Novel Local Calibration Method for Chemical Oxygen Demand Measurements by Using UV–Vis Spectrometry

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Abstract. In recent years, ultraviolet–visible spectroscopy has been widely used for chemical oxygen demand (COD) measurements of water. However, chemical compositions of substance in different water samples can cause measurement deviations, so a local calibration is needed. In this study, a novel local calibration method is proposed. The absorption spectra of COD standard solutions and wastewater samples taken from four factories were collected. We analyzed the impact of chemical compositions of substance in different water samples and extracted the morphology features of their absorptive spectra for recognition models. Furthermore, we calculated the local calibration parameters of the four categories of real water samples by specific modification based on the ability of light absorption in various water environments. After the process of local calibration, the root mean square errors (RMSEs) of the predictions were very small, which highlights the potential of this method for improving the accuracy and adaptability of COD measurements based on ultraviolet–visible spectrum.

1. Introduction

Water contamination is an important environmental concern, and there is a great need for reliable information on contaminant concentrations in natural waters. Chemical oxygen demand (COD) is an important parameter that reflects the concentrations of organic pollutants in water. In recent years, ultraviolet–visible (UV–Vis) spectroscopy, as an indirect method, relies on the regressing model standards provided by chemical methods [1]. It has been widely used for chemical oxygen demand and other parameters measurements of water, because its procedure is easy and can achieve fast detections with no secondary pollution [2].

Langergraber’s research group [3, 4] developed a submersible UV–Vis spectrometer for in-situ real-time measurements and put forward the concepts of global and local calibration. Lourenço ND et. Al [5] researched the water quality monitoring method and applied it in a fuel park wastewater treatment plant. Zhao [6, 7] developed an online spectrometer with an open flow pool based on the UV–Vis absorption spectrum for water quality monitoring. Mi [2] predicted COD by using machine learning methods and the result was better than that of the least squares method. Wang [8] established the prediction models for seawater COD by using partial least squares and the results were consistent with real values. Hu [1] and Tang [9] studied algorithms to compensate the turbidity in the COD measurement.

In spite of this research, these systems and algorithms suffer from lower accuracy in different application environments, in other words, the adaptability is poor. Actually, the chemical component determines the shapes of absorption spectra, i.e., absorbance response position and degrees; so, the
detection of conventional parameters such as COD, total organic carbon (TOC), total suspended solids (TSS), and dissolved organic carbon (DOC) is seriously impacted by the presence of diverse chemical components in water [10]. Therefore, a local calibration is needed in various water environments. However, algorithms for the local calibration in COD measurements have not been studied in detail and intensively.

In this study, we analyzed the impact of chemical compositions of substance in different water samples and proposed a local calibration method theoretically and experimentally. Detection results suggest that this local calibration method can be used to improve the measurement accuracy and adaptability, to some extent, during UV–vis-based COD measurements.

2. Materials and methods

2.1. Experimental setup
The UV–Vis spectral acquisition system consisted of a light source, a sample cell, a spectrometer, and a microcomputer (figure 1). The pulsed xenon light source produced 220–750 nm light, which was collimated by a lens and then passed through the sample cell and air respectively, as the measurement beam and the reference beam. The emergent light was collected into the spectrometer by the converging lens. An optical fiber was used to connect the xenon lamp and the sample cell, and the sample cell and spectrometer as well. The data processing was realized by an embedded system.

For the convenience of online and in situ measurement, a groove was designed in the submerged structure. In addition, the present state of light source can be caught in the double light path. The instrument was shown in figure 2, with the length of 550 mm, the diameter of 110 mm, and the light path of 35mm.

2.2. Water sample
In this study, the COD standard solutions were prepared by dissolving potassium hydrogen phthalate in deionized water supplied by a MilliQ water purification system (Millipore, Billerica, MA, USA). The concentrations included 5, 7.5, 10, 15, 20, 30, 60 mg/L.

The real wastewater samples were taken from two dyeing and printing plants and two paper mills in Zhejiang Province, China. We took water samples near the sewage-draining exits respectively and diluted with deionized water to expand the concentration range. The dilution multiples included 2, 3, 4, 5, 6, 8, 10, 12, 16, 18, 20, 25, 30, 32. Moreover, the real COD values were detected by chemical titration for the verification experiment.

