

# Spectrophotometric Catalytic Determination of Micro-amount Chromium in Steel Based on Oxidation of Bromopyrogallol Red by Hydrogen Peroxide

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**Abstract:** Chromium (VI) was determined based on its catalytic effect on the decolorization reaction of Bromo-Pyrogallol Red with hydrogen peroxide in weakly acidic solutions. The optimum condition for indicator reaction and interference effect of various ions have also been studied. The apparent activation energy of catalytic and non-catalytic reactions were calculated by Arrhenius equation. The calibration curve is linear in the range of 0.1 to 0.6  $\mu\text{g Cr(VI)}/25\text{ mL}$ . The detection limit reached down to  $9.1 \times 10^{-10}\text{ g/mL}$ . The method was successfully applied to the determination of micro amount Chromium in the steel.

**Key words:** Trace analysis, Spectrophotometric catalytic determination, Chromium, steel

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The catalytic kinetic method (CKM)<sup>[1]</sup> is one of the most attractive procedures for achieving trace determinations of chromium. Many indicator reactions for CKM have been reported to determine trace copper, iron, silver *etc.*, but there have been few methods sensitive enough for determination of Cr(VI)<sup>[2~4]</sup>.

In this paper a new sensitive catalytic method of analysis of Cr(VI) is reported based on the oxidation of Bromo-Pyrogallol Red (BPR) with hydrogen peroxide. The procedure was applied to the determination of trace chromium in steel with satisfactory results.

## 1 Experimental

### 1.1 Apparatus

A thermostatic water bath made in China with a contact conductive thermometer, a relay and a stirrer were used. The temperature stability should be controlled within  $\pm 0.2\text{ K}$ . A spectrophotometer made in China with a 2 cm absorption cell and several 25 mL colorimetric tubes were also used.

### 1.2 Reagents

Deionized distilled water, all chemicals used were of A. R. grade and without further purification.

BPR,  $2.0 \times 10^{-4}\text{ mol/L}$ , 20% ethanol solution.

Urotropine, 20% solution.

Aqueous hydrogen peroxide solution, 30%.

Standard solution of chromium:

(a) Stock solution. (1 L = 1 mg of Cr(VI)): weigh out 0.2827 g of  $\text{K}_2\text{Cr}_2\text{O}_7$ , dissolve  $\text{K}_2\text{Cr}_2\text{O}_7$  in deionized distilled water and transfer the mixture into 100 mL volumetric flask and dilute to graduation with the same water.

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(b) Working solution (1 L= 1 mg of Cr(VI)): dilute stock standard solution 1 to 1 000(1+ 999) with deionized distilled water.

1.3 Procedure

Into both 25 mL colorimetric tubes with a glass stopper, add 0.7 mL of BPR, 1.5 mL urotropine, 0.6 mL H<sub>2</sub>O<sub>2</sub>, in that order. Into the first tube add appropriate amount of Cr(VI), the absorbance of which is A. Into the second tube add no Cr (VI), the absorbance of which is A<sub>0</sub>. The both were diluted to 25 mL with deionized distilled water. Mix thoroughly. Place the both into 373.2 K boiling bath, thermostat each tube exactly for 2 min. After the tubes were removed from the bath, cool each in flowing water for 5 min in order to stop the reaction. Lastly a portion of both solutions was transferred into 2 cm path length cell to measure the absorbance at 560 nm. The absorbance of every solution should be quickly read out at the same time. ΔA = A<sub>0</sub>– A was calculated.

2 Results and discussion

2.1 Absorption spectra of the reaction solutions

From successive visible absorption spectra of the noncatalytic and catalytic reaction solution containing 0.3 μg of Cr (VI), it is clear that at 560 nm ΔA = A<sub>0</sub>– A is the maximum. The working wavelength was therefore chosen to be 560 nm.

2.2 The kinetic condition for determining Cr (VI)

The optimal amounts of the reagents were determined by the orthogonal experiment<sup>[4]</sup> at 373.2K and 2 min of reaction time. Orthogonal table L<sub>16</sub>(4<sup>3</sup>) (Table 1 and 2) was chosen in this work. The optimal action conditions were determined by comparing the values ΔA (the difference of the absorbances between noncatalytic and catalytic reactions). From the maximum difference (R), it was clear that urotropine had the strongest effect on the determination and hydrogen peroxide was weaker.

