Comparative study on ozone oxidation chemiluminescence method and classical alkaline potassium permanganate method for determination of chemical oxygen demand in seawater

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Abstract. Seawater in the coastal waters of Qingdao, China was collected, and COD was measured by ozone oxidation chemiluminescence method and alkaline potassium permanganate method which was adopted in China as the standard method for measuring COD in seawater, respectively. The results show that when COD was less than 1 mg/L, the absolute error of ozone oxidation chemiluminescence method was less than 0.1 mg/L, and when COD was more than 1 mg/L, the relative error was less than 10%. The relative standard deviation of ozone oxidation chemiluminescence method was lower than 5%, and the detection limit was 0.0022 mg/L. The results of ozone oxidation chemiluminescence method were close to those of alkaline potassium permanganate method. With higher precision, lower detection limit, faster measurement, and online measurement, ozone oxidation chemiluminescence method is an ideal monitoring method for COD in seawater in the field.

1. Introduction

Chemical oxygen demand (COD), which is used to characterize organic pollution, is a routine monitoring parameter for marine ecological environment. COD is the main pollutant discharged into the sea in China. Long-term monitoring of COD in seawater in the field can help us to understand the degree of organic pollution in seawater in time, to formulate a reasonable target to control organic pollutants discharged, and then improve the marine ecological environment [1] [2].

In order to prevent chloridion from oxidation, the standard method for measuring COD in seawater adopted in China is the alkaline potassium permanganate method (GB17378.4). The water samples need to be taken back to the laboratory for heating and titration, which is time-consuming.

Commercial COD on-line and in-situ measuring instruments are available. On-line COD measuring instruments based on potassium dichromate method or permanganate index method [3], such as products of HACH and Systea S.p.A. Company, can monitor the COD in freshwater such as surface water, domestic sewage and industrial wastewater. Owing to the ability to oxidize chloridion, these...
instruments are not suitable for the measurement of COD in seawater. Spectrometric COD sensor [4], such as S::CAN and TriOS products, can measure COD in situ. Such instruments can measure dissolved organic matter with strong absorption in the ultraviolet region, such as organic matter containing benzene ring, and can not measure organic matter without ultraviolet absorption such as alcohols, sugars and organic acids. The data obtained by this sensor are not well correlated with those obtained by alkaline potassium permanganate method. Instruments based on other principles, such as electrochemical method [5], photocatalytic method [6], also have the problem of oxidizing chloridion or poor correlation between the measured data and the data obtained by alkaline potassium permanganate method.

Chemiluminescence has attracted considerable attention due to its high sensitivity, wide linear range, good reproducibility and portable devices [7]. Ozone is a kind of green strong oxidant. After Bowman [8] reported the ozone oxidation chemiluminescence system, ozone as a luminescent reagent attracted much attention. Some studies have shown that there was chemiluminescence in the reaction between ozone and organic matter. Zhang et al. [9] showed that there was chemiluminescence in the reaction of ozone with alcohols, phenols and carbohydrates. Bulgakov [10] found that the spectral integral values between 450nm and 600 nm had a good correlation with the CDOM concentration.

We attempt to measure COD in seawater based on the principle of ozone oxidation chemiluminescence. Ozone is produced by high pressure electrical discharge in the air. Chemiluminescence signals produced by the reaction of ozone with organic matter are measured. The quantitative relationship between chemiluminescence signal and COD concentration was established, and then the concentration of COD in seawater was calculated. This method is fast and does not need additional reagents. It is an ideal method for monitoring seawater COD in the field. In this paper, the comparative study of ozone oxidation chemiluminescence method and alkaline potassium permanganate method for measuring COD in seawater was carried out, in terms of accuracy, precision and detection limit. It is hoped that the ozone oxidation chemiluminescence method can be used to monitor COD in seawater in the field.

