) Graduate Institute of Ferrous Technology, Pohang University of Science and Technology, Pohang 790-784, Korea.
2) Chemical Testing Section, Quality Control Department of POSCO, Kwangyang 545-010, Korea.
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A quantitative analysis method used to analyze chlorine, iron and zinc in electroplating solutions, using X-ray spectrometry in atmospheric He mode, is proposed. The present research concerns the replacement of the conventional analyses of electroplating solutions with rapid and reproducible quantification using X-ray fluorescence spectrometer. An in-depth investigation conducted in the present study identifies the species present in the real electroplating solutions. XRD patterns and semi-quantitative results for the electroplating solutions show synthetic standards based on the compositional range of solutions by analyzing the electroplating solutions obtained in real processes. 28 calibration standard solutions are prepared by diluting liquid standard solutions certified by titration and ICP-OES analyses used to construct the XRF calibration curves for Cl, Fe and Zn. The suggested method showed satisfactory precision and accuracy in the analysis of electroplating solutions. The present study provides evidences that the proposed XRF spectrometry could be an alternative analytical method to replace the conventional techniques by comparing the uncertainties estimated for each method.

KEY WORDS: electroplating solutions; chlorine; iron; zinc; atmospheric He mode; calibration standards; XRF; quantification.

1. Introduction

A growing emphasis has been placed on improving the quality of the surface-treated steel sheets using copper, nickel, tin, chromium and zinc since their applications have been extended to the field of electric home appliances, automobiles, building materials, etc. In particular, large development of the electroplating of zinc and zinc alloys on continuous steel sheets has been devoted to build a comprehensive edge against hot dip galvanizing. Commercial zinc plating is accomplished in cyanide baths, alkaline non-cyanide baths, and acid chloride baths. In the 1970s, most commercial zinc plating was carried out in conventional cyanide baths, but the strong international effort to reduce pollution emissions has led to the development of other processes. Today alkaline noncyanide and acid chloride baths comprise most of the production.1,2) POSCO is making efforts to improve the surface quality of steel sheets by homogenizing the microstructure of a coated layer by controlling the amount of additive and the composition of electroplating solutions in the acid chloride baths for continuous electroplating lines of zinc and zinc alloys. In particular, the concentrations of important elements such as chloride, iron, zinc, etc., in the electroplating solutions must be closely monitored and controlled because they can significantly affect the quality of the electroplated steel sheets. POSCO is currently analyzing the amount of Zn, Cl and Fe in acid chloride electroplating solutions of zinc in terms of inductively coupled plasma optical emission spectrometer (ICP-OES).3) NH₄SCN and K₂Cr₂O₇ titrations,4,5) respectively. However, it is required to perform some preliminary treatment prior to employing the methods mentioned above during the analysis. Furthermore, environmental concerns put restriction on the chemical use required for the treatment. In addition, significant errors may arise from diluting weight/volume percent of constituents in solutions to the ppm level when using the spectroscopic analytical method like ICP-OES.

Over a number of years, X-ray fluorescence spectrometry (XRF) has been widely used as a routine instrumental technique for analyzing liquids produced in the refinery and petrochemical industries. A variety of applications has emerged for this established XRF technique. These include simple and single element calibrations such as sulfur in diesel, lead in gasoline, more complex methods for analyzing sulfur, nickel and vanadium in fuel oils, and additives in lubricating oils, respectively.6–8) In the present study, XRF is applied to the chemical analysis of zinc electroplating solutions, which alleviate the necessity of solution pretreatment and labor intensive analysis procedure.

2. Experimental

2.1. X-ray Fluorescence Spectrometer Configuration

The Bruker-AXS S4 Pioneer uses a 4 kW ceramic end-window X-ray tube with an ultra-thin 75 μm beryllium win-
This X-ray tube is positioned below the sample to optimize the presentation of liquid sample to the X-ray beam. A closely coupled optical path helps to provide high intensities and low detection limits for all elements. Automatic computer control of the generator allows the kV and mA settings to be adjusted automatically for each element. The measuring conditions and goniometer settings were programmed by the Bruker-AXS software “SpectraPlus” and summarized in Table 1. This application software was employed to calculate theoretical “variable α coefficients”. The α coefficients correct the absorption or enhancement of secondary radiation due to inter-element or matrix effects.

