

# A Modified Method for the Accurate Determination of Chemical Oxygen Demand (COD) in High Chloride Oilfield Wastewater

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## Abstract

In this work, in order to find a method for the accurate determination of chemical oxygen demand ( $\text{COD}_{\text{Cr}}$ ) in high chloride oilfield wastewater, the interferences of chloridion ( $\text{Cl}^-$ ) on  $\text{COD}_{\text{Cr}}$  determination were first studied based on the Chinese national standard GB 11914-89. The results showed that the  $\text{COD}_{\text{Cr}}$  values and deviations determined by the classical potassium dichromate ( $\text{K}_2\text{Cr}_2\text{O}_7$ ) method increased gradually with the increase of  $\text{Cl}^-$  mass concentration in water samples. Then, theoretical and experimental studies on reducing interferences of  $\text{Cl}^-$  on  $\text{COD}_{\text{Cr}}$  determination were carried out. The results showed that different concentrations of  $\text{K}_2\text{Cr}_2\text{O}_7$  exhibited different oxidation capacities on  $\text{Cl}^-$ , while having little effects on the oxidation of organic compounds. More specifically, when the concentration of  $\text{K}_2\text{Cr}_2\text{O}_7$  was  $0.025 \text{ mol}\cdot\text{L}^{-1}$  and the mass ratio of  $\text{HgSO}_4:\text{Cl}^-$  was 10:1, the interferences of  $\text{Cl}^-$  on  $\text{COD}_{\text{Cr}}$  determination were the slightest. Finally, a low concentration oxidant method was proposed for the accurate determination of  $\text{COD}_{\text{Cr}}$  in high chloride oilfield wastewaters. The performances of the proposed method were verified by the simulated and actual high chloride oilfield wastewater. The results showed that when  $\text{Cl}^- \leq 20,000 \text{ mg}\cdot\text{L}^{-1}$  and  $\text{COD} < 100 \text{ mg}\cdot\text{L}^{-1}$ , the relative prediction errors of  $\text{COD}_{\text{Cr}}$  provided by the proposed method were acceptable, which revealed that the low concentration oxidant method is feasible and reliable for the determination of  $\text{COD}_{\text{Cr}}$  in high chloride oilfield wastewater.

## Keywords

High Chloride Oilfield Wastewater, Chloridion Interference, Chemical Oxygen Demand, Potassium Dichromate Method, Low Concentration Oxidant Method

## 1. Introduction

Chemical oxygen demand (COD) is one of the most important indexes to assess the pollution of organic compounds in water systems [1]. In China, potassium dichromate ( $K_2Cr_2O_7$ ) method is legalized by the Chinese government to determine  $COD_{Cr}$  in water samples [2] [3]. In practical operation, the high level of chloridion ( $Cl^-$ ) in water samples would cause serious interferences on  $COD_{Cr}$  determination [4] [5]. Therefore, the Chinese national standard method *Water Quality—Determination of Chemical Oxygen Demand—Dichromate Method* (GB 11914-89) regulated that when the content of  $Cl^-$  is less than  $1000\text{ mg}\cdot\text{L}^{-1}$ , mercuric sulfate ( $HgSO_4$ ) can be added to eliminate the interferences of  $Cl^-$  [6]. For the samples with  $Cl^-$  content more than  $1000\text{ mg}\cdot\text{L}^{-1}$ , they should be firstly diluted quantitatively so as to reduce their  $Cl^-$  contents to less than  $1000\text{ mg}\cdot\text{L}^{-1}$  and then determine their  $COD_{Cr}$  according to the Chinese national standard GB 11914-89. Research revealed that, the COD values of water samples with high  $Cl^-$  concentration and low COD content were still large after diluting, although  $HgSO_4$  was used to mask  $Cl^-$ , and the relative errors of  $COD_{Cr}$  increased with the increase of  $Cl^-$  concentration. However, during the process of monitoring and analysis, the high chloride wastewaters are often encountered, such as chemical wastewater, marine products processing wastewater, rare-earth mineral refining wastewater, oil produced wastewater. For example, Chen *et al.* [7] reported that the mass concentration of  $Cl^-$  in wastewater of an oilfield was more than  $120000\text{ mg}\cdot\text{L}^{-1}$ , whose COD content was low, and the COD values would become smaller after treatment. But the local environmental protection department used the Chinese national standard GB 11914-89 to monitor its COD concentration with results fluctuating significantly and gave the actual measured  $COD_{Cr}$  values ranging from several hundreds to  $2500\text{ mg}\cdot\text{L}^{-1}$ , which greatly exceeded the national requirements of wastewater discharge ( $COD < 100\text{ mg}\cdot\text{L}^{-1}$ ) [8]. This dilemma brings huge troubles to the wastewater disposal departments, local environmental monitoring and law enforcement departments as well as the water quality analysis workers. Therefore, how to eliminate the interferences of  $Cl^-$  on the  $COD_{Cr}$  determination has become a research hot for environmental monitoring workers [9].

At present, there are many methods for reducing the interferences of  $Cl^-$ , such as chlorine correction method, low concentration oxidant method, silver salt precipitation method, sealed digestion method, mercury salt method and no external heating method [10] [11] [12] [13] [14], which have not yet been unified. However, in the practical operations of the environmental monitoring department, the national or industrial standards recommended by the Chinese Ministry of Environmental Protection are still used as the reference method. Among them, potassium dichromate method (GB 11914-89, abbreviated as the classical method) [6] is the mandatory national standard, whereas fast digestion-spectrophotometric method (HJ/T 399-2007) [15], chlorine correction method (HJ/T 70-2001) [16] and potassium iodide-alkaline potassium permanganate determination method (HJ/T 132-2003) [17] are the standards released by the National

Environmental Protection Department, which are the supplements to the national standard, and whose legal status are naturally lower than that of the classical method (GB 11914-89) [6]. Consequently, during the supervision of law enforcement, the COD determination of samples with high requirements such as discharge sample, assessment sample, arbitration analysis sample is preferred by the classical method (GB 11914-89).

Considering the current research situation mentioned above, the aim of the work is to develop a method that can meet the national standard, and can accurately determine the  $\text{COD}_{\text{Cr}}$  in wastewaters with high content of  $\text{Cl}^-$ . In this work, the interferences of  $\text{Cl}^-$  on  $\text{COD}_{\text{Cr}}$  determination were first investigated by experiments based on the Chinese national standard GB 11914-89, and then the mechanism of interferences was explained. After that, based on the theoretical analysis of electrode potential, a low concentration oxidant method was proposed for the determination of  $\text{COD}_{\text{Cr}}$  in high chloride wastewaters. The performances of the proposed method were verified by simulated and actual high chloride oilfield wastewater. The results demonstrated that the proposed low concentration oxidant method based on GB 11914-89 was accurate and reliable, and thus it is a feasible method for the determination of  $\text{COD}_{\text{Cr}}$  in high chloride oilfield wastewater.