A series of spectral experiments of these samples were carried out with the instrument shown in figure 1. The intensity spectrum of each water sample was measured 15 times and the spectra were averaged to reduce random error from 2.67% to 1%. We measured and deducted the dark spectrum before each measurement.

![Figure 1. The schematic diagram of the spectral data acquisition system with double paths.](image-url)
2.3. Global and local calibration

Ultraviolet–visible (UV–vis) spectroscopy, as an indirect method, relies on the regression model standards provided by chemical methods. The regression process includes global calibration and local calibration, which are used for a universal and a targeted regression model respectively. In this paper, the partial least squares (PLS) was used because of the mature theory and simple calculation. The process of global calibration was shown in figure 3. The COD values of standard solutions and the corresponding absorbance at eight wavelengths close to the absorption peaks were put into the PLS model to train the regression parameters. When applied in different water environments, the COD can be roughly calculated using the global calibration model.

Actually, chemical compositions of substance in water samples varied, which impacts the detection of COD because of the variation in spectral shapes. In order to adapt the variation in different water environments, i.e. to insure the accuracy even for different applications, a local calibration is needed. As a premise, the classification and recognition of water samples should be carried out. In a local calibration, the results calculated by using the global calibration model should be specifically modified based on the ability of light absorption in each water environment. In theory, absorbance follows the Beer–Lambert law:

\[ A = \log \left( \frac{I_0}{I} \right) = kCL \]

where \( k \) is the absorption coefficient, \( C \) is the substance concentration, \( L \) is the optical path, \( I_0 \) and \( I \) are the original and emergent light intensity, respectively, and \( A \) is the absorbance.

As for a real water sample, the absorption coefficient of COD standard solutions was used in the global calibration rather than the real absorption coefficient of the sample. Therefore, it was the fundamental cause of measurement deviation. The local calibration parameter was defined as following:

\[ \tau = \frac{k_0}{k_1} = \frac{C_1}{C_0} \]

where \( \tau \) is the local calibration parameter, \( k_1 \) and \( k_0 \) are the absorption coefficient at a characteristic wavelength of the real water sample and COD standard solution respectively, \( C_0 \) is the COD value calculated by using the global calibration model, and \( C_1 \) is the real COD detected by chemical titration.

In measurements, we calculated the COD by using the global calibration model and identified the category and the corresponding local calibration parameter first, and then multiplied the COD by the local calibration parameter to modify it.
3. Results and discussion

3.1. Impact analysis of chemical compositions of substance in water samples

Through research and investigation, the organic contaminants in water come mainly from sanitary sewage and industrial wastewater. In theory, unsaturated functional groups absorb ultraviolet light, such as C=O bonds, C=C bonds, and benzene rings. Apparently, the location of absorption peaks and the strength of absorption are various because of the chemical components in different water samples. As shown in figure 4, the absorptive characteristics of COD standard substance and wastewater samples were different. The COD standard substance had two distinct absorptive peaks at about 230 and 280 nm; the two absorptive peaks of wastewater samples in dyeing and printing plants were vague; the wastewater samples in paper mills only had one absorptive peak. Actually, dyeing and printing plants mainly contained dyes, phenol, sorts of benzene and its derivatives, so the second absorptive peaks around 280 nm existed. On the contrary, the mono-peak absorbance curves of paper mill wastewater were caused by the lignin-like substance. Although the sewage discharged by the same kind of factories had similar spectral shapes, there were slight variations among different factories.

In addition, the actual COD values of wastewater samples were detected by means of dichromate titration (table 1). In order to compare with the COD standard solutions, the absorbance at 280 nm and the absorption coefficient per unit length and unit concentration were also listed. The table 1 showed that the light absorbing ability of different water samples varied from the COD standard substance. The dyeing and printing plant sewage with more aromatic compounds had a stronger ability of light absorbing than potassium acid phthalate, while the ability of lignin-like substance in paper mills was weaker. Therefore, the different chemical compositions of substance in water samples affect the accuracy of prediction results, if the global calibration of COD standard substance was only used.

