

Determination of chemical oxygen demand in water using near-infrared transmission and UV absorbance method

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Chemical oxygen demand (COD) is a synthetic indicator that represents the degree of organic pollution in water. Compared with the conventional wet chemical method, near-infrared (NIR) transmission and ultraviolet (UV) absorbance method based on photoelectric detection technology and spectroscopy analysis offer advantages such as high precision, speed, non-contact, and absence of secondary pollution, to name a few. NIR transmission spectra and UV absorbance spectra of standard solution configured with phthalate hydrogen potassium were collected using multi purpose analyzer (MPA) Fourier transform infrared (FT-IR) spectrometer and AvaSpec-2048-2 UV spectrometer, respectively. After different pretreatment of the spectra, COD quantitative analysis model was established using partial least squares (PLS) regression and linear regression. The statistical analysis of COD quantitative model was implemented, and the result revealed that UV absorbance method had higher relevance but lower forecast accuracy and precision than the NIR transmission method.

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Because of expanding human production scale and activity areas, water pollution has been continuously aggravated, seriously threatening the living environment and hindering economic and social development. Thanks to enhanced environmental protection awareness, people have sought to live in harmony with nature, with the goal of achieving sustainable social and economic development under the premise of scientific advancement. Therefore, protecting the water environment and controlling pollution are extremely urgent.

Organic pollution is one of the most serious and fastest growing types of pollution. Chemical oxygen demand (COD) is a synthetic indicator that represents the degree of organic pollution in water; it is defined as the amount of oxygen equivalents consumed in oxidizing the organic compounds of samples by strong oxidizing agents such as dichromate or permanganate (unit mg/L)^[1]. The traditional method estimates COD via the oxidative degradation of organic matter presented in water and waste water with strong oxidizing agents such as dichromate or permanganate^[2], specifically traditional wet chemical method. On that basis, a number of digestion process improvement methods are available, such as digestion method, switch heating, microwave digestion method, energy-saving heating, and ultrasonic digestion^[3]. Other methods such as coulometry, spectrophotometry, potentiometry, dynamics, and polarography and atomic absorption spectrometry^[4] are available as well. However, these methods have defects in the form of secondary pollution, high measuring cost, complex pipeline, and high failure rate, which limit their application in the field of water quality monitoring.

Near-infrared (NIR) spectroscopy has been acknowledged as the fastest growing and most compelling spectrum analysis technique since the 1990s. Its properties include short test time, ability to reflect in real time the state of measured object without sample pretreatment, ability to be measured directly, and suitability for on-site

determination. In addition, it does not consume chemical reagents, and almost all of the main structure and composition of organic matter can be found in their NIR spectrum and the stable spectrum^[5].

Meanwhile, ultraviolet (UV) absorbance method is based on the Lambert-Beer law, and COD value can be obtained indirectly by establishing a relationship between COD concentration and UV absorbance. Due to the characteristics of their molecular structure, most organic matters have absorption peaks in the UV region. After water sample is irradiated with 254 nm of UV light, extent of water pollution can be judged from the absorbance value^[6]. The NIR method is appropriate for short path because the light scattering coefficient is larger than UV method in water, and the UV method is difficult for water quality online measurement.

Different sources of pollution have varying organic composition. However, the same water quality composition has a unique calibration curve for NIR and UV methods. In this letter, the standard solution configured with potassium hydrogen phthalate is the experimental subject. NIR transmission spectra and UV absorbance spectra of standard solution were collected. After different pretreatment of the spectra, COD quantitative analysis model was established using partial least squares (PLS) regression and linear regression. By comparing the results of data statistics of the two methods, analysis of the feasibility and merits of measuring COD using them was performed.

Experimental instruments used in this letter include the multi purpose analyzer (MPA) Fourier transform infrared (FT-IR) spectrometer (Bruker Optics Inc., Germany), AvaSpec-2048-2 UV spectrometer (Avantes Inc., Netherlands), 10-mm quartz cuvette, OPUS spectral acquisition and analysis software, and AvaSoft 7.2 spectral acquisition and analysis software. The standard solution configured with potassium hydrogen phthalate, measuring 1000 mg/L, was purchased from the National Nonfer-

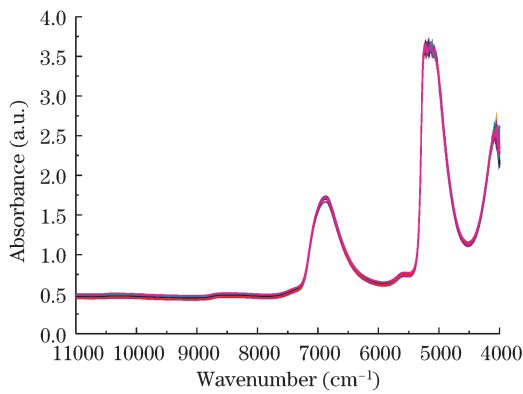


Fig. 1. NIR spectra of samples.

