On-line Analyzer for Ni–Zn Alloy Electroplating Bath

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In the production of Ni–Zn alloy electroplated sheet steels, the concentrations of Ni$^{2+}$ and Zn$^{2+}$ ions in the plating bath are necessary to be controlled. An automatic on-line analyzer has been developed for the process control. The on-line analysis system consists of a sampling system and an energy-dispersive X-ray fluorescence analyzer. The plating process solution is continuously supplied to the X-ray fluorescence analyzer through the sampling system. The concentrations of the Ni$^{2+}$ and Zn$^{2+}$ ions are determined from the intensities of Ni, Zn, Fe and S fluorescent lines. The intensities of the S and Fe lines are measured for interelement correction. The intensity of the S line is easily measured after a drop in air with the energy-dispersive X-ray spectrometer. The S line is excited by chromium, and the Ni, Zn and Fe lines are by tungsten X-ray source, for obtaining a higher excitation efficiency. The analysis can be completed within 8 min. The analytical accuracies on the production line were 0.77 g/l for Ni$^{2+}$ and 0.48 g/l for Zn$^{2+}$ ion.

KEY WORDS: Ni–Zn alloy electroplating; concentration determination; plating bath; on-line analyzer; X-ray fluorescence analysis.

1. Introduction

In the production of alloy electroplated steel sheets, the concentrations of bath components must be maintained within limited ranges to ensure optimum performance. For this purpose bath compositions are necessary to be monitored and the concentration of each bath component is determined by means of an on-line analyzer. Some types of on-line analyzers for electroplating baths have been reported. Yasui et al. developed an on-line system for X-ray fluorescence analysis of droplet-drying technique. A filter paper containing the plating solution substances is analyzed with a wavelength-dispersive X-ray fluorescence spectrometer after pre-treatments such as dilution, dropping on to a filter, and drying. Kondo et al. developed an on-line analyzer by inductively coupled plasma spectrometry (ICP). The plating solution is diluted and continuously analyzed. The present paper describes an on-line energy-dispersive X-ray fluorescence analysis system for a Ni–Zn alloy plating bath. The plating process solution is supplied during processing to the analytical system to be analyzed without needs of complex pre-treatments such as dilution and addition of any reagent. This analytical system has been operated for 7 years without any trouble.

2. Outline of System

Fig. 1 shows the block diagram of the present on-line analysis system. The on-line analyzer consists of a sampling system in the production line and an energy-dispersive X-ray fluorescence analyzer in an enclosed analyzer house near the process line. The analyzer house is air-conditioned to protect the instruments from the corrosive environment of plant for stable operation of the analyzer. The plating process solution is continuously pumped to the X-ray fluorescence analyzer and flows through the sampling system so that it is acceptable to the X-ray fluorescence analyzer. The sampling system consists of a cooler for cooling the sampled solution, a filter for separating solid suspensions, and an overflow tank for removing bubbles. The main components of the plating solution are Ni$^{2+}$, Zn$^{2+}$ and SO$_4^{2-}$ ions and minor components Na$^+$ and Fe ions. The intensities of Ni, Zn, Fe and S fluorescent X-rays are measured. The measured intensities are converted to the concentration of each component by iteration procedure and the analytical results are displayed on CRT's installed in the analyzer house and in the plant control room. Since each concentration of Fe$^{2+}$ and Fe$^{3+}$ ions is difficult to be determined separately by X-ray fluorescence spectrometry the concentration of Fe$^{2+}$ and Fe$^{3+}$ ions is obtained as a total Fe ion concentration.