![Figure 4.](image)

**Figure 4.** (a) Absorption spectra of COD standard solutions with different concentrations. (b) Absorption spectra of wastewater in two paper mills and two dyeing and printing plants.

| Water samples                  | COD(mg \cdot L^{-1}) | Absorbance at 280nm | Absorption coefficient at 280nm(L \cdot mg^{-1} \cdot m^{-1}) |
|--------------------------------|-----------------------|----------------------|---------------------------------------------------------------|
| Paper mill 1                   | 238.5                 | 1.92                 | 0.23                                                          |
| Paper mill 2                   | 39.4                  | 0.53                 | 0.38                                                          |
| Dyeing and printing plant 1    | 57.8                  | 1.36                 | 0.67                                                          |
| Dyeing and printing plant 2    | 62.9                  | 1.72                 | 0.78                                                          |
| COD standard solution          | 20.0                  | 0.33                 | 0.47                                                          |

**Table 1.** The concentration, absorbance at 280 nm, and the absorption coefficient at 280 nm of four wastewater samples and a COD standard solution.
Table 2. The morphology features and output values of 5 categories of water samples. The peaks or valleys of each water sample were taken the first three, and the difference of absorbance was the latter one subtracted by the prior one.

| No. | Water samples                  | Peak 1 (nm) or valley | Peak 2 (nm) or valley | Peak 3 (nm) or valley | Difference 1 | Difference 2 | Output |
|-----|--------------------------------|-----------------------|-----------------------|-----------------------|--------------|--------------|--------|
| 1   | Paper mill 1                   | 256                   | 0                     | 0                     | 0            | 0            | 1      |
| 2   | Paper mill 2                   | 255                   | 0                     | 0                     | 0            | 0            | 0      |
| 3   | Dyeing and printing plant 1    | 257                   | 289                   | 307                   | -1.92        | 0.02         | 0      |
| 4   | Dyeing and printing plant 2    | 256                   | 300                   | 316                   | -0.92        | 0.05         | 0      |
| 5   | COD standard solution          | 230                   | 268                   | 282                   | -1.93        | 0.23         | 0      |

3.2 Classification and recognition of water samples
In order to reduce the impact from chemical compositions of substance in different water samples, it is necessary to classify the water samples based on morphology features of their absorptive spectra and construct effective recognition models before local calibration. For better recognizing, the morphology features included the positions of absorptive peaks and valleys (the first three), and the difference of absorbance between two adjacent peaks and valleys. In addition, back-propagation algorithm was used in the artificial neural networks training to establish the recognition models. In the process of sample training, 28 water samples of four factories with seven dilution multiples and seven COD standard solutions were taken as the training set. The dilution multiples included 1, 2, 4, 8, 10, 16, 20. In table 2, the morphology features of every category of water samples were listed and only one sample with the largest concentration of each category was shown here. When training one category of the water samples, the output values of the category were set to 1 and the others were set to 0. For following categories of water samples, the same progress was done.

In the validation process, the rest samples of the four factories were taken as the validation set and the sample size was 32, including 8 dilution multiples of 3, 5, 6, 12, 18, 25, 30, 32. The experimental result was that the correct recognition ratios reached 94%, which proved that the models were rational and effective to identify the category of water samples.

3.3 Parameters of local calibration
A local calibration of wastewater samples belonging to four factories carried out using the method in 2.3 on the premise of correct recognition. Only the original concentration of samples taken from every factory was selected in the calibration process to streamline the operation. The characteristic wavelengths were set at the second absorbance peaks or 280 nm if without the second peaks. The calibration parameters were calculated and listed in table 3.

In practical application, the calibration parameter can be determined after classification recognition and the prediction results can be modified by multiplying the local calibration parameters on the basis of using global calibration models. Therefore, the proposed local calibration method efficiently broadens the range of application through a simple operation, in which only one sample needs chemical titration and spectrum collection.
Table 3. The characteristic wavelengths and calibration parameters of four wastewater samples.

| Water samples            | Characteristic wavelengths (nm) | Calibration parameters (τ) |
|-------------------------|---------------------------------|----------------------------|
| Paper mill 1            | 280                             | 2.03                       |
| Paper mill 2            | 280                             | 1.24                       |
| Dyeing and printing plant 1 | 303                             | 0.75                       |
| Dyeing and printing plant 2 | 315                             | 0.64                       |
| COD standard solution   | 280                             | 1                          |

3.4. Results for predictions using local calibration model

In order to validate the effectiveness of this method for improving the accuracy in various water samples, we predicted the COD of seven standard solutions and 60 wastewater samples of four factories with 15 dilution multiples by using the global calibration model only and both global and local calibration models. After 67 samples were predicted, the results for two types of processing methods were plotted in figure 5, and their correlation coefficient ($R^2$) and root mean square error (RMSE) values are shown in table 4. The results for the proposed method of local calibration are generally consistent with the actual values and the RMSE values are very small.