## 2. Experimental Section

### 2.1. Reagents and Instruments

Reagents: potassium dichromate solution ( $1/6\text{K}_2\text{Cr}_2\text{O}_7$ ) with concentrations of  $0.25\text{ mol}\cdot\text{L}^{-1}$ ,  $0.10\text{ mol}\cdot\text{L}^{-1}$  and  $0.025\text{ mol}\cdot\text{L}^{-1}$ ; ammonium ferrous sulfate solution [ $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2\cdot 6\text{H}_2\text{O}$ ] with concentrations of  $0.1\text{ mol}\cdot\text{L}^{-1}$ ,  $0.04\text{ mol}\cdot\text{L}^{-1}$  and  $0.01\text{ mol}\cdot\text{L}^{-1}$ ; mercury sulfate ( $\text{HgSO}_4$ , A.R.), silver sulfate ( $\text{Ag}_2\text{SO}_4$ , A.R.); sulfuric acid ( $\text{H}_2\text{SO}_4$ , 98%); seven hydrated ferrous sulfate ( $\text{FeSO}_4\cdot 7\text{H}_2\text{O}$ , A.R.); standard potassium acid phthalate ( $\text{KC}_8\text{H}_5\text{O}_4$ , G.R.); sodium chloride ( $\text{NaCl}$ , A.R.); 1,10-phenanthroline. All these reagents were purchased from the Sinopharm Chemical Reagent Co., Ltd. and used without further purification (Shanghai, China).

Instruments: JH-12 COD constant temperature heater (Laoshan Electronic General Factory Co., Ltd., Qingdao, China); ICS-2100 ion chromatography (Thermo Fisher Scientific, U.S.A.).

### 2.2. Experimental Methods

1) Classical  $\text{K}_2\text{Cr}_2\text{O}_7$  method: this classical method was described in detailed in the Chinese national standard *Water Quality—Determination of Chemical Oxygen Demand—Dichromate Method* (GB 11914-89) [6]. Before determination, the method was calibrated by the standard solution of  $\text{KC}_8\text{H}_5\text{O}_4$  with a reference  $\text{COD}_{\text{Cr}}$  of  $500\text{ mg}\cdot\text{L}^{-1}$  for 5 times, giving the relative errors of  $\text{COD}_{\text{Cr}}$  less than 4%, which indicated that the operation technique, instrument and chemical reagents used in this work meet the requirements.

2) Low concentration oxidant method: this method was modified based on the classical standard method described above. More specifically, during the COD<sub>Cr</sub> determination, 0.1 mol·L<sup>-1</sup> or 0.025 mol·L<sup>-1</sup> of 1/6K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> standard solution was used instead of 0.25 mol·L<sup>-1</sup> of 1/6K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> standard solution as the oxidant, whose residual content was then back titrated by corresponding 0.04 mol·L<sup>-1</sup> and 0.01 mol·L<sup>-1</sup> of [(NH<sub>4</sub>)<sub>2</sub>Fe(SO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O] standard solution, respectively.

### 3. Results and Discussion

#### 3.1. Interferences of Cl<sup>-</sup> on COD<sub>Cr</sub> Determination in Simulated High Chloride Oilfield Wastewater

##### 3.1.1. Determination of High COD<sub>Cr</sub> in Simulated High Chloride Oilfield Wastewater by Classical K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> Method

A series of standard water samples with a theoretical COD<sub>Cr</sub> value of 500 mg·L<sup>-1</sup> and Cl<sup>-</sup> mass concentrations of 100, 500, 1000, 2000, 4000, 8000, 10,000, 15,000 and 20,000 mg·L<sup>-1</sup> were prepared as simulated high chloride oilfield wastewater by using standard KC<sub>8</sub>H<sub>5</sub>O<sub>4</sub> and standard NaCl. According to the classical K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> method, 20 mL of each water sample was transferred into a COD digestion tube, then 0.4 g HgSO<sub>4</sub> and 30 mL AgSO<sub>4</sub>-H<sub>2</sub>SO<sub>4</sub> were added to the sample solution, and finally the mixture of each water was oxidized with 10 mL of 0.25 mol·L<sup>-1</sup> K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> standard solution. After heating reflux for about 2 h, the residual content of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> was back titrated by corresponding 0.1 mol·L<sup>-1</sup> [(NH<sub>4</sub>)<sub>2</sub>Fe(SO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O] standard solution. The obtained COD<sub>Cr</sub> results in the prepared water samples are summarized in **Table 1**.

**Table 1.** Results of determination of high chlorine and high COD (500 mg·L<sup>-1</sup>) standard water samples by classical K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> method.

Sample No.	KC <sub>8</sub> H <sub>5</sub> O <sub>4</sub> theoretical COD/(mg·L <sup>-1</sup> )	Cl <sup>-</sup> content/(mg·L <sup>-1</sup> )	Dilution fold	Found COD/(mg·L <sup>-1</sup> )	Relative error/%
1	500	100	1	507.3	1.5
2	500	500	1	498.7	-0.3
3	500	1000	1	509.3	1.9
4	500	2000	1	528.4	5.7
5	500	4000	2	602.5	20.5
6	500	8000	4	795.8	59.2
7	500	15,000	8	961.4	92.3
8	500	20,000	10	1291.1	158.2

As can be seen from **Table 1**, for the simulated high chloride oilfield wastewater samples with a theoretical COD<sub>Cr</sub> of 500 mg·L<sup>-1</sup> and high level of Cl<sup>-</sup>, when the mass concentration of Cl<sup>-</sup> was less than 2000 mg·L<sup>-1</sup>, the relative errors of COD<sub>Cr</sub> determined by the classical K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> method were relatively small (< 5.7%), which almost accorded with the national requirements that the relative error of COD<sub>Cr</sub> determination should be within ±5% [18] [19]. This is because

the addition of 0.4 g HgSO<sub>4</sub> in 20 mL water samples was perfectly able to coordinate 2000 mg·L<sup>-1</sup> Cl<sup>-</sup> in wastewater, and then the interferences of Cl<sup>-</sup> on COD<sub>Cr</sub> determination can be virtually eliminated. However, with the increase of Cl<sup>-</sup> mass concentration in water samples, the Cl<sup>-</sup> in water samples could not be completely coordinated by 0.4 g HgSO<sub>4</sub>, resulting in the obtained concentration of COD<sub>Cr</sub> in water samples increased gradually, and the differences between the experimental values and theoretical ones also increased gradually. All the above results indicated that pseudo COD<sub>Cr</sub> was introduced during the determination of COD<sub>Cr</sub> in high chloride wastewater by the classical K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> method. As a result, if the interferences of Cl<sup>-</sup> cannot be effectively eliminated, the obtained inaccurate COD<sub>Cr</sub> results will cause wrong expert conclusion for water quality.