The results indicate that the optimal amounts of reagents are A<sub>3</sub>B<sub>3</sub>C<sub>2</sub>. Hence the working condition for determining Cr (VI) in this work are as follows: 0.7 mL of BPR, 1.5 mL of urotropine, 0.6mL of hydrogen peroxide.

The effect of heating time was investigated in the range of 0.5~ 3.0 min.

The results showed that heating for 2 min could obtain large and stable value of ΔA. Therefore the heating time was fixed to be 2 min.

The effect of reaction temperature was also investigated in the range of 348.2~ 373.2 K. ΔA at 2 min increased with temperature. ΔA at about 358.2 K was

Table 1 Factors and Levels in orthogonal Experiment

level	factors		
	A : BPR/ mL	B : urotropine/ mL	C: hydrogen peroxide/ mL
1	0 5	0. 5	0. 4
2	0 6	1. 0	0. 6
3	0 7	1. 5	0. 8
4	0 8	2. 0	1. 0

Table 2 Results of The Orthogonal Experiment

No.	factors			
	BPR A	Urotropine B	H <sub>2</sub> O <sub>2</sub> C	Results ΔA
1	1	1	4	0. 100
2	2	1	1	0. 190
3	3	1	3	0. 180
4	4	1	2	0. 160
5	1	2	3	0. 186
6	2	2	2	0. 228
7	3	2	4	0. 330
8	4	2	1	0. 388
9	1	3	1	0. 146
10	2	3	4	0. 380
11	3	3	2	0. 408
12	4	3	3	0. 358
13	1	4	2	0. 116
14	2	4	3	0. 132
15	3	4	1	0. 080
16	4	4	4	0. 226
I	0. 548	0. 630	0. 804	I+ II+ III= 3. 608
II	0. 930	1. 132	0. 912	
III	0. 998	1. 292	0. 856	
IV	1. 132	0. 554	1. 036	
R	0. 584	0. 730	0. 232	

larger than those at lower or higher temperature. In order to reduce the error caused by temperature control and for the sake of easily controlling the temperature, the heating temperature was set at 373.2 K.

### 2.3 Order of the catalytic reaction

At above fixed conditions the absorbance  $A$  for catalytic reaction system [ addition of 0.3  $\mu\text{g}$  of Cr (VI) ] was measured at various times (0.5~ 3.0 min). In the time range of 0.5~ 2.5 min,  $A$  is linear with  $t$ , from this it was concluded that the catalytic reaction was quasi—zero order reaction.

### 2.4 Apparent activation energy of reactions

Absorbance  $A_{t=0}$  (at beginning of reactions, i. e. at  $t=0$ ) and  $A$  at  $t=2$  min for the catalytic [ added 0.5  $\mu\text{g}$  Cr (VI) ] and the noncatalytic reactions were measured at the range of 350.2~ 373.2 K.  $\lg(A_{t=0}-A)_{\text{cat}}$  and  $\lg(A_{t=0}-A)_{\text{noncat}}$  were calculated at all temperatures. When plotting  $\lg(A_{t=0}-A)_{\text{cat}}$  vs  $1/T$ , a straight line with the slope ( $-1220$ ) was obtained. When plotting  $\lg(A_{t=0}-A)_{\text{noncat}}$  vs  $1/T$ , while a straight line with the slope ( $-1650$ ) was also obtained. According to Arrhenius equation, apparent activation energy of catalytic and noncatalytic reactions was calculated. The values were 23.36 kJ/mol and 31.59 kJ/mol for catalytic and noncatalytic reactions respectively.