2.1. Sampling System

Successful analysis by the process analyzer depends to a large extent on the sampling system. The function of the sampling system is to prepare the sample acceptable to the analyzer. The schematic diagram of the present sampling system is shown in Fig. 2. The solution is cooled to room temperature in the
cooler by circulating water. Excessive cooling of the solution may lead to the formation of dews on the Mylar (polyethylene terephthalate) film window of the sample cell of the X-ray fluorescence analyzer and insufficient cooling may cause an expansion of the Mylar film. These phenomena have influence on X-ray intensities and cause determination errors. A cross section of the filtering system is shown in Fig. 3. A filter consists of elements of hollow polyvinyl alcohol fiber membrane sheathed in a shell of polyvinyl chloride. The elements in a filter are 1 000 mm in length and 7 m² in effective area resistant to SO₂⁻. The membrane can remove suspended particles in the minimum size of about 0.1 to 0.5 μm from the plating solution. The filter system is composed of two filter units; one filter unit is cleaned by means of air back-flushing while the other filter is in operation. The overflow tank is low headed for constant flow into the sample cell of the X-ray analyzer. The overflow tank is introduced into the sample cell at a constant flow rate. Entrapped air and bubbles in the plating solution can escape from the overflow tank. If the plating operation stops and the plating solution does not flow to the on-line analysis system, water is supplied from the water-tank to the sample cell to prevent drying and precipitation of plating solution substances on the wall of the flow tube and the sample cell. The flow rate of sample through the cell is 0.2 l/min. The plating solution is pumped at a flow rate of 20 l/min from plating trays to the on-line analysis system to reduce the time lag between sampling and analysis, and most of the solution is immediately returned to the plating trays. Measurement can be performed within 15 min after sampling.

2.2. X-ray Fluorescence Analyzer

The schematic diagram of the X-ray fluorescence analyzer is shown in Fig. 4: a sample cell, a reference plate, an excitation source instrument and an X-ray spectrometer with a Si (Li) detector. Some cells were used for continuous analysis of liquid samples like slurry. A sample cell shown in Fig. 5 was newly designed for the present on-line analyzer. The cell window is a Mylar film of 6 μm thick. The plating solution does not damage the Mylar window in practice only to be replaced after use of two years. The solution conditioned in the sampling system flows to the sample cell and the inside surface of the Mylar window does not fog. A reference plate is attached to the other side of the sample holder for correction of instrumental drift. The reference plate is made of a mixture of FeSO₄, NiSO₄ and ZnSO₄ reagents. The excitation source is a Cr and a W target X-ray tube immersed in cooling oil. A vessel holding tubes is mechanically rotated to choose the tube suitable for measuring characteristic lines. The Cr and the W radiations are used for excitation of the S line and the Fe, Ni and Zn lines, respectively. The Cr X-ray
3. Interelement Effect

The influence of coexistent-components on the analytical value (the X-ray fluorescence intensity) was studied before designing the on-line analyzer. The primary fluorescent X-ray intensities excited with a monochromatic source were calculated from the following equation.8)
\[
I_i = \frac{k \cdot I_0 \cdot W_i}{\sum_j (\mu_j \cdot W_j)} \quad \text{...................(1)}
\]

\[
\mu_j = \rho_j^i \sin \phi + \rho_j^p \sin \phi
\]

where,
- \( k \): Constant
- \( I_i \): X-ray fluorescence intensity of an analyzing element (ion) \( i \)
- \( I_0 \): Intensity of incident X-rays (monochromatic)
- \( W_i \): Weight fraction of an analyzing element (ion) \( i \)
- \( W_j \): Weight fraction of coexistent element (ion) \( j \)
- \( \mu_j^i \): Mass absorption coefficient of element \( j \) for X-rays of wavelength \( \lambda \)
- \( \rho_j^p \): Mass absorption coefficient of element \( j \) for characteristic X-rays, \( p \)-line of element \( i \)
- \( \phi, \phi \): Incident and takeoff angles, respectively

\( (j \text{ includes } i \text{ in } \sum_j) \)

The plating solution includes \( \text{Ni}^{2+}, \text{Zn}^{2+}, \text{Fe}^{2+} + \text{Fe}^{3+}, \text{Na}^{+}, \text{H}^+, \text{SO}_4^{-} \) ions and \( \text{H}_2\text{O} \). The Ni\( \text{K}\alpha \) line intensity is given by

\[
I_{\text{NiK}\alpha} = k \cdot I_0 \cdot W_{\text{Ni}^{2+}}(\mu_{\text{Ni}^{2+}} \cdot W_{\text{Ni}^{2+}} + \mu_{\text{Zn}^{2+}} \cdot W_{\text{Zn}^{2+}} + \mu_{\text{Fe}^{2+}+\text{Fe}^{3+}} \cdot W_{\text{Fe}^{2+}+\text{Fe}^{3+}} + \mu_{\text{Na}^{+}} \cdot W_{\text{Na}^{+}} + \mu_{\text{H}^+} \cdot W_{\text{H}^+} + \mu_{\text{SO}_4^{-}} \cdot W_{\text{SO}_4^{-}} \cdot W_{\text{H}_2\text{O}}) \quad \text{.............(2)}
\]