### 3.1.2. Determination of Low COD<sub>Cr</sub> in Simulated High Chloride Oilfield Wastewater by Classical K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> Method

A series of standard water samples with a theoretical COD<sub>Cr</sub> value of 100 mg·L<sup>-1</sup> and Cl<sup>-</sup> mass concentrations of 100, 500, 1000, 2000, 4000, 8000, 10,000, 15,000 and 20,000 mg·L<sup>-1</sup> were prepared as simulated high chloride oilfield wastewater by using standard KC<sub>8</sub>H<sub>5</sub>O<sub>4</sub> and standard NaCl. According to the classical K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> method, 20 mL of each water sample was transferred into a COD digestion tube, then 0.4 g HgSO<sub>4</sub> and 30 mL AgSO<sub>4</sub>-H<sub>2</sub>SO<sub>4</sub> were added to the sample solution, and finally the mixture of each water was oxidized with 10 mL of 0.25 mol·L<sup>-1</sup> K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> standard solution. After heating reflux for about 2 h, the residual content of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> was back titrated by corresponding 0.1 mol·L<sup>-1</sup> [(NH<sub>4</sub>)<sub>2</sub>Fe(SO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O] standard solution. The obtained COD<sub>Cr</sub> results in the prepared water samples are summarized in **Table 2**.

**Table 2.** Results of determination of high chlorine and low COD (100 mg·L<sup>-1</sup>) standard water samples by classical K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> method.

Sample No.	KC <sub>8</sub> H <sub>5</sub> O <sub>4</sub> theoretical COD/(mg·L <sup>-1</sup> )	Cl <sup>-</sup> content/(mg·L <sup>-1</sup> )	Dilution fold	Found COD/(mg·L <sup>-1</sup> )	Relative error/%
1	100	100	1	100.0	0
2	100	500	1	108.0	8.0
3	100	1000	1	113.7	13.7
4	100	2000	1	175.9	75.9
5	100	4000	1	324.3	224.3
6	100	8000	1	627.3	527.3
7	100	15,000	1	981.6	881.6
8	100	20,000	1	981.6	881.6

As can be seen from **Table 2**, for the simulated high chloride oilfield wastewater samples with a theoretical COD<sub>Cr</sub> of 100 mg·L<sup>-1</sup> and high level of Cl<sup>-</sup>, when the mass concentration of Cl<sup>-</sup> was less than 500 mg·L<sup>-1</sup>, the relative errors of COD<sub>Cr</sub> determined by the classical K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> method almost conformed to the allowable error range required by the Chinese government. But with the increase

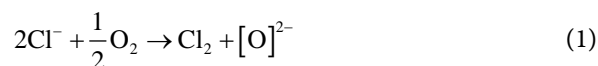
of  $\text{Cl}^-$  mass concentration in water samples, not only the  $\text{COD}_{\text{Cr}}$  values determined by the classical  $\text{K}_2\text{Cr}_2\text{O}_7$  method increased gradually, but also the differences between the experimental values and theoretical ones increased gradually. And the relative errors obtained in low COD water samples are more remarkable than those of high COD water samples as described in Section 3.1.1, which is mainly due to the higher relative concentration of  $\text{Cl}^-$  in low COD water samples than those in high COD water samples under the same mass concentration of  $\text{Cl}^-$ . Therefore, it is very necessary for pollutant discharging companies, environmental monitoring and legislation departments to develop a method for the accurate determination of COD in high chloride wastewater.

### 3.1.3. Analysis of Interference Mechanism

At present, the classical  $\text{K}_2\text{Cr}_2\text{O}_7$  method (GB 11914-89) is used to determine COD in water sample by concentrated  $\text{H}_2\text{SO}_4$ -assisted heating reflux. During the reaction process, not only organic compounds but also  $\text{Cl}^-$  in water sample were oxidized by  $\text{K}_2\text{Cr}_2\text{O}_7$ . The interferences of  $\text{Cl}^-$  are mainly attributed to the following two aspects:

#### 1) Consumption of oxidant $\text{K}_2\text{Cr}_2\text{O}_7$

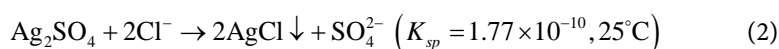
Regarding water sample containing  $\text{Cl}^-$ , apart from the reaction between organic compounds and  $\text{K}_2\text{Cr}_2\text{O}_7$ , the  $\text{Cl}^-$  can be also oxidized by  $\text{K}_2\text{Cr}_2\text{O}_7$  and thus consumes some oxidants, which will affect the accuracy of COD determination. The corresponding reaction equation about  $\text{Cl}^-$  in the water sample can be expressed as follows:



Theoretically, 0.226 mg oxygen is needed for complete oxidation of 1 mg  $\text{Cl}^-$  [ $15.999/(2 \times 35.453) = 0.226$ ]. Taking the above reason into account,  $\text{Cl}^-$  can cause huge positive interferences on  $\text{COD}_{\text{Cr}}$  determination because of its consumption of oxidant  $\text{K}_2\text{Cr}_2\text{O}_7$  under the condition of Chinese national standard GB 11914-89.

#### 2) Consumption of catalyst $\text{Ag}_2\text{SO}_4$

In the mixture system of  $\text{H}_2\text{SO}_4$ - $\text{K}_2\text{Cr}_2\text{O}_7$ , acidified  $\text{K}_2\text{Cr}_2\text{O}_7$  can just oxidize most of the organic compounds in the water sample. Only after adding catalyst  $\text{Ag}_2\text{SO}_4$ , can the straight chain aliphatic compounds be completely oxidized, which increases the oxidation rate of organic compounds and makes the oxidation reaction proceed more completely. However, if the water sample contains  $\text{Cl}^-$ , it will combine with  $\text{Ag}^+$  to produce  $\text{AgCl}$  precipitate, resulting in poisoning of the catalyst, then decreasing the oxidation rate of the sample, and finally affecting the final determination results of COD. The reaction between  $\text{Cl}^-$  and  $\text{Ag}_2\text{SO}_4$  is expressed as follows:



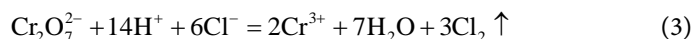
In addition, the resulting  $\text{AgCl}$  precipitate can be further oxidized by  $\text{K}_2\text{Cr}_2\text{O}_7$ , which also consumes some oxidants. Moreover, the white precipitate makes the

solution color at the end of titration become grey and difficult to be titrated accurately.