2. Material and methods

2.1. Measuring process

The process of alkaline potassium permanganate method is as follows. Under alkaline and heating conditions, excessive potassium permanganate is used to oxidize oxygen-demand substances in seawater. Then in acidic environment, potassium iodide is used to reduce the remaining potassium permanganate and manganese dioxide. Finally, the generated free iodine is titrated with sodium thiosulfate. The reaction equation is as follows:

\[
\begin{align*}
\text{MnO}_4^- + 3\text{C} + 2\text{H}_2\text{O} & = 4\text{MnO}_2 \downarrow + 3\text{CO}_2 + 4\text{OH}^- \\
2\text{MnO}_4^- (\text{remaining}) + 10\text{I}^- + 16\text{H}^+ & = 2\text{Mn}^{2+} + 5\text{I}_2 + 8\text{H}_2\text{O} \\
\text{MnO}_2 \downarrow + 2\text{I}^- + 4\text{H}^+ & = \text{Mn}^{2+} + \text{I}_2 + 2\text{H}_2\text{O} \\
\text{I}_2 + \text{S}_2\text{O}_3^{2-} & = \text{S}_4\text{O}_6^{2-} + 2\text{I}^- 
\end{align*}
\]

We have developed an on-line measuring instrument based on the principle of ozone oxidation chemiluminescence method (Figure 1). The measuring time is less than 5 minutes. The measurement process is as follows. Ozone generator produces ozone by high pressure discharge of air. Ozone passes through the hydrophobic and permeable membrane and reacts with oxygen-demand substances in seawater. The generated chemiluminescence signal is continuously detected by photomultiplier tube, and the COD concentration is calculated by combining with the obtained chemiluminescence kinetic curve integral model.
2.2. Experimental methods

In order to obtain seawater with high, medium and low COD concentration gradients, the seawater near Xiaogang Port, Zhongyuan Port, Shilaoren bathing beach and Shazikou of Qingdao, China was collected. COD in seawater was measured by ozone oxidation chemiluminescence on-line measuring instrument and alkaline potassium permanganate method respectively. Each method was measured five times in parallel. When the COD value of seawater sample was less than 1 mg/L, the accuracy of the method was expressed by absolute error according to formula 1; when the COD value of seawater sample was more than 1 mg/L, the accuracy of the method was expressed by relative error according to formula 2. The relative standard deviation was used to express the precision of the method according to formula 3. Distilled water was measured 11 times in parallel, and the detection limit was calculated by formula 4.

\[ \Delta C = C_p - C_s \]  
\[ \delta C = \frac{C_p - C_s}{C_s} \times 100\% \]  
\[ RSD\% = \sqrt{\frac{\sum(x_i - \bar{x})^2}{n - 1}} \frac{1}{\bar{x}} \]  
\[ DL = 3.3 \times SD_B \]  

Where \( \Delta C \) is the absolute error of ozone oxidation chemiluminescence method (mg/L), \( \delta C \) is the relative error of ozone oxidation chemiluminescence method, \( C_p \) is the average value of ozone oxidation chemiluminescence method (mg/L), and \( C_s \) is the average value of alkaline potassium permanganate method (mg/L).

3. Results and discussions

The COD in the coastal waters of Qingdao, China were measured by ozone oxidation chemiluminescence on-line measuring instrument and alkaline potassium permanganate method,
respectively. The results of 23 samples are shown in Table 1. COD in seawater ranged from 0.256 mg/L to 4.57 mg/L. The correlation of measurement data between ozone oxidation chemiluminescence method and alkaline potassium permanganate method was good ($R^2 = 0.985$, Figure 2). The results of the two methods were close. When COD was less than 1 mg/L, the absolute error of ozone oxidation chemiluminescence method was less than 0.1 mg/L; when COD was more than 1 mg/L, the relative error was less than 10%. This may be due to the similarity of the organic species oxidized by the two methods. Alkaline potassium permanganate is relatively weak in oxidation ability, easy to oxidize simple organic compounds, like hydrocarbons, alcohols, phenols and aldehydes, and poor in the oxidation of complex organic compounds, such as organic compounds containing benzene rings. Zhang et al. [9] have shown that ozone can react with alcohols, phenols and carbohydrates to form intermediate ROOH, which is unstable and can rapidly release emissive $^{1}O_2$ species, causing chemiluminescence. Organic compounds with simpler structure and less space hindrance have stronger chemiluminescence intensity. Complex benzene ring structure will lead to weak chemiluminescence intensity.