2.2. Analytical Procedure

It is crucial to find the proper standard materials certified by accurate and precise test methods for XRF measurement of electroplating solutions because XRF spectrometry is a secondary analytical technique. In other words, XRF spectrometer should be calibrated using certified standard materials before unknown samples are analyzed. However, reliable standard solutions in accordance with zinc electroplating solutions are not available in markets. In the present study, the electroplating solutions sampled from the surface treatment processes were used as standard solutions by determining their compositions via ICP-OES and titration methods. Each value in Table 2 was obtained by three repeated measurements of each element in the solutions, and the precision RSD values showed less than 1.5%. This result indicates that the analysis methods employed could be considerably reproducible for certifying standard electroplating solutions.

In the substantial analyses of the electroplating solutions, 10 mL of an unknown solution was transferred to 100-mL of a volumetric flask and 5 mL of HNO₃(1+1) was added for dissolving some residue in the original solutions. Then the solution was diluted to the mark with water, which was in turn mixed for homogeneous liquid. Individual specimens were prepared by pouring 7 g of the diluted solution into 40 mm diameter plastic cells that were fitted with 12 mm polypropylene windows. These liquid cells were then placed into sample cups fitted with stainless steel masks having openings of 34 mm in diameter. Each cell was vented during the analysis in order to prevent the polypropylene window from bulging.

The X-ray tube excitation was controlled according to the optimal condition of each spectral line of chlorine, iron and zinc. The whole calibration and the resulting standard deviation of the calibration curve were calculated using the 32 bit software SPECTRAplus. The measurement of each solution takes about three minutes with the SPECTRAplus automatic measurement time optimization set to check for the maximum 0.2 % deviation of counting statistics.

3. Results and Discussion

3.1. X-ray Diffraction Analysis of the Zinc Electroplating Solutions Dried onto the Filter Paper and Semi-quantitative XRF Measurement

It is necessary to identify the zinc electroplating solu-

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Table 1. Summary of the analyzing parameters used to measure chlorine, potassium, iron and zinc in electroplating solutions of zinc.

| Element   | Cl | Fe | Zn |
|-----------|----|----|----|
| Analyte line | Cl Kα | Fe Kα | Zn Kα |
| Analyzer crystal | PET | LiF200 | LiF200 |
| 2d=0.8752 nm | 2d=0.4026 nm | 2d=0.4026 nm |
| Reflection order | 1° | 1° | 1° |
| Peak 20 angle | 65.440° | 57.536° | 41.809° |
| 20 angle of background 1 (Weight) | 67.606° | 59.483° | 43.304° |
| (1) | (1) | (1) |
| 20 angle of background 2 (Weight) | - | - | - |
| Primary collimator | 0.46° | 0.46° | 0.46° |
| Detector | Flow proportional counter | Scintillation counter | Scintillation counter |
| Mask | 34 mm | 34 mm | 34 mm |
| Mode | Atmospheric He | Atmospheric He | Atmospheric He |
| X-ray tube voltage | 27 kV | 60 kV | 60 kV |
| X-ray tube current | 114 mA | 51 mA | 51 mA |
| Count time | 60 seconds at peak angle | 60 seconds at peak angle | 60 seconds at peak angle |
| | 30 seconds at background angle | 30 seconds at background angle | 30 seconds at background angle |
tions in advance in order to examine the possibility of analyzing them by XRF. The concentration method was employed to indirectly predict the kinds of chemical species that are favorable in the solutions. In other words, the solutions were evaporated straight onto a filter paper of confined spot, which were followed by X-ray diffraction measurement, as shown in Fig. 1. It is believed that the primary chemical species are K₂ZnCl₄ and KCl. This indicates that they comprise the major compounds of the acid chloride electroplating solutions of zinc, which are usually monitored by analyzing the concentrations of chlorine, iron and zinc in the real process.