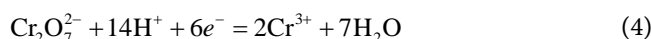
### 3.2. Reducing Interferences of Cl<sup>-</sup> on COD<sub>Cr</sub> Determination in High Chloride Oilfield Wastewater

#### 3.2.1. Theoretical Analysis of Reducing Cl<sup>-</sup> Interference

During the COD determination, the interference reaction of Cl<sup>-</sup> is as follows:



In Equation (3), the electrode reaction of electron pair Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup>/Cr<sup>3+</sup> is:



And the electrode reaction of electron pair Cl<sub>2</sub>/Cl<sup>-</sup> is:



According to the Nernst equation, the electrode potential of electron pair Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup>/Cr<sup>3+</sup> can be calculated as follows:

$$\begin{aligned} \varphi_{\text{Cr}_2\text{O}_7^{2-}/\text{Cr}^{3+}} &= \varphi_{\text{Cr}_2\text{O}_7^{2-}/\text{Cr}^{3+}}^\theta + \frac{RT}{nF} \ln \frac{\alpha_{\text{Cr}_2\text{O}_7^{2-}} \cdot \alpha_{\text{H}^+}^{14}}{\alpha_{\text{Cr}^{3+}}^2} \\ &= \varphi_{\text{Cr}_2\text{O}_7^{2-}/\text{Cr}^{3+}}^\theta + \frac{RT}{nF} \ln \alpha_{\text{H}^+}^{14} + \frac{RT}{nF} \ln \frac{\alpha_{\text{Cr}_2\text{O}_7^{2-}}}{\alpha_{\text{Cr}^{3+}}^2} \end{aligned} \quad (6)$$

Similarly, the electrode potential of electron pair Cl<sub>2</sub>/Cl<sup>-</sup> can be calculated as:

$$\varphi_{\text{Cl}_2/\text{Cl}^-} = \varphi_{\text{Cl}_2/\text{Cl}^-}^\theta + \frac{RT}{nF} \ln \frac{p_{\text{Cl}_2}/p^\theta}{\alpha_{\text{Cl}^-}^2} \quad (7)$$

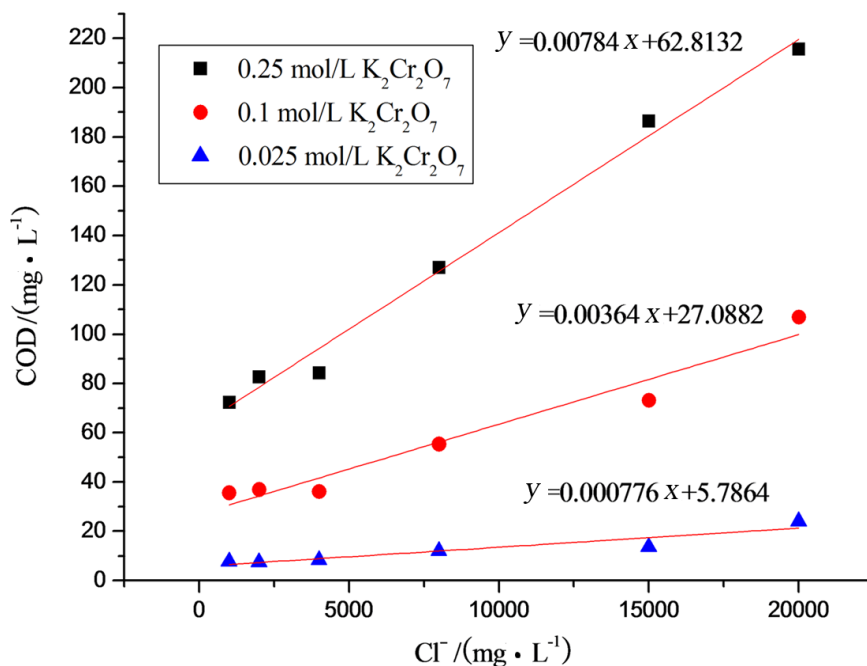
In the determination of COD<sub>Cr</sub>, the conditional electrode potential of oxidant K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> can reach to  $\varphi_{\text{Cr}_2\text{O}_7^{2-}/\text{Cr}^{3+}} = 1.55 \text{ V}$  due to the strong acid medium (in non strong acid medium  $\varphi_{\text{Cr}_2\text{O}_7^{2-}/\text{Cr}^{3+}} = 1.33 \text{ V}$ ) [20], thus the oxidation reaction of Cl<sup>-</sup> can occur completely ( $\varphi_{\text{Cl}_2/\text{Cl}^-} = 1.36 \text{ V}$ ). And the higher the oxidation potential is, the easier the Cl<sup>-</sup> will be oxidized, and consequently the greater the error introduced is.

As can be known from Equation (6), the concentration of Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> and Cr<sup>3+</sup> is one of the main factors that affect the electrode potential. Under certain conditions of COD<sub>Cr</sub> determination, the higher the oxidant concentration is, the more residual amount of oxidant will be after the reaction, which makes the ratio of Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup>/Cr<sup>3+</sup> larger, and results in a higher oxidation potential. Theoretically speaking, the proper reduction of the oxidant concentration is helpful to reduce the oxidation potential of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> and thus reduce the interferences of Cl<sup>-</sup> on COD<sub>Cr</sub> determination.

#### 3.2.2. Effect of Oxidant Concentration on the Oxidation of Cl<sup>-</sup>

In order to investigate the effect of oxidant concentration on Cl<sup>-</sup> oxidation, a series of NaCl solutions with Cl<sup>-</sup> mass concentrations of 1000, 2000, 4000, 8000, 15,000 and 20,000 mg·L<sup>-1</sup> were prepared by standard NaCl. 20 mL of each water sample was transferred into a COD digestion tube, then appropriate amounts of

HgSO<sub>4</sub> [ $m(\text{HgSO}_4) : m(\text{Cl}^-) = 10 : 1$ ] were added to the sample solution, and finally the mixture of each water was oxidized with 10 mL of 0.25, 0.1 and 0.025 mol·L<sup>-1</sup> K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> standard solution, respectively. After heating reflux for about 2 h, the residual content of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> was back titrated by corresponding 0.1, 0.04 and 0.01 mol·L<sup>-1</sup> [(NH<sub>4</sub>)<sub>2</sub>Fe(SO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O] standard solution, respectively. The obtained COD<sub>Cr</sub> results in the prepared water samples are plotted in **Figure 1**.