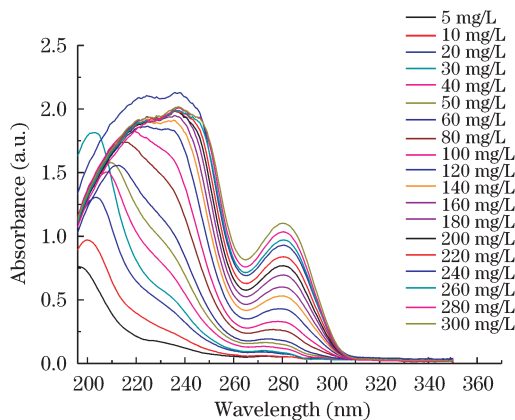


Fig. 2. UV absorbance spectra of samples.

rous Metals and Electronic Materials Analysis and Test Center. It was used as experimental sample and proportionately diluted into a number of 5–400 mg/L copies. Spectral acquisition of the above dilution standard solution was achieved by respectively using NIR spectroscopy and UV spectrometer. NIR transmission spectroscopy and UV absorbance spectra of samples are shown in Figs. 1 and 2, respectively.

Selection of the appropriate spectral region and subsequent spectral pretreatment were completed using MPA spectrometer analysis software optimization function. After pretreatment was conducted using the first derivative, multi-dimensional scattering was adjusted, thus eliminating the constant displacement quantity, vector normalization, and so on. Quantitative analysis model was established using the least PLS, and it was examined with internal cross validation. Order of calibration set with minimal root mean square errors of cross-validation (RMSECV) was selected as the best number of PLS principal component^[6]. Quality of the model was evaluated through the calibration set correlation coefficient R^2 and RMSECV.

UV spectrum, which was collected by UV spectrometer, was saved in microsoft excel using Avaspec Ava-soft software. Subsequently, UV absorbance data of the 254-nm wavelength was gathered. Excel data analysis tools were used for data processing, and the linear regression equation between 254-nm UV absorbance and COD values was obtained. Regression results were composed of regression statistics, variance analysis, regres-

sion coefficient output, and the coefficient significance test, without residual.

The quantitative analysis model was established using MPA analysis software OPUS establishment quota 2 method function. Firstly, NIR transmission spectrum of standard solution was appended. By observing R^2 , which was obtained after modeling in different spectral regions, we found that in the spectrum shown in Fig. 3, maximum R^2 can be obtained. Subsequently, spectral pretreatment was completed using MPA spectrometer analysis software optimization function. The number of principal component and RMSECV was observed under different pretreatments in different modeling spectral regions, and the correction model with relatively small RMSECV was selected as the prediction model. The main component number and RMSECV of the standard solution under the different spectral regions and pretreatment methods are shown in Fig. 4.

As shown in Table 1, when establishing the COD value quantitative analysis model of standard solution using the smallest-biggest normalized pretreatment method and selecting spectral region of 5816.6–5446.3 cm⁻¹, the RMSECV value is smallest at 27.7, and the main component number is 5. As shown in Fig. 4, using the parameter to execute inspection, the correlation curve between COD true value and NIR spectrum quantitative model predicted value of the standard solution was obtained. The horizontal axis pertains to COD true value while the vertical axis stands for predicted value.

A 200–400-mg/L solution was prepared again and predicted value analysis was performed using the established quantitative model. The result is shown in Table 2. It can be observed that the prediction model has smaller standard residuals.

Table 3 demonstrates UV absorbance of standard solution of the different concentration at the 254-nm wavelength. As shown in Fig. 5, the linear regression equation between 254-nm UV absorbance and COD values was obtained.

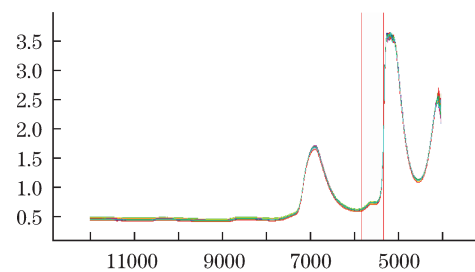


Fig. 3. Spectra range of building model.