### 2.5 Calibration curve and its empirical formula

From the calibration curve, it is obvious that the calibration curve is linear in the range 0.1~ 0.6  $\mu\text{g}/25\text{ mL}$  of Cr(VI). The empirical formula of calibration curve is as follows

$$\text{Cr(VI)} = 1.269 \Delta A - 0.02967 \mu\text{g}/25\text{ mL} \quad (1)$$

with linear coefficient  $r = 0.997$ . ( $n = 5$ )

According to the method described by Hernandez F H and Eschrich J M, it can easily be obtained that the detection limit of the proposed method reaches down to  $9.1 \times 10^{-10}$  g/mL.

### 2.6 Interferences

The effects of diverse ion on the determination of 0.3  $\mu\text{g}/25\text{ mL}$  Cr(VI) are studied. The tolerance limit is defined as the concentration of added ion causing less than 5% relative error. Most metal ions did not interfere with the determination, even when they were present at 500~ 1000 times as much as the amount of chromium. Copper or iron interfered with the determination. Because Cr (VI) is a positive ion, the interference of copper and iron could be successfully eliminated by either ion exchange technique or precipitation separation. Chloride, sulfate, nitrate and phosphate showed no interference with the determination.

### 2.7 Precision and accuracy

Multiplicate determinations have been performed on different Cr (VI) standard concentrations and different steel samples. The results showed that relative standard deviations varied between 0.95% and 3.49% and the recoveries was 98% to 105%. Both can satisfy the requirement for routine analyses, and the precision and accuracy of the proposed method are better than any other methods.

### 2.8 Application

The procedure established was applied to the determination of chromium in steel.

Precisely weighed steel samples (0.10~ 0.13 g) were dissolved in 3 mL of aqua regia, drops of sulfuric acid solution were added to get rid of nitrid acid and hydrochloric acid. The residue was then dissolved in small amount of water. The pH of the test solution was adjusted to strong alkaline by KOH solution. Then 1 mL of  $\text{H}_2\text{O}_2$  solution (30%) was added into test solution to oxidize Cr (III) into Cr(VI). The test solution was filtered to remove the precipitates of  $\text{Fe}(\text{OH})_3$  and  $\text{MnO}_2$ . The precipitates were washed for 3~ 4 times with hot deionized water, and the filtrate was heated to remove excessive  $\text{H}_2\text{O}_2$ . Finally the resulting solution was diluted to 1000 mL.

The test solutions were diluted to an appropriate volume with deionized distilled water. The same procedure was followed as described above for the determination of Cr (VI) in the test solutions. The results of analyses are shown in Table 3.

Table 3 Determination of Chromium in Steel

No.	Sample	Sample taken/g	Aliquot /mL	Cr in sample (standard value) / %	Cr in sample (determined value) / %	Relative error / %	Relative standard deviation/ % (n= 6)
1	Chromium- tungsten -nickel steel	0.1000	1.0	1.84	1.81	1.74	3.49
2	20Cr3MoWV steel	0.1000	1.0	2.58	2.64	2.33	2.42
3	4Cr5MoSiV steel	0.1250	1.0		2.50		2.83

3 Conclusions

This work has shown that the detection limit for chromium could be as low as  $9.1 \times 10^{-10}$  g/mL with no need of any activator. Since the fixed time method could be employed for monitoring the reaction rate, only 2min are required for the absorbance measurement. The method has a higher sensitivity compared to other catalytic kinetic method reported previously. The BPR-H<sub>2</sub>O<sub>2</sub> reaction is catalyzed by not only Cr(VI) but also Fe(III) or Cu(II). This means that the catalytic system is applicable to a new approach for determining Fe(III) or Cu(II).

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借助于过氧化氢氧化溴苯三酚红的催化光度法测定钢样中的微量铬

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[ 摘要] 借助在弱酸性溶液中过氧化氢使溴苯三酚红褪色的催化效应测定了铬(VI), 研究了测定反应的最佳条件及各种离子的干扰效应. 利用 Anhenius 方程计算了非催化和催化反应的表现活化能, 检测限的线性范围为 0.1~ 0.6 μg Cr(VI)/25 mL, 检测限量达到  $9.1 \times 10^{-10}$  g/mL. 可以成功地应用于钢样中微量铬的测定.  
[ 关键词] 微量分析, 催化光度测定, 铬, 钢样

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