**Figure 1.** Effect of oxidant concentration on the oxidation of Cl<sup>-</sup>.

As can be seen from **Figure 1**, on the one hand, under the same Cl<sup>-</sup> mass concentration, both the oxidation rate of Cl<sup>-</sup> and obtained COD<sub>Cr</sub> values increased gradually with the increase of oxidant concentration; on the other hand, under the same oxidant concentration, the obtained COD<sub>Cr</sub> values and their relative errors also increased gradually with the increase of Cl<sup>-</sup> concentration. When the oxidant concentration was about 0.025 mol·L<sup>-1</sup>, the oxidation rate of Cl<sup>-</sup> was the smallest. These results indicated that the oxidant concentration plays a very important role during the determination of COD in high chloride wastewater. Therefore, the proper reduction of oxidant concentration is helpful to reduce the oxidation rate of Cl<sup>-</sup> and improve the accuracy of COD<sub>Cr</sub> determination, which is highly consistent with our theoretical analysis in Section 3.2.1.

### 3.2.3. Effect of Oxidant Concentration on the Oxidation of Organic Compounds

In order to investigate the effect of oxidant concentration on the oxidation of organic compounds, a series of standard KC<sub>8</sub>H<sub>5</sub>O<sub>4</sub> solutions with theoretical COD<sub>Cr</sub> values of 50, 100, 300 and 600 mg·L<sup>-1</sup> were prepared by standard KC<sub>8</sub>H<sub>5</sub>O<sub>4</sub>. After proper dilution, 20 mL of each water sample was transferred into a COD digestion tube, then 30 mL AgSO<sub>4</sub>-H<sub>2</sub>SO<sub>4</sub> was added to the sample so-



lution, and finally the mixture of each water was oxidized with 10 mL of 0.25, 0.1 and 0.025 mol·L<sup>-1</sup> K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> standard solution, respectively. After heating reflux for about 2 h, the residual content of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> was back titrated by corresponding 0.1, 0.04 and 0.01 mol·L<sup>-1</sup> [(NH<sub>4</sub>)<sub>2</sub>Fe(SO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O] standard solution, respectively. The obtained COD<sub>Cr</sub> results in the prepared water samples are summarized in **Table 3**.

**Table 3.** Effect of oxidant concentration on COD determination of standard KC<sub>8</sub>H<sub>5</sub>O<sub>4</sub> water samples.

Theoretical COD/(mg·L <sup>-1</sup> )	Dilution fold	0.25 mol·L <sup>-1</sup> K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> COD/(mg·L <sup>-1</sup> )	Dilution fold	0.1 mol·L <sup>-1</sup> K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> COD/(mg·L <sup>-1</sup> )	Dilution fold	0.025 mol·L <sup>-1</sup> K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> COD/(mg·L <sup>-1</sup> )
50	1	51.0	1	54.6	1	48.1
100	1	97.3	1	100.8	2	93.9
300	1	299.8	1	299.5	5	286.0
600	1	596.8	2	602.1	10	583.3

**Table 3** revealed that under the same condition of COD<sub>Cr</sub> determination, different concentrations of oxidants exhibit almost the same oxidation ability on the standard KC<sub>8</sub>H<sub>5</sub>O<sub>4</sub>, and the measured COD<sub>Cr</sub> values are nearly consistent with the theoretical ones. In addition, with the increase of theoretical COD<sub>Cr</sub> value in the samples, the measured results by different concentrations of oxidants are almost the same, which implied that the concentration of oxidant has little effect on the oxidation of organic compounds as long as the amount of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> is enough.

#### 3.2.4. Effect of the Amount of Masking Agent on COD<sub>Cr</sub> Determination

In order to investigate the effect of the amount of masking agent on COD<sub>Cr</sub> determination, in this part, a series of standard water samples with a theoretical COD<sub>Cr</sub> value of 500 mg·L<sup>-1</sup> and Cl<sup>-</sup> mass concentrations of 1000, 2000, 4000, 8000, 15,000 and 20,000 mg·L<sup>-1</sup> were prepared by standard KC<sub>8</sub>H<sub>5</sub>O<sub>4</sub> and standard NaCl. After 10-folds dilution, 20 mL of each water sample was transferred into a COD digestion tube, then different amounts of HgSO<sub>4</sub> based on the mass ratio of HgSO<sub>4</sub>:Cl<sup>-</sup> together with 30 mL AgSO<sub>4</sub>-H<sub>2</sub>SO<sub>4</sub> were added to the sample solution, and finally the mixture of each water was oxidized with 10 mL of 0.25 mol·L<sup>-1</sup> K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> standard solution. After heating reflux for about 2 h, the residual content of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> was back titrated by corresponding 0.1 mol·L<sup>-1</sup> [(NH<sub>4</sub>)<sub>2</sub>Fe(SO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O] standard solution. The obtained COD<sub>Cr</sub> results in the prepared water samples are summarized in **Table 4**.

As can be seen from **Table 4**, the relative errors of COD<sub>Cr</sub> results decreased gradually with the increase of the mass ratio of HgSO<sub>4</sub>: Cl<sup>-</sup>. When the mass ratio of HgSO<sub>4</sub>: Cl<sup>-</sup> is 10:1, the relative errors are small (<±3%), and they are not significantly improved with the increase of the mass ratio of HgSO<sub>4</sub>: Cl<sup>-</sup>. However, the environmental pollution risk would increase if large amounts of HgSO<sub>4</sub> were used. Therefore, 10:1 was suggested to be the suitable mass ratio of HgSO<sub>4</sub>: Cl<sup>-</sup> for COD<sub>Cr</sub> determination in high chlorine wastewater.

**Table 4.** Effect of mass ratio of  $\text{HgSO}_4:\text{Cl}^-$  on  $\text{COD}_{\text{Cr}}$  determination in high chlorine water samples.

Sample No.	$\text{Cl}^-$ content/( $\text{mg}\cdot\text{L}^{-1}$ )	5:1	10:1	15:1	20:1
1	1000	500.0 [0%]*	511.2 [2.2%]	495.6 [-0.9%]	484.0 [-3.2%]
2	2000	507.2 [1.4%]	514.4 [2.9%]	508.0 [1.6%]	510.4 [2.1%]
3	4000	519.6 [3.9%]	495.6 [-0.9%]	502.4 [0.5%]	492.0 [-1.6%]
4	8000	558.4 [11.7%]	511.6 [2.3%]	532.0 [6.4%]	516.0 [3.2%]
5	15,000	567.2 [13.4%]	508.4 [1.7%]	520.0 [4.0%]	512.8 [2.6%]
6	20,000	551.2 [10.2%]	514.8 [3.0%]	520.0 [4.0%]	520.0 [4.0%]

\*The values in bracket are the relative errors and the same meanings in Table 5 and Table 6.

