Influence of temperature and turbidity on water COD detection by UV absorption spectroscopy*

ZHOU Kun-peng (周昆鹏)[1,2], **BI Wei-hong** (毕卫红)[1]**, **ZHANG Qi-hang** (张启航)[1], **FU Xing-hu** (付兴虎)[1], **and WU Guo-qing** (吴国庆)[1]

1. The Key Laboratory for Special Fiber and Fiber Sensor of Hebei Province, School of Information Science and Engineering, Yanshan University, Qinhuangdao 066004, China

2. School of Physics and Electronic Information, Inner Mongolia University for Nationalities, Tongliao 028000, China

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Ultraviolet (UV) absorption spectroscopy is used to detect the concentration of water chemical oxygen demand (COD). The UV absorption spectra of COD solutions are analyzed qualitatively and quantitatively. The partial least square (PLS) algorithm is used to model COD solution and the modeling results are compared. The influence of environmental temperature and turbidity is analyzed. These results show that the influence of temperature on the predicted value can be ignored. However, the change of turbidity can affect the detection results of UV spectra, and the COD detection error can be effectively compensated by establishing the single-element regression model.

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Chemical oxygen demand (COD) is one of the most important indicators in the pollution degree of organic pollutants[1]. There are a lot of methods for COD detection, such as titration method[2], fast digestion-spectrophotometric method[3], electrochemical method[4], spectral method[5-7], et al. In recent years, the spectroscopy method has been widely used in many areas, such as food, biology[8], medicine, safety and environment monitoring[9,10], and so on. Ultraviolet/visible (UV/vis) spectroscopy has been previously used for water quality monitoring[11-16]. However, the studies have not fully taken environmental factors into account, such as the temperature and turbidity.

In this paper, the water COD is detected by UV spectrophotometry, and the influence of environmental factors such as temperature and turbidity on the detection process is analyzed, which has lower detection limit and higher sensitivity. The AvaSpec-2048-2 UV/vis spectroscopy (Avantes, Holland) is used to collect the spectra. The parameters of the UV/vis spectroscopy are set as follows: the spectral scanning range is between 200 nm and 310 nm, with 1 nm resolution, 3 ms integral time, 20 times of scanning and 10 mm optical path length. All of the samples used in the experiment are diluted by COD standard solution (1 000 mg/L) and turbidity standard solution (800 NTU). The digital adjustable precision liquid transfers (Brand, Germany) are used for removing the liquid. 29 COD solutions are prepared, whose concentrations are 1 mg/L, 2.5 mg/L, 5 mg/L, 10 mg/L, 20 mg/L, 40 mg/L, 60 mg/L, … 480 mg/L, 500 mg/L, respectively. The spectra are obtained by the spectra data collecting system shown in Fig.1, and the spectral scanning results are shown in Fig.2.

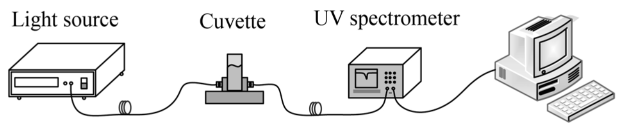

Fig.1 UV spectrum collecting system

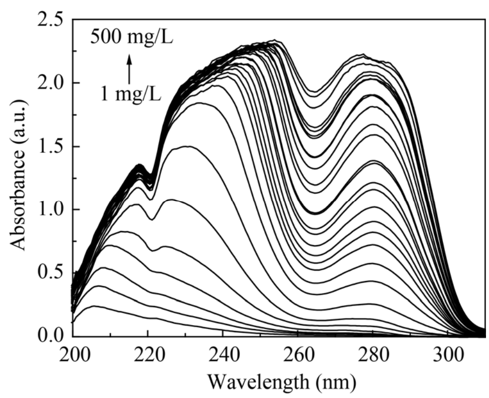

Fig.2 UV spectra of COD standard solutions

Partial least squares (PLS) regression is used for mod-

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** E-mail: whbi@ysu.edu.cn

eling in this study, and the prediction performance evaluation of the model is based on several performance indices, such as determination correlation (R^2), root-mean-squared error of calibration (*RMSEC*) and residual standard deviation (*RSD*). The equations of those performance indices are given as follows:

$$R^2 = 1 - \frac{\sum_{i=1}^{n} (\hat{y}_i - y_i)^2}{\sum_{i=1}^{n} (y_i - \bar{y})^2} , \quad (1)$$

$$RSD = \frac{RMSEP}{\frac{1}{n}\sum_{i=1}^{n} y_i} \times 100\% , \quad (2)$$

$$RMSEC = \sqrt{\frac{\sum_{i=1}^{n} (\hat{y}_i - y_i)^2}{n - A - 1}} . \quad (3)$$

