An On-Site Colorimetric Technique for Routine Determination of Chromium, Iron and Copper in Bath Solutions for Chromium(III) Conversion Coating

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An on-site colorimetric technique was developed for the routine determination of chromium, iron and copper in bath solutions for the chromium(III) conversion coating. A portable colorimeter with a red-green-blue light emitting diode was used for the absorbance measurements. Iron and copper were determined as Fe(III)-thiocyanate and Cu(I)-bathocuproindisulfonate, respectively. Chromium(III) was determined simultaneously with iron or copper using green and blue light. A correction method of the matrix effect was proposed and its applicability was demonstrated. Analytical errors were within 500, 5 and 0.3 mg L⁻¹ for chromium(III), iron and copper, respectively.

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Introduction

Iron and copper are typical contaminants limiting the bath life in the chromium conversion coating.^{1,2} Chromium(III) compounds are used as alternatives of chromium(VI) compounds for the implementation of RoHS (Restriction of the use of certain Hazardous Substances in electrical and electric equipment). Therefore, rapid and on-site determination of iron, copper and chromium(III) in the bath solution is required for the routine process control; *e.g.*, less than 1 and 100 mg L⁻¹ level for copper and iron, respectively. A visual colorimetric method (duplication method) was proposed for the determination of iron in chromium plating solutions.³ This method is simple, but a skillful analyst is required to minimize the personal error. A test kit using a portable colorimeter is commercially available for the determination of chromium with a detection limit of 0.01 mg L⁻¹.⁴ This kit is based on the diphenylcarbazide method. The determinations of total chromium and of hexavalent chromium are required for the monitoring of chromium(III).

In this paper, a simple two-component analysis using a palmtop-size portable colorimeter⁵ with a red-green-blue light emitting diode was proposed for the on-site determinations of iron, copper and chromium(III) in bath solutions of the chromium(III) conversion coating. Iron and copper were determined as Fe(III)-thiocyanate complex and Cu(I)-bathocuproindisulfonate complex, respectively. Chromium(III) was simultaneously determined with iron or copper by an absorbance measurement for green and blue light. A correction technique was introduced to minimize the influence of matrix effect. Applicability of the method was tested for different types of bath solutions.

Experimental

Reagents and apparatus

Unless stated otherwise, all chemicals were of analytical-reagent grade and were used without any purification. Water (≥ 18 M Ω cm) prepared by Millipore Simpli Lab system was used throughout. Metal stock solution (1.00 g Fe, Cu or Cr L⁻¹) was prepared by dissolving Fe(NH₄)(SO₄)₂·12H₂O, CuSO₄·5H₂O or Cr(NO₃)₃·9H₂O, respectively, with 0.1 M HCl. Working standard solutions were prepared by diluting stock solutions with 0.1 M or 1 mM HCl. Bathocuproine disulfonic acid (BCS) was prepared by dissolving the reagent (2,9-dimethyl-4,7-diphenyl-1,10-phenanthrolinedisulfonic acid, disodium salt) (Dojindo Laboratories) with water.

The absorbance measurement was carried out using a laboratory-made colorimeter (10 × 7 × 5 cm, 280 g) with a RGB LED (with three light emitters, Nichia TSTM515M) as a light source.⁵ Emission wavelengths and spectral band widths of emitters are 630 and 25 for red, 525 and 45 for green, and 470 and 30 nm for blue. A photodiode (Hamamatsu Photonics, S2386-18K) was used for the absorbance measurements. The same type of photodiode was equipped to correct the fluctuation of emission intensity. Signal detection for red, green or blue emission was synchronized with the blinking of emitters. A 10-mm glass cell was used for the absorbance measurement. A Shimadzu UV-160 double-beam spectrophotometer was used for the measurement of absorption spectra.

Samples

Twenty samples were collected from working bath solutions. They included two types of treatment solution supplied by the same maker; 15 samples were grouped into an inorganic acid type and 5 samples into an organic acid type. In the inorganic acid type samples, 10 samples were used for the barrel treatment

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and the residuals were for the rack treatment. The samples contained zinc at 0.01 – 10 g L⁻¹ levels.