In addition, semi-quantitative XRF analysis was also performed to acquire some information on zinc electroplating solutions, as shown in Fig. 2. The XRF spectral lines of Cl, K, Fe and Zn were identified and the effective penetration depth of each characteristic radiation was estimated due to the automated calculation, as indicated in Fig. 2. Considering that about 7 g of liquid sample could fill the cup up to the height of about 7.4 mm, it is believed that XRF analysis is not influenced by the amount of liquid sample.

### 3.2. Preparation of Standard Solutions by Certifying Factory Electroplating Solutions

Two kinds of modes available in the XRF spectrometer for liquid measurements were employed, in this study. The He mode is usually selected for the analysis of most of non-volatile liquids with spectrometer kept in vacuum. The second mode, atmospheric He mode, is selected for the measurement of volatile elements in solutions where reproducible measurement should be required for acid-based solutions. The previous research\(^{10}\) convey that the precision RSD values of the volatile element like chlorine measured in atmospheric He mode were significantly smaller than those in He mode. This might indicate that the X-ray radiation has an influence on the heating of acid-based solutions and on the rapid decrease of solution acidity with time. Henceforth, the present study employed the atmospheric He mode for XRF measurement of zinc electroplating solutions.

### Table 2. The analysis results of 14 factory electroplating solutions of zinc certified by titrations and ICP-OES.

| Sample | Cl | Fe | Zn |
|--------|----|----|----|
|        | NH₄SCN Titrations\(^b\) | K₂Cr₂O₇ Titrations by SnCl₂•H₂O reduction\(^b\) | ICP-OES\(^\ast\) |
| 01-ZF  | 26.49 w/\% | 1.30 w/\% | 7.49 w/\% |
| 02-ZF  | 23.45    | 1.16   | 5.760 |
| 03-ZF  | 23.45    | 1.17   | 5.711 |
| 04-ZF  | 23.45    | 1.15   | 5.779 |
| 05-ZF  | 23.51    | 1.16   | 5.759 |
| 06-ZF  | 23.21    | 1.08   | 5.485 |
| 07-ZF  | 23.27    | 0.99   | 5.487 |
| 08-ZF  | 23.63    | 1.16   | 5.728 |
| 09-ZF  | 16.34    | 0.76   | 3.750 |
| 10-ZF  | 17.74    | 1.01   | 4.656 |
| 11-ZF  | 19.56    | 0.89   | 4.836 |
| 12-ZF  | 24.29    | 1.33   | 5.751 |
| 13-ZF  | 24.79    | 1.42   | 6.573 |
| 14-ZF  | 25.46    | 1.60   | 6.465 |

\(^{b}\) Determined by titration.
\(^{\ast}\) Determined by ICP-OES.

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From fourteen standard solutions in Table 2, 28 liquid calibration standards were prepared by means of diluting the solutions with water 15 and 10 times. Their compositions were calculated and expressed in units of weight/volume percent (w/v%) considering only the dilution factors of 15 and 10 since the densities of diluted solutions in Table 3 could be approximated to be 1.00 g/mL. This provided not only an appropriate compositional range, but also a wide spread of calibration data points over the range of each component to be calibrated.