Table 1. COD results by ozone oxidation chemiluminescence method and alkaline potassium permanganate method.

| Sample | Measuring results of ozone method (mg/L) | Measuring results by alkaline permanganate method (mg/L) | Absolute/relative error of ozone method | Relative standard deviation of ozone method | Relative standard deviation of alkaline permanganate method |
|--------|------------------------------------------|--------------------------------------------------------|-----------------------------------------|---------------------------------------------|----------------------------------------------------------|
| 1      | 0.701                                    | 0.688                                                  | 0.013 mg/L                              | 2.01%                                       | 3.23%                                                    |
| 2      | 0.634                                    | 0.656                                                  | -0.022 mg/L                             | 1.89%                                       | 2.16%                                                    |
| 3      | 0.662                                    | 0.672                                                  | -0.01 mg/L                              | 3.26%                                       | 3.72%                                                    |
| 4      | 2.72                                     | 2.95                                                   | -7.80%                                  | 1.25%                                       | 3.89%                                                    |
| 5      | 3.02                                     | 3.09                                                   | -2.27%                                  | 3.31%                                       | 4.93%                                                    |
| 6      | 3.07                                     | 2.98                                                   | 3.02%                                   | 3.67%                                       | 4.58%                                                    |
| 7      | 3.10                                     | 3.42                                                   | -9.36%                                  | 0.89%                                       | 1.63%                                                    |
| 8      | 0.488                                    | 0.446                                                  | 0.042 mg/L                              | 4.45%                                       | 4.91%                                                    |
| 9      | 0.541                                    | 0.606                                                  | -0.065 mg/L                             | 2.98%                                       | 3.61%                                                    |
| 10     | 1.55                                     | 1.42                                                   | 9.15%                                   | 1.18%                                       | 3.85%                                                    |
| 11     | 2.55                                     | 2.32                                                   | 9.91%                                   | 1.03%                                       | 2.75%                                                    |
| 12     | 3.80                                     | 3.48                                                   | 9.20%                                   | 0.94%                                       | 1.46%                                                    |
| 13     | 0.375                                    | 0.436                                                  | -0.061 mg/L                             | 4.86%                                       | 6.53%                                                    |
| 14     | 0.428                                    | 0.492                                                  | -0.064 mg/L                             | 4.07%                                       | 4.63%                                                    |
| 15     | 0.766                                    | 0.742                                                  | 0.024 mg/L                              | 4.80%                                       | 1.75%                                                    |
| 16     | 0.573                                    | 0.598                                                  | -0.025 mg/L                             | 2.27%                                       | 2.74%                                                    |
| 17     | 0.540                                    | 0.448                                                  | 0.092 mg/L                              | 1.39%                                       | 6.47%                                                    |
| 18     | 0.639                                    | 0.670                                                  | -0.031 mg/L                             | 4.56%                                       | 2.35%                                                    |
| 19     | 0.554                                    | 0.482                                                  | 0.072 mg/L                              | 1.02%                                       | 4.25%                                                    |
| 20     | 4.12                                     | 4.57                                                   | -9.85%                                  | 0.41%                                       | 1.02%                                                    |
| 21     | 1.52                                     | 1.39                                                   | 9.35%                                   | 1.96%                                       | 1.06%                                                    |
| 22     | 4.10                                     | 4.52                                                   | -9.29%                                  | 0.69%                                       | 0.19%                                                    |
| 23     | 0.176                                    | 0.256                                                  | -0.08 mg/L                              | 4.45%                                       | 5.92%                                                    |
Figure 2. Correlation analysis by ozone oxidation chemiluminescence method and alkaline potassium permanganate method.