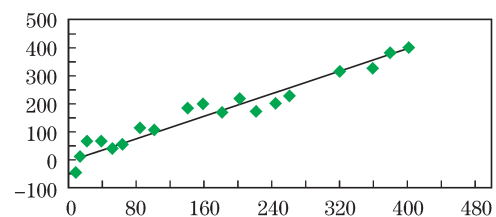


Fig. 4. Correlation curve of predicted values and true values of standard solution.

Table 1. Parameters of Different Spectra Pretreatment Methods in NIR Spectra of Samples

Value	RMSECV	Dimension	Range	Pretreatment
13	27.7	5	5816.6–5446.3	Min-max Normalization
3	34.9	7	48.16.6–5318.0	No Spectral Pretreatment
12	36.2	5	5816.6–5319.0	Standard Normal Variate
18	36.2	5	5816.6–5319.0	Multiplicative Scatter Correction
8	36.7	3	5450.1–5319.0	Subtract a Straight Line
6	37.0	6	5816.6–5319.0	Min-max Normalization
9	40.3	4	5816.6–5319.0	Subtract a Straight Line
15	40.7	5	5816.6–5319.0	Min-max Normalization
5	42.1	4	5450.1–5319.0	Standard Normal Variate
11	43.9	2	5450.1–5319.0	Multiplicative Scatter Correction
17	43.9	2	5450.1–5319.0	Multiplicative Scatter Correction
14	48.4	3	5450.1–5319.0	Min-max Normalization
35	48.5	8	5631.4–5446.3	Min-max Normalization
24	48.6	4	5816.6–5319.0	Second Derivative
10	53.6	5	5816.6–5446.3	Standard Normal Variate
16	53.6	5	5816.6–5446.3	Multiplicative Scatter Correction
2	55.3	4	5450.1–5319.0	No Spectral Pretreatment
7	57.6	5	5816.6–5446.3	Subtract a Straight Line

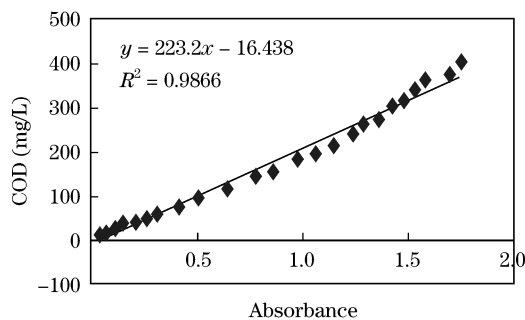


Fig. 5. Single linear regression of UV absorbance in 254 nm and COD value.

Table 2. Forecasting Analysis Based on the Quantitative Analysis Model

Predicted Value (mg/L)	Mahalanobis Distance	Range	Residual	F	F -Probability
404.90	0.32	1.1	0.0237	1.120	0.696
385.06	0.35	1.1	0.0178	0.631	0.563
357.33	0.23	1.1	0.0194	0.749	0.603
318.46	0.33	1.1	0.0168	0.559	0.536
249.91	0.10	1.1	0.0197	0.776	0.611
234.80	0.33	1.1	0.0254	1.280	0.729
184.99	0.24	1.1	0.2320	1.070	0.687
161.95	0.32	1.1	0.0206	0.842	0.630
141.35	0.25	1.1	0.0317	2.010	0.827
199.04	0.28	1.1	0.0376	2.810	0.890

Hence, a linear regression equation of UV absorbance and COD values is

$$y = 223.2x - 16.438. \quad (1)$$

The correlation coefficient is 0.9866. Regression results are shown in Tables 4–7 below.

In Table 4, one can observe that the regression correlation coefficient adjusts the correlation coefficient. The standard errors are 0.993285, 0.986006, and 15.26344, respectively. Although the correlation coefficient is high, the standard error is larger.

Table 7 shows the regression variance analysis. F test of the regression is 1.18365×10^{-22} , considerably less than 0.05. Therefore, this regression result is considered remarkable.

Table 6 presents the regression coefficient significance tests and confidence intervals. Based on the data, the regression coefficient is considered remarkable, and confidence intervals are 28.3973–4.47927 and 211.708–234.6988, respectively.

Table 7 presents the predicted results and corresponding residual analysis, which indicate that the inaccuracy remains remarkable. The reason is that the sample number is insufficient.