as a function of the concentrations of the \( \text{Ni}^{2+} \) ion and the other components. Weight fraction of all components in the plating solution is summed to be unity;

\[
W_{\text{Ni}^{2+}} + W_{\text{Zn}^{2+}} + W_{\text{Fe}^{2+}+\text{Fe}^{3+}} + W_{\text{Na}^{+}} + W_{\text{H}^+} + W_{\text{SO}_4^{-}} + W_{\text{H}_2\text{O}} = 1. \quad \text{.............(3)}
\]

The term, \( W_{\text{H}_2\text{O}} \), in Eq. (2) is omitted and the concentrations are represented by the commonly used concentration unit, \( \omega_i \) [g/l], which is given by \( \omega_i = W_i [{g/l}] = W_i [{g/g}]/(1000 \cdot \rho) \), where \( \rho \) [g/cm\(^3\)] is the density of plating solution. The relationship between the plating solution density and the concentrations of \( \omega_{\text{Ni}^{2+}}, \omega_{\text{Zn}^{2+}}, \omega_{\text{Fe}^{2+}+\text{Fe}^{3+}}, \omega_{\text{Na}^{+}} \) and \( \omega_{\text{SO}_4^{-}} \) must be found in order to express the intensity equation as a function of concentrations \( \omega_i \) [g/l]'s. The relationship was experimentally obtained. Reference samples prepared form reagents were used for the experiments and were determined by their densities by means of pycnometers. The density, \( \rho \), also varies with the concentration of \( \omega_{\text{Ni}^{2+}} \) and \( \omega_{\text{H}_2\text{O}} \). However, the terms of these components were omitted in the relation because of the low concentration of each component in the plating bath. The following relationship was obtained by regression analysis

\[
\rho = 1.01 + 0.0000945 \cdot \omega_{\text{Ni}^{2+}} + 0.0000894 \cdot \omega_{\text{Zn}^{2+}} + 0.000761 \cdot \omega_{\text{Na}^{+}} + 0.000816 \cdot \omega_{\text{SO}_4^{-}} \quad \text{.............(4)}
\]

For systematic incidence and takeoff of 45° with an incident X-ray wavelength of 0.6 Å (the maximum intensity wavelength of continuous X-rays at 30 kV excitation), the Ni\( \text{K}\alpha \) line intensity ratio is approximately expressed by Eq. (5). The mass absorption coefficients tabulated by BIRKS\(^8\) were used for calculation.

\[
I_{\text{NiK}\alpha} = \frac{w_{\text{Ni}^{2+}}}{kI_0}
\]

\[
= \frac{86 \cdot w_{\text{Ni}^{2+}} + 105 \cdot w_{\text{Zn}^{2+}} + 35 \cdot w_{\text{Na}^{+}} + 47 \cdot w_{\text{SO}_4^{-}} + 13450}{1} \quad \text{.............(5)}
\]

The interelement effect was experimentally studied in the laboratory. A wavelength-dispersive X-ray fluorescence spectrometer was used with a source of Cr target operated at 30 kV-5 mA. A sample holder with a thin 6 μm Mylar film for liquid samples was used. The specimen chamber of the X-ray fluorescence spectrometer was not evacuated to avoid the damage of the Mylar film in vacuum. Reference samples were prepared from the reagents of nickel sulfate and zinc sulfate. The concentrations of the reference materials were determined by atomic absorption spectrometry. Fig. 7 shows the relationship between the Ni\( \text{K}\alpha \) line intensity and the concentrations of the Ni\( ^{2+} \) and Zn\( ^{2+} \) ions. The Ni\( \text{K}\alpha \) line intensity was influenced by the concentrations of both Ni\( ^{2+} \) and Zn\( ^{2+} \) ions. The relationship between the Ni\( \text{K}\alpha \) line intensity and the concentration of the Ni\( ^{2+} \) ion was represented by a single working curve at a given Zn\( ^{2+} \) ion concentration. The Ni\( \text{K}\alpha \) line intensity decreased with increasing the Zn\( ^{2+} \) ion concentration due to absorption of the Ni\( \text{K}\alpha \) line by Zn\( ^{2+} \) ion. In these results the SO\(_4\)\(^{-}\) ion also had influence on the measured intensity. Similarly the intensity of the Zn\( \text{K}\alpha \) line was influenced by the Ni\( ^{2+} \) ion as shown in Fig. 8. Further, the influence of Na\( \text{SO}_4 \) on the intensities of the Ni\( \text{K}\alpha \) and Zn\( \text{K}\alpha \) lines was studied. The intensities of the Ni\( \text{K}\alpha \) and Zn\( \text{K}\alpha \) lines were measured when the concentration of Na\( \text{SO}_4 \) varied by keeping the concentrations of Ni\( ^{2+} \) (Ni\( \text{SO}_4 \)) and Zn\( ^{2+} \) (Zn\( \text{SO}_4 \)) constant. The apparent concentrations of the Ni\( ^{2+} \) and Zn\( ^{2+} \) ions were determined with the calibration curves of Figs. 7 and 8, respectively. The amount of Na\( \text{SO}_4 \) affected the analytical values of Ni\( ^{2+} \) and Zn\( ^{2+} \) ions as shown in Fig. 9. The concentrations of the Na\(^+\), Fe and SO\(_4\)\(^{-}\) ions