For 23 seawater COD samples, the relative standard deviation of ozone oxidation chemiluminescence method was less than 5%, and the maximum relative standard deviation of alkaline potassium permanganate method was 6.53% (Table 1). The repeatability of ozone oxidation chemiluminescence method was better than that of alkaline potassium permanganate method in 82.6% samples, indicating that ozone oxidation chemiluminescence method had higher precision. This is mainly because the ozone oxidation chemiluminescence method is an automatic measurement method, which avoids the human interference in the sampling process and the measurement process.

Ozone oxidation chemiluminescence on-line measuring instrument was used to measure distilled water 11 times in parallel. The results are shown in Table 2. The detection limit of ozone oxidation chemiluminescence method was 0.0022 mg/L, lower than 0.15 mg/L of alkaline potassium permanganate method, indicating that ozone oxidation chemiluminescence method has higher sensitivity.

| Sample | COD value of distilled water (mg/L) | Standard deviation (mg/L) | Detection limit (mg/L) |
|--------|-----------------------------------|---------------------------|------------------------|
| 1      | 0.006                             |                           | 0.0022                 |
| 2      | 0.006                             |                           |                        |
| 3      | 0.005                             |                           |                        |
| 4      | 0.006                             |                           |                        |
| 5      | 0.006                             |                           |                        |
| 6      | 0.005                             | 0.0007                    | 0.0022                 |
| 7      | 0.005                             |                           |                        |
| 8      | 0.006                             |                           |                        |
| 9      | 0.005                             |                           |                        |
| 10     | 0.004                             |                           |                        |
| 11     | 0.005                             |                           |                        |

4. Conclusion
The results of seawater samples with different COD concentrations show that the correlation between ozone oxidation chemiluminescence method and alkaline potassium permanganate method was good,
and the results were close. Compared with the alkaline potassium permanganate method, ozone oxidation chemiluminescence method has higher precision, lower detection limit, faster measurement, and can realize on-line monitoring without additional reagents. It is suitable for monitoring COD in seawater in the field.

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References
[1] Liu, L., Chen, D., Ren, M., Ge C. (2009) Study on total quantity control of pollutant in Xiangshan Bay. Mar. Environ. Sci., 28: 13–15.
[2] Tang, J., Shao, M., Tao, P., Chen L., Wang T. (2016) The further research on seawater exchange and diffusion ability of pollutant COD of Pulandian Bay in Dalian. Trans. Oceanol. Limnol., 1: 37–44.
[3] Maya, F., Estela, J.M., Cerdà, V. (2010) Flow analysis techniques as effective tools for the improved environmental analysis of organic compounds expressed as total indices. Talanta, 81: 1-8.
[4] Zhao, M., Tang, P., Tang, B. (2018) Research on Denoising of UV-Vis Spectral Data for Water Quality Detection with Compressed Sensing Theory Based on Wavelet Transform. Spectrosc. Spect. Anal., 38: 844-850.
[5] Cao, X., Zhou, M., Ma, Y. (2018) A rapid potentiometric titration method for measuring low-level chemical oxygen demand in organic wastewater containing the synthetic phenothiazine dyes. Anal. Methods-UK, 10: 1902-1910.
[6] Liang, L., Yin, J., Bao, J. (2019) Preparation of Au nanoparticles modified TiO2 nanotube array sensor and its application as chemical oxygen demand sensor. Chinese Chem. Lett., 30: 167-170.
[7] Gill, A., Zajda, J., Meyerhoff, M.E. (2019) Comparison of electrochemical nitric oxide detection methods with chemiluminescence for measuring nitrite concentration in food samples. Anal. Chim. Acta, 107: 167-173.
[8] Bowman, R.L., Alexander, N. (1966) Ozone-Induced Chemiluminescence of Organic Compounds. Science, 154: 1454-1456.
[9] Zhang, D., Zheng, Y., Dou, X., Lin, H. (2017) Heterogeneous Chemiluminescence from Gas-Solid Phase Interactions of Ozone with Alcohols, Phenols, and Saccharides. Langmuir, 33: 3666-3671.
[10] Bulgakov, R.G., Musavirova, A.S., Abdakhmanov, A.M. (2002) Chemiluminescence in ozonolysis of solutions of fullerene C60. J. Appl. Spectrosc+, 69: 220-224.