# Simultaneous Determination of Chromium(VI) and Manganese(VII) by Differential Kinetic Rate Spectrophotometry of Direct Yellow Brown D3G

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In this study, the fading reaction of Cr(VI) and Mn(VII) oxidating direct yellow brown D3G, a textile dyes, was investigated. In sulfuric acid medium, at 90 in water bath, both Cr(VI) and Mn(VII) could fade direct yellow brown D3G, but the fading rate was different. Moreover, there was no obvious synergistic effect between them. A new method to determine Cr(VI) and Mn(VII) by differential reaction rate kinetic direct yellow brown D3G fading spectrophotometry was purposed. The effect of medium acidity, the dosage of direct yellow brown D3G, reaction temperature and time on fading reaction was studied and the proportion equation was established. This method could be used to determine Cr(VI) and Mn(VII) in industrial wastewater and the results were according to the flame atomic absorption spectrophotometry.

**Key Words: Direct yellow brown D3G, Fading spectrophotometry, Differential kinetic rate, Cr(VI), Mn(VII), Wastewater.**

## INTRODUCTION

At present, in environmental monitoring, the determination of Cr(VI) and Mn(VII) usually uses spectrophotometry, atomic absorption spectrophotometry and ICP, *etc.*[1-4]. Spectrophotometry can only determine chromium and manganese respectively. Their operations are complicated. Moreover, atomic absorption spectrophotometry and ICP needs expensive instrument. Fading spectrophotometry has been used in the respective determination of Cr(VI) and Mn(VII) for its simple operation and low cost[5-7]. Combination of simple fading spectrophotometry and differential reaction rate kinetic method could realize simultaneous determination of multi-components[8-10]. Reference cost used bordeauxred R or amaranth as indicator and realized simultaneous determination of Cr(VI) and Mn(VII) in steel and wastewater. However, bordeauxred R and amaranth were high price. But using direct yellow brown D3G, a low price textile dyes, has not been studied. In this study, based on the different reaction rate of Cr(VI) and Mn(VII) with direct yellow brown D3G, a new method for simultaneous determination of Cr(VI) and Mn(VII) was developed using the proportion equation method. This method was used to synchronously determine Cr(VI) and Mn(VII) in industrial wastewater.

## EXPERIMENTAL

723 Spectrophotometer (Shanghai Precision Science Instrument Co. Ltd.); CS501 super temperature thermostat (Shanghai Experiment Instrument Company); Standard Mn(VII) stock solution: 0.1 g of potassium permanganate was dissolved in proper amount of water and then filtered with glass sand funnel (G3). The filtrate was decanted into 1 L volumetric flask, diluted to scale and calibrated with sodium oxalate. It should be diluted to standard 10 mg/L working solution. 100 mg/L standard Cr(VI) stock solution: 0.2829 g of potassium dichromate (reference reagent) was weighed and dried at 105 ℃ for 1 h. The sample was dissolved in water, decanted into 1 L volumetric flask and diluted to scale; it should be diluted to standard 10 mg/L working solution. Direct yellow brown D3G (a textile dyes, come from a textile factory) solution: 1 mmoL/L. All the reagents were analytically pure except otherwise specified and the water was distilled water.

**Experimental principal:** In sulfuric acid medium, both Cr(VI) and Mn(VII) could fade direct yellow brown D3G and the fading rate was different. The absorbance $A_0$, of non-oxidative system at $t_1$ and the absorbance $At_1$ after oxidized by Cr(VI) and/or Mn(VII) at $t_1$ were measured. According to the additivity of absorbance[10], the difference $\Delta At_1$ was:

$$\Delta A_{t1} = A_0 - A_{t1} = \Delta A_{t1(Mn)} + \Delta A_{t1(Cr)} = K_{t1(Mn)} \cdot \rho Mn + K_{t1(Cr)} \cdot \rho Cr + \alpha_{t1(Mn)} + \alpha_{t1(Cr)}$$

Similarly, at $t_2$ the difference $\Delta A_{t2}$ ($t_2 > t_1$) could be also obtained:

$$\Delta A_{t2} = A_0 - A_{t2} = \Delta A_{t2(Mn)} + \Delta A_{t2(Cr)} = K_{t2(Mn)} \cdot \rho Mn + K_{t2(Cr)} \cdot \rho Cr + \alpha_{t2(Mn)} + \alpha_{t2(Cr)}$$

Based on the standard curve of Cr(VI) and Mn(VII) at $t_1$ and $t_2$, the proportionality coefficients $K_{t1(Mn)}$, $K_{t1(Cr)}$, $K_{t2(Mn)}$ and $K_{t2(Cr)}$ and constants $\alpha_{t1(Mn)}$, $\alpha_{t1(Cr)}$, $\alpha_{t2(Mn)}$ and $\alpha_{t2(Cr)}$ could be obtained.

The mass concentration of Cr(VI) and Mn(VII) ($\rho_{Mn}$ and $\rho_{Cr}$, in mg/L) could be then obtained.