![Figure 5. Prediction results for two types of processing methods.](image)

Table 4. Prediction results of different processing methods for water samples.

| Processing methods                  | Relative error (%) | $R^2$  | RMSE(mg/L) |
|-------------------------------------|--------------------|--------|------------|
| Only global calibration             | 42.94%             | 0.77   | 44.72      |
| Both global and local calibration  | 8.43%              | 0.99   | 5.62       |

4. Conclusion

In this study, we sampled the absorption spectra of COD standard solutions and wastewater samples taken from four factories and proposed a novel local calibration method during COD measurements.
employing the UV–vis spectrum. This method improved the measurement accuracy and adaptability by specific modification for various water environments. We analyzed the impact of chemical compositions of substance in different water samples and extracted the morphology features of their absorptive spectra for recognition models. The dyeing and printing plant sewage with more aromatic compounds had a stronger ability of light absorbing than potassium acid phthalate, while the ability of lignin-like substance in paper mills was weaker. Furthermore, we calculated the local calibration parameters of the four categories of real water samples. Moreover, 67 samples of standard solutions and real wastewater with 15 dilution multiples were predicted and the results by using local calibration were consistent with the actual. In conclusion, this local calibration method can be used to improve the measurement accuracy and adaptability, to some extent, during UV–vis-based COD measurements.

5. Acknowledgements
The study was supported by the National High Technology Research and Development Program of China (863 Program) (Project No. 2014AA06A504).

6. References
[1] Hu YT, Wen YZ and Wang XP 2016 Novel method of turbidity compensation for chemical oxygen demand measurements by using UV–vis spectrometry Sensor Actuat. B-Chem.227 393-8
[2] Mi YP, Wang XP and Jin X 2008 Water COD prediction based on machine learning J. Zhejiang Univ. Sci. A42(5) 790-3
[3] Langergraber G, Weingartner A and Fleischmann N 2004 Time-resolved delta spectrometry: a method to define alarm parameters from spectral data Water Sci. Technol. 50(11) 13-20
[4] Rieger L, Langergraber G, Thomann M, Fleischmann N and Siegrist H 2004 Spectral in-situ analysis of NO2, NO3, COD, DOC and TSS in the effluent of a WWTP Water Sci. Technol. 50(11) 143-52
[5] Lourenço ND, Chaves CL, Novais JM, Menezes JC, Pinheiro HM and Diniz D 2006 UV spectra analysis for water quality monitoring in a fuel park wastewater treatment plant Chemosphere 65(5) 786-91
[6] Zhao YQ, Li YC, Guo Y, Gu BJ and Yang Z 2012 A Novel Technology for Water Quality Testing Based on UV Spectral Analysis Spectrosc. Spec. Anal.32(5) 1301-5
[7] Zhao YQ, Wang HM, Liu ZY, Li YC and Fan SF 2010 Novel method for on-line water COD determination using UV spectrum technology Chinese Journal of Scientific Instrument 31(9) 1927-32
[8] Wang LL, Liu XH, Shi XX, Lu YR, Qi Y and Wang MY 2013 Study on Real-Time Monitoring of Seawater COD by UV-Vis Spectroscopy Adv. Mat. Res.726-731 1534-7
[9] Tang B, Wei B, Wu DC, Mi DL, Zhao JX, Feng P, Jiang SH and Mao BJ 2014 Experimental Research of Turbidity Influence on Water Quality Monitoring of COD in UV-Visible Spectroscopy Spectrosc. Spec. Anal. (11) 3020-4
[10] Hu YT and Wang XP 2017 Application of surrogate parameters in characteristic UV–vis absorption bands for rapid analysis of water contaminants Sensor Actuat. B-Chem.239 718-26