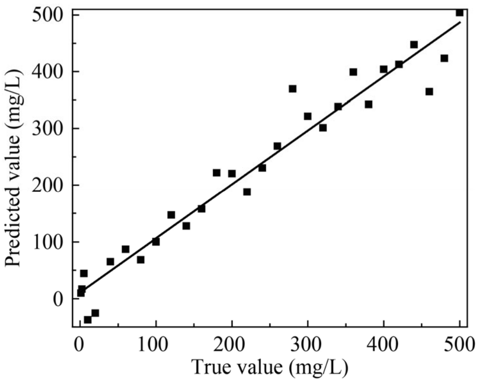
In Eq.(2), *RMSEP* represents the root-mean-squared error of prediction, and its equation is

$$RMSEP = \sqrt{\frac{1}{m}\sum_{i=1}^{m} (\hat{y}_i - y_i)^2} , \quad (4)$$

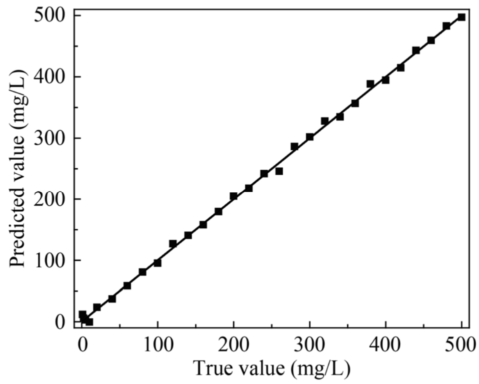
where $\hat{y}_i$ is the predicted value by calibration model, $\bar{y}$ is the mean of measured values, y_i is the measured value based on the reference method, n is the number of calibration samples, m is the number of validation samples, and A is the number of regression factors.

In Fig.2, we can see that the COD solution absorption phenomenon exists mainly in the near UV region, where 200—225 nm, 225—265 nm and 265—310 nm correspond to the E1, E2 and B absorption bands of $C_8H_5KO_4$ (solute of the COD standard solution), respectively[17]. The PLS algorithm is used to model the COD solution based on the data in UV spectrum (200—225 nm, 225—265 nm, 265—310 nm and 200—310 nm, respectively). The results are shown in Fig.3.

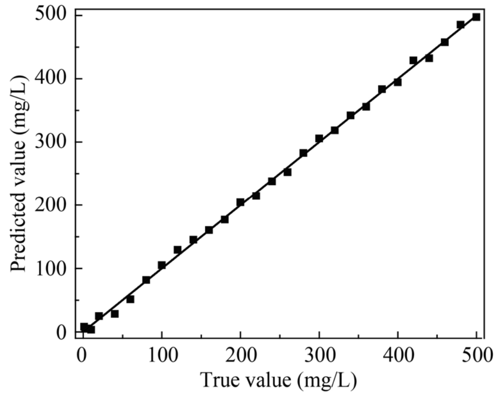
The evaluation indices of the models in different spectral regions are shown in Tab.1.



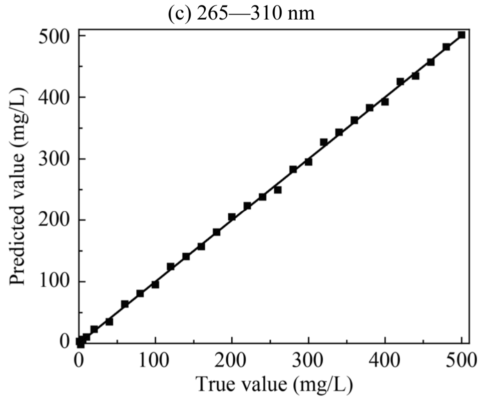
(a) 200—225 nm



(b) 225—265 nm



(c) 265—310 nm



(d) 200—310 nm

Fig.3 Results of different spectral ranges of modeling

Tab.1 Evaluation indices of different spectral models

Model No.	Spectral range (nm)	R^2	*RMSEC* (mg/L)	*RSD* (%)
1	200—225	0.949 7	36.975 3	35.29
2	225—265	0.997 4	13.473 1	5.47
3	265—310	0.998 8	11.635 1	5.56
4	200—310	0.999 3	10.549 8	4.31

In Tab.1, the smallest R^2, the largest *RMSEC* and *RSD* appear in Model 1. However, Model 4 has the largest R^2, the smallest *RMSEC* and *RSD*, which indicates the highest prediction accuracy. That is, Model 4 is the optimal one.

The COD solution with concentration of 80 mg/L is chosen as the sample, which is set at different temperatures. When the temperature range is from 18 °C to

48 °C, the spectra are shown in Fig.4. Obviously, the absorption of COD solution at different temperatures is almost the same in the UV band.