3 mL of direct yellow brown D3G solution, 0.5 mL of sulfuric acid (l+1) was added into two colourimetric cylinders in order and then diluted to about 15 mL with water. Standard Cr(VI) and/or Mn(VII) solution (oxidative system) was added into one colourimetric cylinder and the other colourimetric cylinder was added nothing (non-oxidative system). The solutions were diluted to 25 mL with water, shaken up and placed into a thermostatic water bath at 90 ºC, determined the absorbance at 1 min and 15 min (terminated the reaction with running water), the absorbance difference ($\Delta A_{t1}$ and $\Delta A_{t2}$) of oxidative system and non-oxidative system were measured at 480 nm with 10 mm colourimetric cuvette, taking water as reference, respectively.

## RESULTS AND DISCUSSION

**Absorption spectra:** The absorption spectra curves of each solution were shown in Fig. 1 after heating for 15 min at 90 ºC in water bath. It could be seen that in acid, direct yellow brown D3G itself did not fade, while existence of Cr(VI) and Mn(VII) could make it fade. Moreover, there was no obvious synergistic effect between them. All curves had maximal absorption peak and $\Delta A$ reached maximum at 480 nm. Therefore, 480 nm was selected as measuring wavelength in this study.
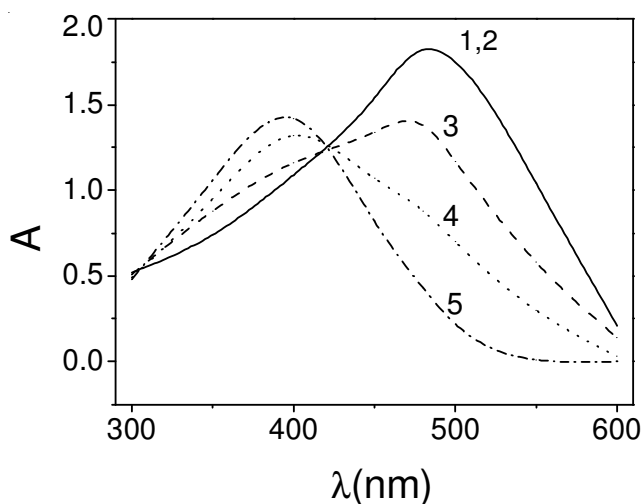


Fig. 1.  Absorption spectra; (1) Direct yellow brown D3G; (2) 1 + H₂SO₄; (3) 2+1 µg/mL Mn(VII); (4) 2+2 µg/mL Cr(VI); (5). 2+1 µg/mL Mn(VII) + 2 µg/mL Cr(VI)

**Acid and its dosage:** The effect of H₂SO₄, HCl, HNO₃ and H₃PO₄ and their dosage on the oxidation reaction was investigated. The results showed that whether for Cr(VI) and Mn(VII), $\Delta A$ had maximum in H₂SO₄, when the dosage was 1 mL. Therefore, 1 mL of 9 moL/L H₂SO₄, was used in this study.

**Optimal experimental conditions:** The effect of reaction time at different temperatures and different dosage of direct

yellow brown D3G on $\Delta A$ was investigated. The results showed that whether for Cr(VI) and Mn(VII), the sensitivity increased with the increase of direct yellow brown D3G dosage and reaction temperature. When the dosage of 1mmoL/L direct yellow brown D3G was 3 mL, the reaction sensitivity reached maximum in water bath at 90 ºC. Higher dosage and temperature resulted in lower sensitivity. The reaction of Mn(VII) was complete in water bath at 90 ºC in 0.5 min and the reaction of Cr(VI) in 15 min. Cr(VI) did not react with direct yellow brown D3G at room temperature. Therefore, the oxidation reaction of Cr(VI) could be terminated by flowing water. The dosage of direct yellow brown D3G in this study was 3 mL and the reaction time in water bath at 90 ºC was 1 min and 15 min for Cr(VI) and Mn(VII), respectively.

**Working curve, detection limit and precision:** The results showed that, Beer's law was obeyed in 0-11 µg/mL and 0-9.8 µg/mL for Cr(VI) and Mn (VII). The linear regression equations were:

$$\Delta A_{t1(Cr)} = 0.085\, \rho_{Cr} + 0.029\ (R = 0.9989)$$
$$\Delta A_{t2(Cr)} = 0.157\, \rho_{Cr} - 0.004\ (R = 0.9967)$$
$$\Delta A_{t1(Mn)} = \Delta A_{t2(Mn)} = 0.194 \cdot \rho_{Mn} + 0.113\ (R = 0.999)$$

Based on the above equations, the proportion equation group was obtained:

$$\Delta A_{t1(Cr,\, Mn)} = 0.085\, \rho_{Cr} + 0.194\, \rho_{Mn} + 0.142$$
$$\Delta A_{t2(Cr,\, Mn)} = 0.157\, \rho_{Cr} + 0.194\, \rho_{Mn} + 0.109$$

The detection limits ($3\sigma/k$) of Cr(VI) and Mn(VII) were 0.81 µg/mL and 0.11 µg/mL, respectively. 11 determinations for 2 µg/mL Cr(VI) were conducted and the RSD tor 1 min and 15 min were 3.11 % and 1.01 %, respectively. For 11 determinations of 1 µg/mL Mn(VII), the RSD in 1 min and 15 min were 1.87 % and l.23 %, respectively.