As shown by the NIR spectra of the standard solution in Fig. 1, the standard solution in 7000, 5500, 5000, and 4000 cm^{-1} around has a strong absorption peak. Through experiments, the best prediction model has been obtained in the 5816.6–5446.3 cm^{-1} spectral region. Meanwhile, 7000, 5000, and 4000 cm^{-1} around represent the first-level frequency doubling of O-H stretching vibration of water, and 5500 cm^{-1} around is the first-level frequency doubling of C-H and O-H in -COOH stretching vibration of phthalate hydrogen potassium in standard solution.

The quantitative analysis model has been established

Table 3. Standard Solution COD Value and Corresponding Absorbance in 254 nm

Absorbance	COD	Absorbance	COD	Absorbance	COD	Absorbance	COD
0.065544354	5	0.308390325	60	0.97588956	180	1.427480804	300
0.084917403	10	0.423232361	80	1.061978214	200	1.481703196	320
0.134000456	20	0.511389699	100	1.158132721	220	1.535094298	340
0.154099282	30	0.648923267	120	1.255357361	240	1.584664311	360
0.214021697	40	0.775672418	140	1.292572045	260	1.692548096	380
0.263515985	50	0.863691398	160	1.358370827	280	1.738866797	400

Table 4. Regression Statistics

Regression Statistics	
Multiple <i>R</i>	0.993285
<i>R</i> Square	0.986614
Adjusted <i>R</i> Square	0.986006
Standard Error	15.26344
Observation Counts	24

Table 5. Variance Analysis

	Df	SS	MS	<i>F</i>	Significance <i>F</i>
Regression Analysis	1	377773.6	377773.6	1621.536	4.18365×10^{-22}
Residual	22	5125.4	232.9727		
Sum	23	382899			

Table 6. Regression Coefficient Output and Coefficient Significance Test

	Coefficient	Standard Error	<i>t</i> Stat	<i>P</i> -Value	Lower 95%	Upper 95%
Intercept	-16.4383	5.766514	-2.850	0.009299	-28.397304	-4.47927
<i>X</i> Variable 1	223.2035	5.54291	40.268	4.18×10^{-22}	211.708239	234.6988

Table 7. Residual Out

Experimental Group	Predicted Value <i>Y</i>	Residual	Std. Residual	Experimental Group	Predicted Value <i>Y</i>	Residual	Std. Residual
1	-1.80856	6.808556	0.456095	13	201.3837	-21.3837	-1.43246
2	2.515577	7.484423	0.50137	14	220.599	-20.599	-1.3799
3	13.47109	6.528912	0.437362	15	242.061	-22.061	-1.47783
4	17.95722	12.04278	0.806728	16	263.7619	-23.7619	-1.59177
5	31.33211	8.667888	0.580649	17	272.0684	-12.0684	-0.80844
6	42.37941	7.620589	0.510492	18	286.7549	-6.75488	-0.4525
7	52.39552	7.604477	0.509412	19	302.1805	-2.18047	-0.14607
8	78.02867	1.971329	0.132056	20	314.2831	5.716901	0.382966
9	97.7057	2.2943	0.153692	21	326.2002	13.79982	0.924429
10	128.4037	-8.40368	-0.56295	22	337.2644	22.73562	1.523024
11	156.6945	-16.6945	-1.11834	23	361.3444	18.65557	1.249708

using the NIR transmission method. Here, the correlation coefficient is up to 0.9521, relative percentage deviation (RPD) is 4.57%, and offset is 0.582. Table 2 shows that the prediction model obtained using infrared trans-

mission method has good predictability.

Figure 2 shows a strong absorption peak at 254 nm, which weakened with reduction in COD value. As demonstrated in Fig. 5, the linear regression model of

the COD value and UV absorbance shows that they have a good linear relationship, with correlation coefficient of up to 0.9866. F test to regression variance shows that the regression results are significant. However, COD value measured by UV absorbance method is greater when the residual in Table 7 is analyzed, and the accuracy requires further enhancement. This may possibly be attributed to insufficient sample number, which causes low predictive ability of the quantitative analysis model.

In conclusion, the quantitative analysis model of COD of the standard solution is obtained through infrared transmission method and UV absorbance method. By comparing experimental results, several conclusions are derived. Both methods can be used to measure COD. The correlation coefficients by infrared transmission method and UV absorbance method are 0.9521 and 0.9866, respectively. The UV absorbance method has the higher correlation degree. Comparing the predicted value residuals reveals that the infrared transmission method has smaller standard residuals and higher accuracy than the UV absorbance method. These results are based on the standard solution as measuring objects; they are not extensive, and they do not consider the impact of turbidity and PH value, for example, on the accuracy of measurement.

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