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Fig. 7. Relationship between Ni\( \text{K}\alpha \) line intensities and concentrations of plating solution components.
were necessary to be determined for interelement correction. Among them the Na$^+$ ion had less influence on the intensities of the NiKα and ZnKα lines than the other components. The concentration variation of the Na$^+$ ion was small in the plating process bath. In practice, the Na$^+$ ion had little influence on the NiKα line intensity. In addition, the intensity of the Na line is difficult to be measured with the present on-line analyzer. For these reasons the intensities of the S and Fe lines were measured in the on-line analyzer to correct the interelement effect.

4. Analytical Methods and Results

4.1. Analytical Methods

4.1.1. Correction Equation

Various correction models\(^{10,11}\) have been proposed and JIS, \(d_j\) method\(^{12}\) has been adopted for alloy-plating solution analysis. In the present on-line analyzer, the following correction equation is used. The constituent of H$\text{}_2$O is regarded as a residual component and the analyte "\(i\)" concentration was taken in the correction term.

\[
w_i = R_i (1 + \sum M_{ij} \cdot w_j) \cdot I_i + \varepsilon_i \quad \ldots \ldots \ldots (6)
\]

where, \(I_i\): X-ray fluorescence intensity of analyte ion
\(M_{ij}\): Correction coefficient (including \(M_{ii}\))
\(R_i\): Coefficient
\(w_i\): Concentration of analyte ion (g/l)
\(w_j\): Concentration of each ion (Ni$^{2+}$, Zn$^{2+}$, Fe and SO$_4^{2-}$) (g/l)
\(\varepsilon_i\): Coefficient of error correction term.

The coefficients of \(R_i\)'s, \(M_{ij}\)'s and \(\varepsilon_i\)'s were obtained from the intensities and component concentrations of reference samples by regression analysis. The ion concentrations of an unknown sample were obtained by the following iteration method. First, each of \(w_i\)'s was calculated as

- the first approximation: \(w_i^1 = R_i \cdot I_i + \varepsilon_i\)
- the second: \(w_i^2 = R_i \cdot (1 + \sum M_{ij} \cdot w_j^1) + \varepsilon_i\)
- until \(n\)-th: \(w_i^n = R_i (1 + \sum M_{ij} \cdot w_j^{n-1}) + \varepsilon_i\).

The iteration was performed until the value, \((w_i^n - w_i^{n-1})/w_i^{n-1}\), converges below \(10^{-5}\). The resultant values, \(w_i\)'s, were taken as the analytical values.

4.1.2. X-ray Spectrum and Background Correction

The most significant contribution to background is due to the X-ray tube spectrum scattered by the specimen. Scattering of the X-ray tube continuum and the characteristic anode lines from the specimen is an important source of interference. Fig. 10 shows the scattered spectrum from a water specimen obtained by using the Cr target X-ray tube. The ArKα line (2.96 keV) interferes with the Skα line (2.31 keV). The ArKα line is emitted from argon in the atmosphere (0.93 %). Fig. 11 shows the background spectrum obtained by using the W target X-ray tube. The Wλα (\(\alpha_1\): 8.40 keV, \(\alpha_2\): 8.34 keV) and Wλβ (\(\beta_1\): 9.67 keV, \(\beta_2\): 9.96 keV) lines interfered with the ZnKα (8.63 keV) and ZnKβ (9.57 keV) lines, respectively.

