# A Study of Rapid Direct Potentiometry To Measure Trivalent Chromium Content In a Chromic Anhydride Plating Bath

By Huang Yongxia, Zhang Yizhen and Huang Dingqi

The quantity of trivalent chromium has a significant effect on the characteristics of a chromic anhydride plating bath. It is desirable, therefore, to be able to measure the quantity in the bath rapidly and accurately. Measurements were made with platinum and saturated calomel electrodes on a series of baths having different quantities of trivalent chromium to get stable readings of potential within two minutes by adding eerie sulfate, Ce(SO<sub>4</sub>)<sub>2</sub>. The potential readings were treated by the least squares method, and standard curves of potential vs. concentration of trivalent chromium were constructed for temperatures of 15, 25, and 300 C. The measurement procedure requires less than eight minutes. The quantity of trivalent chromium measured in this way ranges from 1 to 15 g/L.. Traces of copper and iron do not affect the determination. The result is comparable to measurement by ferrous titration.

n the usual measurements of trivalent chromium, the typical quantity is several percent from chromic acid and measures from 3 to 6 g/L. The method of measuring trivalent chromium in the presence of chromic acid has been reported previously.<sup>14</sup> The method described here (rapid potentiometry) has not been reported. It is simple and reliable, and makes use of the relation between potential and concentration.

The electrode potential for an oxidation-reduction couple may be described by the Nernst equation, i.e.,

$$E = E^{\circ} + \frac{RT}{nF} \ln \frac{a_{oxid}}{a_{red}}$$

For the plating bath,

$$Cr_2O_7^{2^-}$$
 + 14H<sup>+</sup> + 6e<sup>-</sup>  $\rightleftharpoons$  2Cr<sup>3+</sup> + 7H<sub>2</sub>O

E = 1330 mV (Ref. 5)

then

$$\mathsf{E}_{\mathrm{Cr}_{2}\mathrm{O}_{7}^{2^{-}}/\mathrm{Cr}^{3^{+}}}^{2^{-}} = \mathsf{E}^{\circ}_{\mathrm{Cr}_{2}\mathrm{O}_{7}/\mathrm{Cr}^{3^{+}}}^{3^{+}} + \tag{1}$$

$$\frac{\mathsf{RT}}{\mathsf{nF}} \ln \frac{\mathsf{f}_{\mathrm{Cr}_2 \mathrm{O}_7 \mathrm{2}^-} [\mathsf{Cr}_2 \mathrm{O}_7 \mathrm{2}^-] (\mathsf{fH}^+ [\mathsf{H}^+])^1}{(\mathsf{f}_{\mathrm{Cr}}^{3^*} [\mathsf{Cr}^{3^*}]^2}$$

Under the condition that the concentration of chromic anhydride remains constant, (i.e., the concentration of  $Cr_2O_7^{2*}$  is constant), and a definite quantity of sulfuric acid is added to the bath, the concentration of H<sup>\*</sup> and the ionic

strength of the solution will also remain constant. The activity coefficient f will be constant and Eq. 1 may be simplified:

$$E_{Cr_{2}O_{7}2^{-}/Cr^{3+}} = E^{\circ}cr_{2}O_{7}2^{-}/Cr^{3+} + \frac{RT}{nf} \ln C = \frac{RT}{nf} \ln (Cr^{3+})^{2} = (2)$$
$$E^{\circ'} - \frac{RT}{nf} \ln (Cr^{3+})^{2}$$

where C is a constant.

Because trivalent chromium and  $SO_4^{22}$  form a complex with stability constant of  $10^{14}$  the concentration of free trivalent chromium and the total concentration T exist in the following relation:

$$[Cr^{3+}] = \phi_{Cr^{3+}} T_{Cr^{3+}} = \frac{T_{Cr^{3+}}}{1 + \beta(SO_4^{\frac{2}{2}})}$$

where  $\phi_{Cr^{3+}}$  is the ratio of free trivalent chromium to total **Cr**<sup>3+</sup> ion concentration in solution.

In addition, under strong acidic conditions, hydrolysis of trivalent chromium may be neglected. Equation 2 may then become:

$$E_{Cr_{2}O_{7}^{2^{-}}/Cr^{3+}} = E^{\circ}_{Cr_{2}O_{7}^{2^{-}}/Cr^{3+}} - \frac{RT}{3F} \ln T_{Cr^{3+}} +$$
(3)

Therefore, under the condition that the concentration of CrO₃and sulfuric acid are well-controlled, the electrode potential depends upon the total concentration, Tcr³+only. Measurement of the quantity of trivalent chromium in the

bath can be accomplished by measuring the potential with a platinum electrode and a saturated calomel electrode. The time required for the potential between  $Cr_2O_7^{-2}/Cr^{-3+}$ and the platinum to reach equilibrium is about an hour, disqualifying it for rapid measurement. A strong oxidizing agent, eerie sulfate, is added to the original  $Cr_2O_7^{-2}/Cr^{-3+}$ system to oxidize the  $Cr^{-3+}$ . A  $Cr_2O_7^{-2}/Cr^{-3+}-Ce^{-4+}/Ce^{-3+}$  mixed system is formed through the following equilibrium:

 $6Ce^{4+} + 2Cr^{3+} + 7H_2O \rightleftharpoons 6Ce^{3+} + Cr_2O_7^{2-} + 14H^{+}$ 

Table 1					
Preparation	of	the	Standard	Solutions	

Solution No.	Added CrO₃solution in 200 g/L, mL <sup>`</sup>	CrO₃quantity in standard solution, g/L	Added Cr³ quantity in 25 g/L mL	Cr³⁺quantity in standard solution, g/L
1	25	100	2	1
2	25	100	4	2
3	25	100	6	3
4	25	100	8	4
5	25	100	10	5
6	25	100	12	6
7	25	100	14	7
8	25	100	16	8
9	25	100	18	9
10	25	100	20	10
11	25	100	22	11
12	25	100	24	12
13	25	100	13	13/2
14	25	100	14	14/2
15	25	100	15	15/2

Now, in this system

 $E_{Cr_2O_7^{2^-}/Cr^{3+}} = E_{Ce^{4+}/Ce^{3+}}$ 

because equilibrium between Ce<sup>4+</sup>/Ce<sup>3+</sup> and the platinum electrode can be reached quickly, a stable potential reading can be obtained in two minutes.

If an excessive quantity of eerie sulfate, b, is added, then

$$E_{Ce^{4+}/Ce^{3+}} = E^{\circ}_{Ce^{4+}/Ce^{3+}} + \frac{RT}{nF} \ln \frac{b - 3T_{Cr^{3+}}}{3T_{Cr^{3+}}}$$
(4)

where b is expressed in mol/L.

Under the experimental conditions, from the  $E_{ce}^{a+}/c_{e}^{a+}$ -Tcr<sup>3+</sup> standard curve drawn from a set of measured data, the quantity of trivalent chromium in the bath can be determined. Regression analysis of the measured data yields the curve shown in the figure. In addition, a suitable value of *b* can be chosen to make the slope of the standard curve greater than that of the pure  $Cr_2O_7^2/Cr^{3+}$  system. Under such conditions, measurement accuracy would be increased The actual measured data are shown in Table 1.



Cr<sup>\*</sup>concentration curves plotted from regression analysis of data of Table.

# **Experimental Procedure**

To obtain the  $E_{ce}^{4*}/c_{e}^{3*}$ -  $T_{cr}^{3*}$  curve, 15 standard solutions were made up with the concentrations shown in Table 2. For each temperature, potential was measured, with results as indicated. Regression analysis yielded the following equations:

15 °C: E = 1249.53700- 16.2159400  $(T_{cr}^{3+})$  + 1.43017900 $(T_{cr}^{3+})^2$ - 0.06267808  $(T_{cr}^{3+})^3$ (mV)

25 °C: E = 1272.20000- 23.9847300  $(T_{cr}^{3*})$  + 2.54542700  $(T_{cr}^{3*})^2$ - 0.10884440 $(T_{cr}^{3*})^3$ (mV)

30 °C: E = 1284.16100- 24.0574900  $(T_{c_{1}}^{3+})$  + 2.71408800  $(T_{c_{1}}^{3+})^{2}$  - 0.12073490 $(T_{c_{1}}^{3+})^{3}$ (mV)

### **Results and Discussion**

After addition of  $Ce^{4+}$ , it appeared that the quantity of trivalent chromium had increased over that measured in the original solution. This required checking. Forth is purpose, a set of solutions was prepared in which the trivalent chromium is constant and the quantity of  $CrO_3$  is changed

Table 2ElectrodePotentialsFor the Standard Solutions

Solution	,				
No.	30 °C	25° C	15° C		
1A	1260.4	1252.8	1237.0		
2A	1247.0	1233.0	1224.0		
3A	1237.0	1218.0	1207.0		
4A	1223.0	1208.0	1200.0		
5A	1216.0	1202.0	1196.0		
6A	1211.0	1198.0	1192.0		
7A	1207.0	1193.0	1186.0		
8A	1202.0	1188.0	1181.0		
9A	1198,0	1183.0	1175.0		
10A	1194.0	1178.0	1168.0		
11A	1189.0	1173.0	1159.0		
12A	1180.0	1166.0	1153.0		
13A	1166.0	1144.0	1139.0		
14A	1145.0	1132.0	1129.0		
15A	1127.0	1123.0	1120.0		

### Table 3 Comparison with Variable CrO₃/Cr<sup>3+</sup>Ratio

CO	Test nditions	Reference concentrations		
Temp., °C	CrO₃conc., g/L	Cr³∗, 5 g/L E, mV	Cr³⁺, 10 g/L E, mV	
15	98	1195.0	1168.0	
15	100	1195.0	1166.0	
15	102	1196.0	1169.0	

(i.e., the solutions were prepared with different ratios of CrO<sub>3</sub>/trivalent chromium). The potentials were measured at 15 °C. The results are given in Table 3. From these data and the Nernst equation, it is known that at constant temperature, when the quantity of chromic anhydride is

0.34

changed by a small amount, the change in potential is also small, assuring the reliability of this method. As a further check, the quantity of CrO<sub>3</sub> may be measured by the specific gravity method.