### 3.3. Constructing of XRF Calibration Curves of Chlorine, Iron and Zinc Using Twenty-eight Liquid Standards

The calibration curves for chlorine, iron and zinc were constructed from 28 liquid standards by plotting the corrected intensities and chemical concentrations of the standards as shown in Figs. 3–5. The results illustrate excellent linear correlations between corrected X-ray intensities and concentrations of chlorine, iron and zinc. The SPECTRAplus software includes the data of variable $\alpha$ absorption coefficients which were derived from first principles using matrix data, spectrometer geometry and primary X-ray characteristics, based on the de Jongh’s model. In addition, the overlap of spectral lines from different elements in electroplating solutions was corrected by a mathematical curve fitting technique whose applications were performed by the software in the user-friendly manner.

| Standards | Cl (w/v%) | Fe (w/v%) | Zn (w/v%) |
|-----------|-----------|-----------|-----------|
| Std01-ZF  | 1.766     | 0.087     | 0.499     |
| Std02-ZF  | 1.563     | 0.077     | 0.384     |
| Std03-ZF  | 1.563     | 0.078     | 0.381     |
| Std04-ZF  | 1.563     | 0.077     | 0.385     |
| Std05-ZF  | 1.567     | 0.077     | 0.384     |
| Std06-ZF  | 1.547     | 0.072     | 0.366     |
| Std07-ZF  | 1.551     | 0.066     | 0.366     |
| Std08-ZF  | 1.575     | 0.077     | 0.382     |
| Std09-ZF  | 1.089     | 0.051     | 0.250     |
| Std10-ZF  | 1.183     | 0.067     | 0.310     |
| Std11-ZF  | 1.304     | 0.059     | 0.322     |
| Std12-ZF  | 1.619     | 0.089     | 0.383     |
| Std13-ZF  | 1.653     | 0.095     | 0.438     |
| Std14-ZF  | 1.697     | 0.107     | 0.431     |
| Std15-ZF  | 2.649     | 0.130     | 0.749     |
| Std16-ZF  | 2.345     | 0.116     | 0.576     |
| Std17-ZF  | 2.345     | 0.117     | 0.571     |
| Std18-ZF  | 2.345     | 0.115     | 0.578     |
| Std19-ZF  | 2.351     | 0.116     | 0.576     |
| Std20-ZF  | 2.321     | 0.108     | 0.549     |
| Std21-ZF  | 2.327     | 0.099     | 0.549     |
| Std22-ZF  | 2.363     | 0.116     | 0.573     |
| Std23-ZF  | 1.634     | 0.076     | 0.375     |
| Std24-ZF  | 1.774     | 0.101     | 0.466     |
| Std25-ZF  | 1.956     | 0.089     | 0.484     |
| Std26-ZF  | 2.429     | 0.133     | 0.575     |
| Std27-ZF  | 2.479     | 0.142     | 0.657     |
| Std28-ZF  | 2.546     | 0.160     | 0.647     |

Fig. 3. Cl calibration curve for electroplating solutions of zinc by XRF using the proposed method with dilution of 10 and 15 times.
In constructing the calibration curves, several standards out of 28 standard solutions were first measured in scan mode in order to determine the most optimal positions of peak and background signals for the highest intensities of each element radiation before calibration. Then, the subsequent measurements were made in fixed mode. This procedure plays a key role in improving the spectral line sensitivities of chlorine, iron and zinc, resulting in decreasing the minimum detection limit (MDL). The minimum detection limit is frequently considered to compare the detection limits of elements to be analyzed among comparative analytical methods. It is defined as the concentration of an element that gives a signal is equal to three times the standard deviation of the background level.

Since both the background intensity and the sensitivity of a spectral line are affected by the matrix, the minimum detection limit is determined not only by the atomic number of the measured element but also by the sample matrix. The MDL for the elements in electroplating solutions were calculated at a counting time of 60 s for the peak and 30 s for background. Based on the measurement parameters in Table 1, the calculated value of MDL for each element is listed in Table 4. The detection limits generated by the electroplating standard solutions are much lower than those for the same elements in condensed matrices such as steels or oxides and they are nearly equivalent to those obtained from the spectroscopic analytical methods like atomic absorption spectroscopy.