Principle of analysis

Various bath solutions are used for numerous types of chromium(III) conversion coatings. The solutions contain chromium(III), organic acid (*e.g.*, malonic, oxalic or citric acid as chelating agent), surfactants, silicates, metal salts and other materials. Chromium(III) conversion coating is mainly used to passivate zinc- and zinc alloy-plated surfaces and thereby the bath solution is contaminated by zinc. The elimination of matrix effects in the colorimetric analysis is probably difficult for such bath solutions. On the other hand, in the routine process of the chromium(III) conversion coating, a type of bath solution is usually fixed and therefore the correction of the matrix effect may be possible for each bath solution system. Among the above coexisting species, the organic acid probably influences the determination of analytes by the formation of metal complexes. In the presence of a color-producing reagent (R) and of complexing species (L) acting as color-inhibitors for an analyte (M), the total concentration of M can be represented by

$$[M]_T = [M] + [MR] + [ML] + [ML_2] + \dots + [ML_n]. \quad (1)$$

When sufficiently excess concentrations of R and L to $[M]_T$ are present in the solution, Eq. (1) becomes

$$[M]_T = [M] + k_1[M][R]_0 + \beta_1[M][L]_0 + \beta_2[M][L]_0^2 + \dots + \beta_n[M][L]_0^n, \quad (2)$$

where k_1 is the stepwise stability constant of MR, β_1 to β_n are the overall stability constants of ML_i complexes, and $[R]_0$ and $[L]_0$ are the concentrations of R and L added, respectively. In the absence of L, *i.e.*, without any matrix effect, the absorbance of MR is represented by

$$A_0 = \varepsilon_0[MR] = \varepsilon_0 k_1[M][R]_0, \quad (3)$$

where A_0 and ε_0 indicate the absorbance and the molar absorption coefficient for MR, respectively. Equation (3) and $[M]_T = [M] + k_1[M][R]_0$ from Eq. (2) at $[L]_0 = 0$ give

$$A_0 = \varepsilon_0 k_1[M]_T[R]_0 / (1 + k_1[R]_0). \quad (4)$$

On the other hand, in the presence of L as a color-exhibitor, the absorbance (A) is represented by

$$A = \varepsilon[MR] = \varepsilon k_1[M][R]_0, \quad (5)$$

where ε denotes the molar absorption coefficient in the presence of the color-exhibitor. Equations (2) and (5) give

$$A = \varepsilon k_1[M]_T[R]_0 / (1 + k_1[R]_0 + \beta_1[L]_0 + \beta_2[L]_0^2 + \dots + \beta_n[L]_0^n). \quad (6)$$

From Eqs. (4) and (6),

$$A/A_0 = (\varepsilon/\varepsilon_0)(1 + k_1[R]_0) / (1 + k_1[R]_0 + \beta_1[L]_0 + \beta_2[L]_0^2 + \dots + \beta_n[L]_0^n). \quad (7)$$

This equation indicates that A/A_0 is constant. When S and α denote $\varepsilon_0 k_1[R]_0 / (1 + k_1[R]_0)$ and A/A_0 (correction coefficient), respectively, Eqs. (4) and (6) give

$$A_0 = S[M]_T \quad (8)$$

and

$$A = \alpha S[M]_T. \quad (9)$$

S is corresponding to the slope of the calibration curve in the absence of the color-inhibitor and the color-exhibitor. The same algorithm indicates that the value of α is also constant in the presence of MR_i ($i > 1$), *e.g.*, $Fe(SCN)_2^{2+}$ and $Fe(SCN)_3$, and other colored or colorless complexes of M. The dilution of each sample should be kept constant, because the matrix effect often changes with the degree of dilution.