Figs. 12 and 13 show the spectra emitted from a plating solution with the Cr and W radiations, respectively; the Cr target tube is efficient for exciting the
SKα line. The net counts of the SKα line, \( I_0 \), are obtained as \( I_0 = R_0 - H_0 \), where \( R_0 \) is the total count number in the channels of 195 to 260 and \( H_0 \) is the background count number in the channels of 100 to 165. The counts of the FeKα and NiKα lines are recorded in the channels of 610 to 675 and of 705 to 790, respectively. Background is not subtracted for the FeKα and NiKα lines. The counts of the ZnKβ line are measured as the Zn analog line intensity because the NiKβ and WLα lines interfere strongly with the ZnKα line. The net counts of the ZnKβ line, \( I_{198} \), are obtained by \( I_{198} = R_{198} - 0.40 \times H_W \), where \( R_{198} \) is the total count number in the channels of 920 to 1000 and \( H_W \) the count number of WL7 line. The background intensity under the ZnKβ line peak, \( H_{198} \), is estimated by \( H_{198} = 0.40 \times H_W \), where \( H_W \) is the number of counts integrated in the WL7 line channel region.

The correction for instrumental drift was also made. The factor, \( k = \frac{I_0}{I_S} \), for each line was derived by measuring \( I_S \) of the reference plate when the calibration equation was obtained using the reference samples and \( I_S \) when the plating process solution was analyzed. The concentrations of plating process solution components were obtained from each corrected intensity, \( kI = \frac{I_S}{I_S + I} \).

4.1.3. Preparation of Calibration Equation

The compositional concentrations and the measured intensities of the reference samples are shown in Tables 2 and 3, respectively. The measured intensities are converted to concentrations by the iteration method described above. Table 4 shows the experimental regression coefficients of \( R_i/s \), \( M_j/s \), and \( s_i/s \)'s. The analytical accuracies \( \sigma_i = \sqrt{\sum I_i^2}/(n = 1), \) and (X-ray analytical value) - (Reference value), \( n \) number of samples are 0.12, 0.30, 1.24 and 0.11 g/l for the Zn2+, Ni2+, SO42-, and Fe ions, respectively.

4.2. Analytical Results of Plating Process Solution

The plating solution was continuously supplied to the on-line analyzer system on the production line for automatic analysis. An on-line analysis example of the plating process solution is shown in Fig. 14. The analytical accuracy, \( \sigma_a \), is: 0.46 g/l for Zn2+, 0.77 g/l for Ni2+ ion. The on-line analyzer has been applied to the analysis of a Zn plating bath and operated for 7 years since 1981 without any trouble.

The features of the present on-line analyzer are summarized as follows:

1. The present on-line analyzer system can be used for other alloy plating solutions. In other analytical methods, e.g., ISEs, the design is usually specific for a particular bath chemistry. A system built to analyze a particular plating bath cannot be used for the other solutions.
2. The present system needs no special sample conditioning such as dilution, addition of other reagents, and ionic strengthening.
3. All the solution can be returned to the plating tank after the analysis is completed. So, even if the analyzer is adopted for a small plating bath the problem of plating solution loss does not arise.
4. Maintenance is easy.

5. Conclusions

An on-line analyzer for a Ni-Zn alloy plating bath has been developed.