3.4. Compatibility of XRF Measurement and Conventional Analytical Methods (Titration and ICP-OES) in Terms of Precision Tests and Uncertainty Quantification

In practice, the fitness for purpose of analytical methods applied for routine testing is most commonly assessed through method validation studies. Such studies produce data on the overall performance and on individual influence factors which can be applied to the estimation of uncertainty associated with the results of the method in normal use. The factors include precision, bias, linearity, detection limit, robustness, etc.

First of all, the precision tests for Cl, Fe and Zn were performed on the 10-time diluted unknown solution (01UZF) obtained from factory electroplating process in order to evaluate the validity of the XRF calibration curves constructed in this study. As shown in Table 5, the precision RSD values for Cl, Fe and Zn in the solutions are less than 0.5%. This indicates that XRF spectrometry is highly precise for the chemical analysis of the 10-time diluted electroplating solutions.

Secondly, the comparison of uncertainty quantification was made for the conventional methods and XRF spectrometry. The techniques necessary to evaluate uncertainty were applied to the chemical analyses of Cl, Fe and Zn in the solutions. The techniques necessary to evaluate uncertainty were applied to the chemical analyses of Cl, Fe and Zn in the

Table 4. Calibration range and calculated minimum detection limit (MDL) of each element in the electroplating solutions.

| Element | Calibration Range (w/v%) | MDL (ppm) |
|---------|--------------------------|-----------|
| Cl      | 1.09 – 2.65              | 5.5 – 8.7 |
| Fe      | 0.054 – 0.173            | 1.1 – 1.6 |
| Zn      | 0.25 – 0.75              | 0.9 – 1.2 |

Table 5. Precision RSD values used in repeatability tests to obtain the 10-time diluted unknown electroplating solution of zinc.

| Solution | Measurements | Cl  | Fe  | Zn  |
|----------|--------------|-----|-----|-----|
| Test1    | 2.558 w/v%   | 0.150 w/v% | 0.731 w/v% |
| Test2    | 2.555        | 0.151 | 0.732 |
| Test3    | 2.550        | 0.151 | 0.732 |
| Average  | 2.554        | 0.151 | 0.732 |
| SD       | 0.004        | 0.000 | 0.000 |
| Precision RSD | 0.16%       | 0.21% | 0.06% |
Electroplating solutions by conventional methods and XRF spectrometry. That is, the uncertainty sources were identified and set out in a cause and effect diagram as in Fig. 6 and Fig. 7. And the figures indicate that numerous factors in the process of sample preparation and calibration work contributed to the concentration uncertainties of Cl, Fe and Zn. In Fig. 8, the measured concentrations of Cl, Fe and Zn obtained by using conventional methods and XRF spectrometry were also compared. The uncertainties estimated for XRF measurement can be comparable to those for conventional methods when comparing them at a 95% confidence level. On the other hand, three standard solutions of chlorine, iron and zinc being certified by ICP analysis were measured by the calibration curves constructed in the pres-
ent study in order to examine the bias of the lines as shown in Table 6. Table 6 showed that the standard solutions are accurate and highly precise even though the concentrations of Cl and Zn are not within the calibration range except for Fe from the view of factory operation. Therefore, it is believed that XRF measurement could be an alternative analytical method for the zinc electroplating solutions considering that the conventional methods employed for determining Cl, Fe and Zn require the complicated procedure comprising numerous steps of pretreatments and consume many hazardous chemicals with labor intensive work.

4. Conclusions

The present study demonstrates that the multi-component analysis of zinc electroplating solutions, using XRF spectrometry, can be performed with simple sample preparation, which is using just 10-time dilution. This technique provides rapid, accurate and precise analytical results with broad applications in solution-involved operations. 28 synthetic standard solutions used in preparation of zinc electroplating solutions provide highly linear calibration curves. In constructing the calibration curves, the corrections for line overlaps and matrix effects were carried out with the help of the application of the “SPECTRAplus” software. The comparison of the uncertainties estimated for XRF measurement and for the conventional analytical methods at a 95% confidence level showed that XRF measurement could be an alternative analytical method of analyzing zinc electroplating solutions from the standpoint of precision and accuracy.

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