Chromium(III) was determined simultaneously with iron or copper based on the algorithm for the two-component analysis using absorbances at two different wavelengths. When iron and chromium are determined simultaneously by the absorbance measurement for green and blue light, absorbances for green and blue light are represented by

$$A_g = \alpha_{gFe} \cdot S_{gFe}[Fe] + \alpha_{gCr} \cdot S_{gCr}[Cr], \quad (10)$$

$$A_b = \alpha_{bFe} \cdot S_{bFe}[Fe] + \alpha_{bCr} \cdot S_{bCr}[Cr], \quad (11)$$

where subscripts g, b, Fe and Cr indicate green light, blue light, iron and chromium(III), respectively. When the spectrum of a sample consists of the two spectra for chromium(III) and iron, *i.e.*, $\alpha_{Cr} \equiv \alpha_{gCr} = \alpha_{bCr}$ and $\alpha_{Fe} \equiv \alpha_{gFe} = \alpha_{bFe}$, Eqs. (10) and (11) give

$$[Fe] = (S_{gCr}A_b - S_{bCr}A_g) / \{\alpha_{Fe}(S_{bFe} \cdot S_{gCr} - S_{bCr} \cdot S_{gFe})\}, \quad (12)$$

$$[Cr] = (S_{gFe}A_b - S_{bFe}A_g) / \{\alpha_{Cr}(S_{bCr} \cdot S_{gFe} - S_{bFe} \cdot S_{gCr})\}. \quad (13)$$

S_{gFe} , S_{bFe} , S_{gCr} and S_{bCr} are obtained by calibration curves for each analyte. Values of α_{Cr} and α_{Fe} are previously obtained by a series of bath solution samples for chromium(III) conversion coating, as described later. Iron and chromium(III) are determined by substituting absorbances A_g and A_b in Eqs. (12) and (13). Copper and chromium(III) are determined simultaneously by the same algorithm.

Analytical procedure

For the determination of iron and chromium(III), 1 mL of 1 M HCl and 1 mL of 4 M NaSCN were placed in a 10-mL glass vial. An aliquot of sample solution was added and diluted to 4 mL with water. Absorbances (A_g and A_b) against the reagent blank solution were measured for green light and blue light, respectively. The calibration curve of iron was constructed by using the working standard Fe(III) solutions. The calibration curve of chromium(III) was constructed by using the working standard chromium(III) solutions (0.1 M HCl) without adding any reagent solution.

For the determination of copper and chromium(III), 0.03 mL of 5 mM BCS, 1 mL of 0.1 M L-ascorbic acid and 1 mL of the citrate buffer solution containing 0.5 M citric acid and 0.48 M sodium citrate were placed in a 10-mL glass vial. An aliquot of sample solution was added and diluted to 4 mL with water. The calibration curve of copper was constructed by using the working standard Cu(II) solutions. The construction of a calibration curve of chromium and the absorbance measurements followed the same procedures as those in the determination of iron and chromium(III).

Fig. 1 Absorption spectra (A) of chromium(III) (0.5 g L⁻¹) (a), Fe(III)-thiocyanate (1 mg Fe L⁻¹) (b) and Cu(I)-bathocuproindisulfonate (1 mg Fe L⁻¹) (c), and those (B) of 4 times diluted solution for an inorganic acid type sample (d) and its solution with NaSCN (e).

Fig. 2 Correlation of concentration of chromium(III) (A), iron (B) and copper (C) between the proposed colorimetry and AAS for the inorganic acid type (○) and organic acid type (△) bath solution samples.

Results and Discussion

Design of colorimetric method

Analytical results obtained by atomic absorption spectrometry (AAS) indicated that concentrations of chromium in bath solution samples were at a 1 g L⁻¹ level and 100 to 10000 times higher than those of iron and copper. Therefore, the use of color-producing reagent for the determination of chromium is not adequate for determination of iron and copper, because a high dilution for chromium deteriorates the analytical sensitivity of iron and copper. In the proposed method, chromium(III) was determined without adding any color-producing reagent. Absorption spectra of tested samples were similar to that for the chromium(III) standard solution, as shown in Fig. 1 (a and d). Sodium thiocyanate^{6,7} and BCS^{6,8} were used as color-producing reagents, regarding the sensitivity and selectivity in the determination of iron and copper. The wavelength ($\lambda_{\max}$) giving maximum absorption was 480 nm for iron-thiocyanate and copper-BCS complexes and 580 nm for chromium(III), as shown in Fig. 1(A). Therefore, the method of two-component analysis was applied to the determination of iron and chromium(III) or to that of copper and chromium(III) with green and blue light. The colorimeter used gave linear calibration curves up to about 2 g L⁻¹ for chromium(III), up to