**Additivity test:** After mixing the standard solution of Cr(VI) and Mn(VII) at different ratios, they were determined according to the experimental method. The contents of Cr(VI) and Mn(VII) were obtained by proportion equation. The recovery was calculated and the results were listed in Table-l. It could be seen from Table-1 that, in this linear range, the additive property of Cr(VI) and Mn(VII) was good.

| TABLE-1 ADDITIVELY TEST OF Cr(VI) AND Mn(VII) | | | | | |
|---|---|---|---|---|---|
| Added (µg) | | Found (µg) | | Recovery (%) | |
| Mn(VII) | Cr(VI) | Mn(VII) | Cr(VI) | Mn(VII) | Cr(VI) |
| 20 | 20 | 21.08 | 19.35 | 105.4 | 96.8 |
| 50 | 20 | 52.31 | 18.96 | 104.6 | 94.8 |
| 100 | 20 | 98.98 | 21.14 | 99.0 | 105.7 |
| 20 | 50 | 20.10 | 51.25 | 100.5 | 102.5 |
| 50 | 50 | 49.33 | 52.31 | 98.7 | 104.6 |
| 100 | 50 | 101.52 | 48.01 | 101.5 | 96.0 |
| 20 | 100 | 21.88 | 97.26 | 109.4 | 97.3 |
| 50 | 100 | 48.92 | 104.58 | 97.8 | 104.6 |
| 100 | 100 | 99.35 | 103.42 | 99.4 | 103.4 |
| 20 | 120 | 20.66 | 124.50 | 103.3 | 103.8 |
| 50 | 120 | 48.11 | 119.40 | 96.2 | 99.5 |
| 100 | 120 | 95.44 | 121.80 | 95.4 | 101.5 |

**Effect of concurrent ions:** In 25 mL of solution, 50 µg of Cr(VI) and 25 µg of Mn(VII) were determined according to experimental method. When the relative error was ≤ ±5 %, the allowable amounts of concurrent ions were (in mg): K⁺,

$Na^+$, $Cl^-$, $NO_3^-$, $PO_4^{3-}$, $CO_3^{2-}$, $NH_4^+$ (50); hydrosulfate, EDTA, urea, $Mg^{2+}$ (10); W(VI), $Ca^{2+}$, $Ni^{2+}$, $F^-$ (3); $Zn^{2+}$, $Co^{2+}$ (5); Cr(III), $Al^{3+}$ (1); $I^-$, tartrate, citrate (0.5); Ti (IV), $V^{5+}$, $Pb^{2+}$, $NO_2^-$ (0.2); $Cu^{2+}$, $Ag^+$, $Fe^{2+}$, $Fe^{3+}$ (0.1). Therefore, most of the common ions did not interfere with the determination.

**Sample analysis:** 200 mL of wastewater sample was put into a beaker. Added 5-10 mL of $HNO_3$, the solution was further heated to about 10 mL. After slightly cooling, 1-2 mL of perchloric acid was added. The solution was heated dark until white smoke appeared. If the colour of solution appeared, $HNO_3$ should be added. The solution was heated until there was no white smoke any more. After cooling, the solid was dissolved with 0.2 % $HNO_3$ (v/v). If some precipitation was present, the solution should be filtered. After the filtrate was cooled to room temperature, it was diluted to 10 mL for determination (Table-2).

TABLE-2
ANALYTICAL RESULTS OF WASTE
WATER SAMPLES n = 6, mg/L

| Samples | Found | | RSD (%) | | Found by FAAS | |
|---|---|---|---|---|---|---|
| | Cr | Mn | Cr | Mn | Cr | Mn |
| Wastewater1 | 0.2501 | 0.3217 | 2.6 | 5.7 | 0.2498 | 0.3316 |
| Wastewater2 | 0.5384 | 0.7528 | 3.1 | 4.9 | 0.5299 | 0.7481 |

**Conclusion**

A new method to determine Cr(VI) and Mn(VII) by differential reaction rate kinetic direct yellow brown D3G fading spectrophotometry was purposed. The Beer's law was obeyed in 0-11 µg/mL and 0-9.8 µg/mL for Cr(VI) and Mn(VII). The detection limits of Cr(VI) and Mn(VII) were 0.81 µg/mL and 0.11 µg/mL, respectively. This method could be used to determine Cr(VI) and Mn(VII) in industrial wastewater with satisfactory results.

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