### 3.3. Determination of $\text{COD}_{\text{Cr}}$ in High Chlorine Oilfield Wastewater by Low Concentration Oxidant Method

#### 3.3.1. Determination of Low $\text{COD}_{\text{Cr}}$ in Simulated High Chloride Oilfield Wastewater by Low Concentration Oxidant Method

A series of simulated high chlorine oilfield wastewater samples with theoretical  $\text{COD}_{\text{Cr}}$  values of 50 and 80  $\text{mg}\cdot\text{L}^{-1}$ , and  $\text{Cl}^-$  mass concentrations of 1000, 2000, 4000, 8000, 15,000 and 20,000  $\text{mg}\cdot\text{L}^{-1}$  were prepared by standard  $\text{KC}_8\text{H}_5\text{O}_4$  and standard  $\text{NaCl}$ . According to the classical  $\text{K}_2\text{Cr}_2\text{O}_7$  method, 20 mL of each water sample was transferred into a COD digestion tube, then appropriate amounts of  $\text{HgSO}_4$  [ $m(\text{HgSO}_4) : m(\text{Cl}^-)=10:1$ ] and 30 mL  $\text{AgSO}_4\text{-H}_2\text{SO}_4$  were added to the sample solution, and finally the mixture of each wastewater was oxidized with 10 mL of 0.25  $\text{mol}\cdot\text{L}^{-1}$ , 0.1  $\text{mol}\cdot\text{L}^{-1}$  and 0.025  $\text{mol}\cdot\text{L}^{-1}$   $\text{K}_2\text{Cr}_2\text{O}_7$  standard solution, respectively. After heating reflux for about 2 h, the residual content of  $\text{K}_2\text{Cr}_2\text{O}_7$  was back titrated by corresponding 0.1, 0.04 and 0.01  $\text{mol}\cdot\text{L}^{-1}$   $[(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2\cdot 6\text{H}_2\text{O}]$  standard solution, respectively. The obtained  $\text{COD}_{\text{Cr}}$  results in the simulated high chlorine oilfield wastewater samples are summarized in Table 5.

**Table 5.** Determination results of high chlorine and low COD simulated oilfield wastewater using different concentrations of oxidants.

Sample No.	$\text{Cl}^-$ content/( $\text{mg}\cdot\text{L}^{-1}$ )	Theoretical $\text{COD}/(\text{mg}\cdot\text{L}^{-1})$	0.25 $\text{mol}\cdot\text{L}^{-1}$ $\text{K}_2\text{Cr}_2\text{O}_7$ $\text{COD}/(\text{mg}\cdot\text{L}^{-1})$	0.1 $\text{mol}\cdot\text{L}^{-1}$ $\text{K}_2\text{Cr}_2\text{O}_7$ $\text{COD}/(\text{mg}\cdot\text{L}^{-1})$	0.025 $\text{mol}\cdot\text{L}^{-1}$ $\text{K}_2\text{Cr}_2\text{O}_7$ $\text{COD}/(\text{mg}\cdot\text{L}^{-1})$
1	1000	50	118.4 [136.8%]	77.3 [54.6%]	45.7 [-8.5%]
2		80	156.4 [95.5%]	109.4 [36.7%]	79.3 [-0.9%]
3	2000	50	138.2 [176.4%]	83.8 [67.6%]	47.1 [-5.8%]
4		80	159.9 [99.9%]	110.6 [38.3%]	80.4 [0.5%]
5	4000	50	170.3 [240.6%]	94.2 [88.4%]	50.8 [1.7%]
6		80	187.4 [134.2%]	120.0 [50.0%]	81.7 [2.1%]
7	8000	50	166.3 [232.6%]	92.0 [84.1%]	49.3 [-1.5%]
8		80	211.3 [164.1%]	115.4 [44.3%]	80.9 [1.2%]
9	15,000	50	183.3 [266.7%]	91.4 [82.8%]	51.5 [3.0%]
10		80	226.6 [183.2%]	118.2 [47.8%]	83.6 [4.5%]
11	20,000	50	174.6 [249.3%]	85.2 [70.4%]	50.0 [0.0%]
12		80	215.2 [169.0%]	109.4 [36.7%]	82.8 [3.5%]

**Table 5** shows that with the increase of  $\text{Cl}^-$  mass concentration in wastewater samples, the relative errors of  $\text{COD}_{\text{Cr}}$  determination increased gradually. However, the obtained results provided by low concentration oxidant method ( $0.025 \text{ mol}\cdot\text{L}^{-1}$ ) are much better than those determined by  $0.25 \text{ mol}\cdot\text{L}^{-1}$  and  $0.1 \text{ mol}\cdot\text{L}^{-1}$  oxidants, and the relative errors conform to the national requirements for  $\text{COD}_{\text{Cr}}$  determination. These experimental results demonstrated that low concentration oxidant method is feasible for the determination of low  $\text{COD}_{\text{Cr}}$  in high chlorine wastewater when  $\text{Cl}^-$  concentration is not more than  $20000 \text{ mg}\cdot\text{L}^{-1}$  and  $\text{COD} < 100 \text{ mg}\cdot\text{L}^{-1}$ .

### 3.3.2. Determination of High $\text{COD}_{\text{Cr}}$ in Simulated High Chloride Oilfield Wastewater by Low Concentration Oxidant Method

It can be inferred from the above experimental results that the determination of high  $\text{COD}_{\text{Cr}}$  in high chlorine wastewater is also possible by low concentration oxidant method. In order to verify this inference, a series of simulated high chlorine oilfield wastewater samples with theoretical  $\text{COD}_{\text{Cr}}$  values of 500, 1000 and  $3000 \text{ mg}\cdot\text{L}^{-1}$ , and  $\text{Cl}^-$  mass concentrations of 5000, 10,000, 50,000, 10,000 and  $200,000 \text{ mg}\cdot\text{L}^{-1}$  were prepared by standard  $\text{KC}_8\text{H}_5\text{O}_4$  and standard  $\text{NaCl}$ . After proper dilution, 20 mL of each water sample was transferred into a COD digestion tube, then appropriate amounts of  $\text{HgSO}_4$  [ $m(\text{HgSO}_4) : m(\text{Cl}^-) = 10:1$ ] and 30 mL  $\text{AgSO}_4\text{-H}_2\text{SO}_4$  were added to the sample solution, and finally the mixture of each wastewater was oxidized with 10 mL of  $0.025 \text{ mol}\cdot\text{L}^{-1}$   $\text{K}_2\text{Cr}_2\text{O}_7$  standard solution. After heating reflux for about 2 h, the residual content of  $\text{K}_2\text{Cr}_2\text{O}_7$  was back titrated by  $0.01 \text{ mol}\cdot\text{L}^{-1}$   $[(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2\cdot 6\text{H}_2\text{O}]$  standard solution. The obtained  $\text{COD}_{\text{Cr}}$  results in the simulated high chlorine oilfield wastewater samples are summarized in **Table 6**.