1. The on-line analyzer consists of a sampling
Table 2. Reference samples. (g/l)

| Sample No. | Zn²⁺ | Ni²⁺ | SO₄²⁻ | Fe⁺⁺ |
|-----------|------|------|-------|------|
| 1         | 25.0 | 0.0  | 36.8  | 0.0  |
| 2         | 0.0  | 5.0  | 8.2   | 0.0  |
| 3         | 0.0  | 20.0 | 32.7  | 0.0  |
| 4         | 0.0  | 40.0 | 65.4  | 0.0  |
| 5         | 0.0  | 80.0 | 130.9 | 0.0  |
| 6         | 0.0  | 0.0  | 100.0 | 0.0  |
| 7         | 0.0  | 0.0  | 150.0 | 0.0  |
| 8         | 0.0  | 0.0  | 200.0 | 0.0  |
| 9         | 10.0 | 20.0 | 62.5  | 1.0  |
| 10        | 20.0 | 40.0 | 125.0 | 2.0  |
| 11        | 40.0 | 80.0 | 250.0 | 4.0  |
| 12        | 0.0  | 0.0  | 0.9   | 0.5  |
| 13        | 0.0  | 0.0  | 3.4   | 2.0  |
| 14        | 0.0  | 0.0  | 0.0   | 0.0  |
| 15        | 10.0 | 10.0 | 32.4  | 9.8  |
| 16        | 20.0 | 20.0 | 64.7  | 1.5  |
| 17        | 40.0 | 40.0 | 129.4 | 3.0  |
| 18        | 2.0  | 20.0 | 36.8  | 0.3  |
| 19        | 5.0  | 40.0 | 73.7  | 0.5  |
| 20        | 10.0 | 80.0 | 147.3 | 1.0  |

Table 3. X-ray fluorescence intensities. (cps)

| Sample No. | ZnKα | NiKα | SKα | FeKα |
|------------|------|------|-----|------|
| 1          | 677.63 | 38.42 | 19.46 | 14.17 |
| 2          | -0.49  | 368.06 | 2.92  | 13.32 |
| 3          | 2.12   | 1795.95 | 17.00 | 14.04 |
| 4          | 3.09   | 2846.35 | 34.69 | 15.23 |
| 5          | 2.62   | 4040.77 | 60.11 | 17.08 |
| 6          | -0.12  | 15.33  | 54.95 | 10.90 |
| 7          | -0.31  | 13.68  | 76.61 | 10.93 |
| 8          | -0.03  | 12.78  | 94.01 | 9.90  |
| 9          | 183.86 | 1591.72 | 33.33 | 47.15 |
| 10         | 231.05 | 2316.67 | 66.38 | 67.32 |
| 11         | 265.66 | 3005.45 | 94.03 | 91.29 |
| 12         | -0.97  | 18.60  | -2.49 | 13.07 |
| 13         | -0.63  | 25.47  | 0.76  | 114.09 |
| 14         | -1.42  | 15.79  | -2.49 | 13.07 |
| 15         | 247.71 | 982.47  | 18.47 | 49.52 |
| 16         | 341.26 | 1581.70 | 35.07 | 77.38 |
| 17         | 420.31 | 2273.64 | 59.24 | 110.95 |
| 18         | 54.92  | 1602.02 | 21.00 | 25.96 |
| 19         | 71.41  | 2782.97 | 39.73 | 36.39 |
| 20         | 81.74  | 3907.69 | 66.08 | 49.24 |

Note: The intensities of the ZnKα and SKα lines are background-corrected.

system and an X-ray fluorescence analyzer. The plating process solution is continuously supplied to the analyzer from the plating trays and the analysis is carried out automatically.

(2) The energy-dispersive X-ray fluorescence analysis method is used. In the determination of the Ni²⁺ and Zn²⁺ ions, the interelement effects of the SO₄²⁻ and Fe⁺⁺ ions are corrected. The intensity of the S line can be efficiently measured after a path in air with the energy-dispersive X-ray spectrometer.

Table 4. Regression coefficients.

| i | j |
|---|---|
| Zn²⁺ | Ni²⁺ | SO₄²⁻ | Fe |
| 0.0143 | 0.0363 | 0.0080 | 0.0654 | 5.98 | -0.045 |
| 0.0035 | 0.0024 | 0.0093 | -0.1237 | 2.51 | -0.260 |
| 0.0033 | 0.0021 | 0.0022 | -0.0094 | 1.36 | 3.310 |
| -0.0092 | -0.0102 | 0.0010 | 0.0014 | 0.76 | -0.362 |

Fig. 14. Analytical results of Ni²⁺ and Zn²⁺ concentrations in an arbitrary unit.

(3) For a higher excitation efficiency, the Ni, Zn and Fe lines are excited by W and the S line is by Cr X-ray tube spectra using an excitation source instrument composed of exchangeable W and Cr X-ray tubes.

(4) The present on-line analyzer has been applied to the analysis of the Zn plating bath and operated for process plating solution analysis without any trouble in both the sampling system and the X-ray analyzer.

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