at least 4 mg L⁻¹ for iron, and up to at least 1 mg L⁻¹ for copper. Respective detection limits were about 30, 0.06 and 0.1 mg L⁻¹ for green light, and about 70, 0.03 and 0.04 mg L⁻¹ for blue light. By the addition of NaSCN, $\lambda_{\max}$ of iron-thiocyanate was shifted toward a longer wavelength, as shown in Fig. 1(B). The concentration of chromium in the sample was determined to be 2 g L⁻¹ by the measurement of absorbance at 580 nm for spectrum (d). The concentration of iron was determined to be 5 mg L⁻¹ by an absorbance difference at 480 nm between the two spectra (d and e). These values were higher than 1.5 g L⁻¹ for chromium and 1 mg L⁻¹ for iron, respectively, obtained by AAS, indicating that the correction of analytical values is required for the colorimetry.

Applicability of the method

The proposed method was designed for routine analyses in order to control the bath conditions under a given matrix system. The correction coefficients, α , for the three analytes were calculated using the analytical values obtained by AAS and the colorimetric method without the correction. For the colorimetry, the sample was diluted 10 times for iron and 4 times for copper. For any arbitrary three inorganic-type samples, differences in the absorbance with and without adding the color-producing reagent were used to calculate rough values of α : $\alpha_{\text{Cr}} = 2.1$, $\alpha_{\text{Fe}} = 1.3$ and $\alpha_{\text{Cu}} = 2.0$. Around these values, values of α

giving good agreement in the analytical result for the proposed method and AAS were searched for all the samples. For the inorganic acid type samples, $\alpha_{\text{Cr}} = 1.7$ and $\alpha_{\text{Cu}} = 1.9$ in the determination of copper; $\alpha_{\text{Cr}} = 2.7$ and $\alpha_{\text{Fe}} = 1.2$ in that of iron. A value of α larger than 1 suggests the presence of a color exhibitor. The value of α_{Cr} for the determination of iron did not agreed with that for copper, perhaps indicating the influence of the different color-producing reagents used and/or different degrees of the sample dilution. For the organic acid type samples, $\alpha_{\text{Cr}} = 3.3$ and $\alpha_{\text{Cu}} = 1.9$ in the determination of copper; $\alpha_{\text{Cr}} = 3.1$ and $\alpha_{\text{Fe}} = 1.2$ in that of iron.

The correlation in the analytical value between the proposed method and AAS is shown in Fig. 2. Plots on lines in this figure indicate the agreement of analytical values between the two methods. Colorimetric results for chromium(III) were obtained by the simultaneous determination of copper and chromium(III). Correlation coefficients were 0.996 for chromium(III), 0.98 for iron and 0.93 for copper, except for three samples (one of the three is not indicated in Fig. 2) with higher concentrations (about 4 mg L⁻¹ or more) of copper. Analytical values of the proposed method agreed with those of AAS within errors of 500, 5 and 0.3 mg L⁻¹ as the concentration in the samples for chromium(III), iron and copper, respectively. For the above three samples, analytical values of copper obtained by the proposed method were lower than those by AAS. Two of them contained high concentrations (9 g L⁻¹) of chromium(III), indicating the inhibition effect of chromium(III)⁸ by forming ternary complexes of chromium(III), Cu(II) and citrate ions.⁹ The proposed method was also applicable to simultaneous determination of iron and chromium(III). However, an analytical error (1 g L⁻¹) of chromium(III) was larger than that indicated above, because a larger dilution of sample was required for the determination of iron.

Conclusion

A simple on-site colorimetric technique using a palmtop-size colorimeter with a RGB LED was proposed for the routine determination of iron or copper simultaneously with chromium(III) in the bath solution for the chromium(III) conversion coatings. A correction method of the matrix effect was also proposed and applied to inorganic-acid type and organic-acid type bath solution samples. Analytical results agreed with those obtained by AAS within errors of 500, 5 and 0.3 mg L⁻¹ for chromium(III), iron and copper, respectively.

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