**Table 6.** Determination results of high chlorine and high COD simulated oilfield wastewater by low concentration oxidant method.

Sample No.	$\text{Cl}^-$ content/ ( $\text{mg}\cdot\text{L}^{-1}$ )	Dilution fold	Theor. COD 500 $\text{mg}\cdot\text{L}^{-1}$ / ( $\text{mg}\cdot\text{L}^{-1}$ )	Dilution fold	Theor. COD 1000 $\text{mg}\cdot\text{L}^{-1}$ / ( $\text{mg}\cdot\text{L}^{-1}$ )	Dilution fold	Theor. COD 3000 $\text{mg}\cdot\text{L}^{-1}$ / ( $\text{mg}\cdot\text{L}^{-1}$ )
1	5000	10	487.3 [-2.5%]	20	992.3 [-0.8%]	60	2887.7 [-3.7%]
2	10000	10	507.5 [1.5%]	20	975.4 [-2.5%]	60	3045.6 [1.5%]
3	50000	10	528.1 [5.6%]	20	999.9 [0.0%]	60	3084.0 [2.8%]
4	100,000	10	537.8 [7.6%]	20	1026.1 [2.6%]	60	3094.9 [3.2%]
5	200,000	10	525.2 [5.0%]	20	10,333.7 [3.4%]	60	3099.7 [3.3%]

As can be seen from **Table 6**, the low concentration oxidant method provides relatively small errors for the determination of high  $\text{COD}_{\text{Cr}}$  in high chlorine wastewater, and the obtained results are accurate and reliable. The above experiments proved that it is feasible to determine  $\text{COD}_{\text{Cr}}$  (including both low COD and high COD) in high chlorine wastewater by low concentration oxidant method. Therefore, in the next part, we intend to extend the low concentration

oxidant method to determine the COD<sub>Cr</sub> values in actual high chloride oilfield wastewater.

### 3.3.3. Determination of COD<sub>Cr</sub> in Actual High Chloride Oilfield Wastewater by Low Concentration Oxidant Method

Six kinds of oilfield wastewater samples named JHSX, JHCL, XJ81J, XJ81C, XJ91J and XJ91C were collected from Jiangnan oilfield and Xinjiang oilfield, China. The Cl<sup>-</sup> contents in the six wastewater samples are 92,744.4, 74,155.4, 7578.5, 7699.7, 2086.8 and 2273 mg·L<sup>-1</sup>, respectively, which were determined by a Thermo Fisher ICS-2100 ion chromatograph. It clearly shows that these wastewater samples belong to typical high chloride oilfield wastewater. Therefore, in this section, the COD<sub>Cr</sub> values in these six high chloride oilfield wastewater samples were determined by the proposed low concentration oxidant method. According to the low concentration of oxidant method, each wastewater sample was diluted 10-folds and 20 mL of diluted wastewater sample was transferred into a COD digestion tube, then appropriate amounts of HgSO<sub>4</sub> [ $m(\text{HgSO}_4): m(\text{Cl}^-)=10:1$ ] and 30 mL AgSO<sub>4</sub>-H<sub>2</sub>SO<sub>4</sub> were added to the sample solution, and finally the mixture of each wastewater was oxidized with 0.025 mol·L<sup>-1</sup> K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> standard solution. After heating reflux, the residual content of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> was back titrated by corresponding 0.01 mol·L<sup>-1</sup> [(NH<sub>4</sub>)<sub>2</sub>Fe(SO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O] standard solution. The obtained COD<sub>Cr</sub> results in the six kinds of actual high chloride oilfield wastewater samples are summarized in **Table 7**.

**Table 7.** Determination results of COD<sub>Cr</sub> in six actual high chloride oilfield wastewater samples by low concentration oxidant method.

Sample No.	Water sample	Cl <sup>-</sup> / (mg·L <sup>-1</sup> )	Dilution fold	Unspiked COD / (mg·L <sup>-1</sup> )	Spiked COD / (mg·L <sup>-1</sup> )	Spiked recovery / %
1	JHSX	92,744.4	10	154.1	631.1	95.4
2	JHCL	74,155.4	10	150.5	630.3	96.0
3	XJ81J	7578.5	10	109.0	641.3	106.5
4	XJ81C	7699.7	10	148.2	635.0	97.4
5	XJ91J	2086.8	10	123.1	626.8	100.7
6	XJ91C	2273.0	10	87.8	606.8	103.8

As shown in **Table 7**, the COD<sub>Cr</sub> values of six kinds of high chloride oilfield wastewater samples are not high, which ranges from 100 to 150 mg·L<sup>-1</sup>. Furthermore, spiked recovery experiments were carried out to verify the accuracy of low concentration oxidant method for COD<sub>Cr</sub> determination in actual high chloride oilfield wastewater. Firstly, 500 mg·L<sup>-1</sup> theoretical COD<sub>Cr</sub> was added to the above six high chloride oilfield wastewater samples, and then the COD<sub>Cr</sub> values of these spiked oilfield wastewater samples were determined by the proposed low concentration oxidant method. The spiked recoveries were calculated as  $c_1/c_2 \times 100\%$ , where  $c_1$  is the difference of measured total COD<sub>Cr</sub> value of the spiked oilfield wastewater samples and unspiked oilfield wastewater samples; and  $c_2$  is the theoretical COD<sub>Cr</sub> value of added standard K<sub>2</sub>C<sub>8</sub>H<sub>5</sub>O<sub>4</sub>. The calculated recovery

results are shown in **Table 7**. It can be seen from **Table 7** that the spiked COD<sub>Cr</sub> recoveries of six high chloride oilfield wastewater samples measured by the low concentration oxidant method were in the range of 95.4-106.5%, which revealed that the low concentration oxidant method is feasible and reliable for the determination of COD<sub>Cr</sub> in high chloride oilfield wastewater.