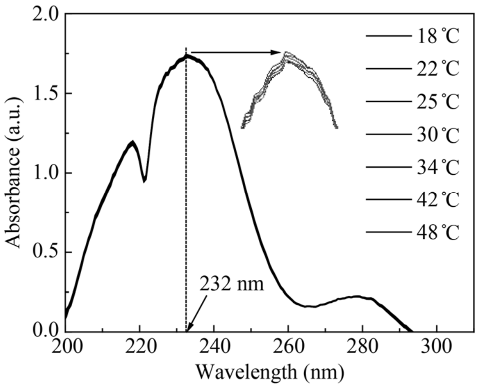


Fig.4 Effect of temperature on the UV absorption of COD solution

In addition, comparing Fig.4 and Fig.2, the change of absorbance caused by every 1 °C temperature change is about 3.1×10^{-4} a.u. in 232 nm, while that caused by every 1 mg/L COD solution concentration change is about 0.004 8 a.u., which is 15 times of the former. Therefore, the temperature influence can be ignored when COD is detected by UV method.

Mixed with COD and turbidity standard solution, 11 sets of solutions are prepared as the samples, the concentration of COD is 130 mg/L and the turbidities are 1.56 NTU, 3.12 NTU, 6.25 NTU, 12.5 NTU, 20 NTU, 25 NTU, 40 NTU, 50 NTU, 60 NTU, 80 NTU, 100 NTU, respectively. The absorbance spectra of the samples in the range of 200—310 nm are collected, as shown in Fig.5. It is shown that the turbidity has a great effect on the absorbance of COD solution in 200—310 nm, and the absorbance gradually increases with the turbidity increasing. The main reason is that the concentration of suspended particles in the solution becomes higher with the increase of the turbidity, the effect of suspended particles on the light blocking increases, and the intensity of transmitted light is reduced, which leads to the absorbance increasing.

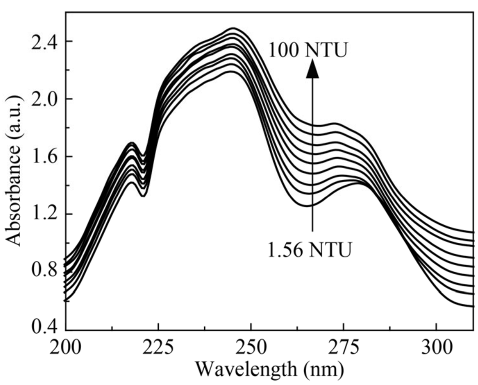


Fig.5 Effect of turbidity on the absorbance of COD solution

The concentrations of COD in those samples are predicted according to Model 4. The predicted results are shown in Tab.2.

Tab.2 Predicted results of Model 4

Turbidity (NTU)	Predicted value (mg/L)
1.56	131.828
3.13	135.950
6.25	136.854
12.5	140.742
20	151.949
25	156.423
40	169.968
50	178.785
60	191.273
80	210.687
100	230.132

The relationship between the predicted value of the COD concentration and the turbidity is shown in Fig.6. The turbidity compensation function is shown as Eq.(5), and its linear correlation coefficient is R^2=0.997 7.

$$y=0.980\,4x+1.724\,1. \quad (5)$$

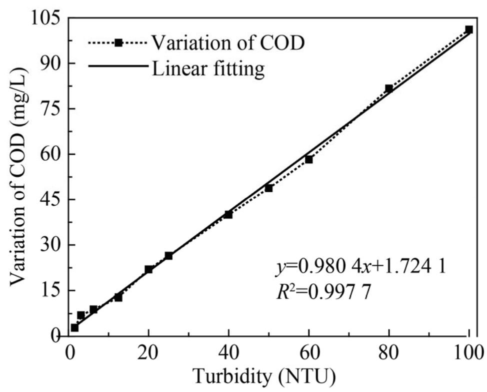


Fig.6 Relationship between turbidity and COD predicted value

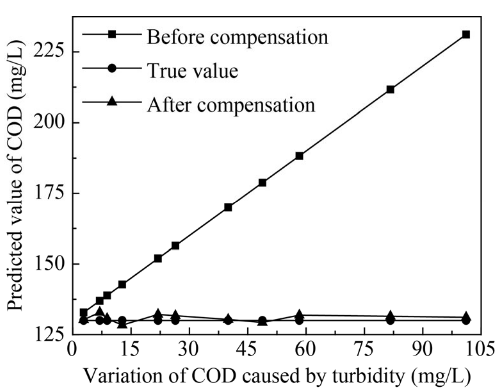


Fig.7 Turbidity compensation result

The COD concentration is predicted under Model 4. As can be seen from Fig.6, the variation of COD concentration and the change of turbidity have the same trend.

In order to verify the compensation effect of Eq.(5), using the one-dimensional regression model, the result of compensation is shown in Fig.7. We can observe that the turbidity can be compensated very well.

The method of UV absorption spectrum detection of water COD is studied in this work. The influence of temperature and turbidity on the predicted results is analyzed. The results show that the influence of temperature on the detection of COD can be ignored, while the measurement error caused by the change of turbidity can be effectively reduced by setting up the compensation function.

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