The results of comparing the rapid potentiometry method with ferrous titration are given in Table 4. The data obtained show that the method of direct potentiometry is accurate.

To determine the effect of ferric ions in the simulated chromic anhydride plating bath (at 30  $^{\circ}$ C), a solution was prepared with 10 g/L of trivalent chromium, a maximum of 10 g/L of ferric iron, and a trace amount of divalent copper. Table 5 shows that the effect of ferric iron is negligible, as is the presence of copper.

As a field test of the method, samples were taken from plating baths of the Hongyang Electroplating Factory, Guangzhou, China. The results of this test, in which the samples were also checked by ferrous titration, are given in Table 6. Comparison shows that rapid potentiometry is useful.

Table 4						
Comparison	of	Rapid	Potentiometry	with	Ferrous	Titration

		Potential, mV		Cr <sup>3+</sup> auontitu (in	Cr <sup>³•</sup> quantity, g/L (ferrous titration)	
Sample no.	Cr³⁺quantity, g/L	Measured value	Mean value	standard curve) g/L	Measured value	Mean value
5	5.0	1216.0		5.0	4.922	
		1216.0	1215.6		4.957	4.957
		1215.0			4.992	
		standard dev	viation: 0.7		standard devi	ation: 0.035
10	10.0	1194.0		10.0	10.50	
		1195.0	1194.3		10.34	10.37
		1194.0			10.26	
		standard dev	viation: 0.7		standaard dev	iation: 0.122

Table 5Measured Values in the Simulated Bath

added in	Cr³⁺found by ferrous	With	out iron	W	With iron	
solution tit ration g/L g/L	tit ration g/L	Potential, mV	Quantity found, g/L	Potential, mV	Quantity found, g/L	
10.0	10.0	1189.0	9.6	1168.0	9.5	
10.0	10.3	1188.0	9.5	1187.0	9.4	
10.0	10.2	1189.0	9.6	1189.0	9.6	
mean	10.33	1188.6	9.57	1188.0	9.5	
standard deviation	0.153	0.583	0.058	1.0	0.1	

# Table 6Measured Values of an Actual BathFrom the Hongyang Electroplating Factory, Guangzhou, China

Ferrous t	itration	Rapid potentiometry			
Cr³∗actual concentration, g/L	Cr <sup>3+</sup> mean concentration, g/L	Actual potential reading, mV	Quantity of Cr³⁺, g/L	Mean, g/L	
3.375		1233.0	3.15		
3.294	3.308	1230.0	3.12	3.123	
3.256		1231.0	3.13		
Standard devi	iation: 0.06	Standard	deviation: 0.02		

#### Conclusions

The quantity of trivalent chromium in a CrO<sub>3</sub>plating bath can be determined by potentiometry in about eight minutes. The method is rapid, simple and reliable. It should be suitable for use in production plating.

This method can also be used for measurement of trivalent chromium with high, medium and low content of chromic anhydride, if a volume matching the actual concentration of chromic anhydride is taken from the bath so as to make the measured concentration of chromic anhydride equal to 1 g/L (neglecting Ce<sup>4+</sup> oxidation).

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Huang

Zhang

Huang

## About the Authors\*

Huang Yongxia is an associate professor in the Chemistry Department, South China University of Technology, Guangzhou, Guangdong Province, P.R. China. Her work includes applied chemistry, analysis, and chemical engineering.

Zhang Yizhen is a graduate of South China University of Technology in chemical engineering. She has been a research assistant and engineer in plastics engineering and production for about 20 years, but is now working in the Department of Applied Chemistry in electrochemical research.

Huang Dingqi is head of the Applied Electrochemistry Research Section of the Chemistry Department, South China University of Technology. For some years he has been engaged in research on coordination chemistry and electrochemistry. He is the author of Inorganic Chemistry, an award-winning textbook for university students. Mr. Huang is also Vice Chairman of the Chemical Society of Guangdong Province and a member of the Council of Guangzhou Electroplating Society.

<sup>\*</sup>Correspondence with these authors should be addressed in care of Mr. Cheng Chee-pui, Department of Biology, Chinese University of Hong Kong, Shatin, Hong Kong.