#### 4. Conclusions

1) As for high chloride water samples, the COD<sub>Cr</sub> values and their deviations determined by the classical potassium dichromate (K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>) method increased gradually with the increase of Cl<sup>-</sup> mass concentration. These effect is more obvious in low COD<sub>Cr</sub> wastewater than that of high COD<sub>Cr</sub> wastewater, which revealed that Cl<sup>-</sup> has serious interferences on the determination of COD<sub>Cr</sub> based on the classical K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> method.

2) During the interference analysis, the oxidation abilities of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> on Cl<sup>-</sup> decreased as its decreasing concentration, while having little effects on the oxidation of organic compounds. More specifically, when the concentration of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> was 0.025 mol·L<sup>-1</sup>, the interferences of Cl<sup>-</sup> on COD<sub>Cr</sub> determination were the slightest. Therefore, the optimum concentration of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> in this study was identified as 0.025 mol·L<sup>-1</sup> for the determination of COD<sub>Cr</sub> in high chloride oilfield wastewater.

3) The relative errors of COD<sub>Cr</sub> determined by the low concentration K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> method were relatively small and the measured results were accurate in simulated and actual high chloride oilfield wastewater. Moreover, like the Chinese national standard GB 11914-89 method, the low concentration K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> method is simple and feasible, and thus it is suitable for the analysis of water samples in large numbers, which proved to be a very effective method for the determination of COD<sub>Cr</sub> in high chloride oilfield wastewater.

4) It was found that low concentration oxidant method has higher requirements on experimental conditions and operator levels due to the use of low concentration of oxidant for the determination of COD<sub>Cr</sub> in high chloride oilfield wastewater. Therefore, during the process of testing, skilled operators and strict operations are crucial for the success of experiments.

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#### Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

## References

- [1] Ma, J. (2017) Determination of Chemical Oxygen Demand in Aqueous Samples with Non-Electrochemical Methods. *Trends in Environmental Analytical Chemistry*, **14**, 37-43. <https://doi.org/10.1016/j.teac.2017.05.002>
- [2] State Environmental Protection Administration of China (2002) Water and Wastewater Monitoring and Analysis Methods. 4th Edition, China Environmental Science Press, Beijing, 210-213.
- [3] Li, J., Luo, G., He, L., Xu, J. and Lyu, J. (2018) Analytical Approaches for Determining Chemical Oxygen Demand in Water Bodies: A Review. *Critical Reviews in Analytical Chemistry*, **48**, 47-65. <https://doi.org/10.1080/10408347.2017.1370670>
- [4] Vaidya, B., Watson, S.W., Coldiron, S.J. and Porter, M.D. (1997) Reduction of Chloride Ion Interference in Chemical Oxygen Demand (COD) Determinations Using Bismuth-Based Adsorbents. *Analytica Chimica Acta*, **357**, 167-175. [https://doi.org/10.1016/S0003-2670\(97\)00541-2](https://doi.org/10.1016/S0003-2670(97)00541-2)
- [5] Vyrides, I. and Stuckey, D.C. (2009) A Modified Method for the Determination of Chemical Oxygen Demand (COD) for Samples with High Salinity and Low Organics. *Bioresource Technology*, **100**, 979-982. <https://doi.org/10.1016/j.biortech.2008.06.038>
- [6] National Standard of the People's Republic of China. Water Quality—Determination of Chemical Oxygen Demand—Dichromate Method (GB 11914-89).
- [7] Chen, P., Zhang, S.H., Lin, N.X. and Chen, W. (2016) Determination of COD in Wastewater Discharged from the Softener in Produced Water of an Oilfield in Xinjiang. *Journal of Yangtze University (Natural Section Edition)*, **13**, 1-6.
- [8] National Standard of the People's Republic of China. Pollutant Discharge Standard of Urban Sewage Treatment Plant (GB 18918-2002).
- [9] Geerdink, R.B., van den Hurk, R.S. and Epema, O.J. (2017) Chemical Oxygen Demand: Historical Perspectives and Future Challenges. *Analytica Chimica Acta*, **961**, 1-11. <https://doi.org/10.1016/j.aca.2017.01.009>
- [10] Baumann, F.J. (1974) Dichromate Reflux Chemical Oxygen Demand. Proposed Method for Chloride Correction in Highly Saline Wastes. *Analytical Chemistry*, **46**, 1336-1338. <https://doi.org/10.1021/ac60345a039>
- [11] Wang, H., Xu, X.L., Han, Y., Le, C. and Zhang, H.Y. (2017) Determination of COD in Effluent with High Chloride from Nanofiltration Membrane for Landfill Leachate Treatment by Chlorine Emendation Method. *China Water & Wastewater*, **33**, 115-117.
- [12] Ma, Y.Y., He, H.J., Yuan, H.Y., Zhang, X.G. and Zhang, X. (2013) Low Concentration COD Analysis Method for Low Concentration of High Chloride Ion Drilling Wastewater in Oil and Gas Field. *Henan Chemical Industry*, **30**, 57-59.
- [13] Domini, C.E., Hidalgo, M., Marken, F. and Canals, A. (2006) Comparison of Three Optimized Digestion Methods for Rapid Determination of Chemical Oxygen Demand: Closed Microwaves, Open Microwaves and Ultrasound Irradiation. *Analytica Chimica Acta*, **561**, 210-217. <https://doi.org/10.1016/j.aca.2006.01.022>
- [14] Yang, H.H., Bu, X.B. and Zhang, T. (2015) Research on the Methods for Eliminating the Interference of Chlorine Ion in COD Determination. *Shandong Chemical Industry*, **4**, 53-54.
- [15] Environmental Protection Industry Standard of the People's Republic of China, Water quality—Determination of Chemical Oxygen Demand—Fast Digestion Spectrophotometric Method (HJ/T 399-2007).

- [16] Environmental Protection Industry Standard of the People's Republic of China, High-Chlorine Wastewater—Determination of Chemical Oxygen Demand—Chlorine Emendation Method (HJ/T 70-2001).
- [17] Environmental Protection Industry Standard of the People's Republic of China, High-Chlorine Wastewater—Determination of Chemical Oxygen Demand—Potassium Iodide Alkaline Permanganate Method (HJ/T 132-2003).
- [18] Chen, G.M. and Zhou, X.L. (2012) Discussion on Determination Methods of COD Concentration in Wastewater Containing High Chloride. *Industrial Water & Wastewater*, **43**, 85-87.
- [19] Liu, X.Y., Zhang, D. and Qi, C.W. (2014) New Methods and Research Progress on Determination of Chemical Oxygen Demand. *Guangdong Chemical Industry*, **41**, 53-54.
- [20] Lu, F. and Wu, C. (2009) Water Quality COD On-Line Monitoring Instrument and Laboratory Analysis Method Difference Comparison and Analysis. *China Resources Comprehensive Utilization*, **27**, 27-29.