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Abstract. Water quality monitoring technology based on optical method isthe trend formodern water environmental monitoring.Compared with the traditional monitoring methods, Spectroscopy is a more simple, a small amount of reagent consumption, good repeatability, high accuracy and rapid detection of significant advantages, which is very suitable for rapid and on-line monitoring determination of environment water samples COD.This paper summarized the status and research progress of optical methods for monitoring of COD in water.The basic principle of traditional analysis methods and optical methods for measuring COD in water were brief described, andcomparedto the characteristic of different waveband of the detection of COD. The principles and applications of spectroscopic methods commonly used spectral preprocessing methods and calibration methods were listed, and also introduced the progress of optical sensors.Finally,the future research focus and direction of spectroscopic methods were prospected.

Keywords： Spectroscopic, Water, COD

1Introduction

Water bodyrefers to the complex of rivers, lakes, ground water and other natural water, which includes water and the living organism and substances present in it.

Water is an important material for human survival. It is also the necessary resources to human life. With the development of the social economy and the occupation and extension for the natural resources constantly by the human activities, the water quality encountered serious pollution which will threaten the security of watersource, the water resource suffered waste that will make the fresh water shortage [1]. The global water source is severely polluted, so that the water cannot reach drinking water quality standards, which exacerbated the shortage of water. In 2012, over ten percent of 972 sections are worse than Grade V,where National Monitoring section of the Yangtze River and Yellow River and other trunk watersheds of china [2].

Water pollution means some chemical or physical parameters of the water donot meet the water quality standards. Industrial wastewater and domestic sewage are important sources of water pollution. Serious water pollution is toxic to aquatic plants and animals and even lead to death, while the harm to human health through the food chain. To ensure the quality and safety and good environmental protection, water quality monitoring work has been increasingly important. COD is one of the main monitoring items of surface water, domestic sewage and industrial waste water, and is an important parameter for water quality monitoring. Both types of industrial waste water or sewage must be treated to meet COD value of environmental emission standards allowed to discharge [3].Therefore, measurement of COD index is particularly important in today's increasingly pay attention to environmental protection. Simultaneously,COD is one of the wastewater pollution indexes of pollutant discharge total amount control engineering[4] .

Chemical Oxygen Demand refers to a substance that can be oxidized in water chemical oxidation under certain conditions, whichcan be consumed amount of oxidant to oxygen mg/L to indicate, it reflects the degree of water and nitrite, ferrous salts, sulfides, etc. So to some extent, COD is one of the important indicators of overall performance characterization of organic pollutants in water [5].

Organic pollutants in the microbial oxidation decomposition requires large amounts of dissolved oxygen in water, and water quality black stinking, choking water creatures, which worsened the aquatic environment and upset the balance of the ecosystem[6], huge losses to aquaculture. Therefore, timely and accurate monitoring water COD concentration is important for the control of pollutant emissions and monitoring water quality.

The standard method for determination of COD is permanganate index and potassium dichromate oxidation method.The former applies to groundwater and relatively clean

surface water, drinking water analysis. The latter used for industrial wastewater and analysis of sewage [7]. The basic principle is potassium dichromate in strongly acidic solution, with an excess of potassium dichromate to reducing substances in water samples, and take ferroinsolution as indicator, back titration with sulfuric acid ferrous ammonium to calculate the amount of reducing substances by the amount of consumed ferrous sulfate of ammonia[8].

This law applies to all types of containing COD value greater than 30 mg/L of water samples, and the upper limit of the undiluted water samples is 700mg/L. Determination of the optimum range of 50-500 mg/L [5]. This method can detect water, sewage treatment plant effluent and moderately polluted wastewater.Be ofsimple detection equipment and accurate measurement results[2]. However, this method has to be consumed expensive silver sulfate and a lot of concentrated sulfuric acid, in order to eliminate the interference of chloride ions [9]. It has the defect of long analysis period, heavy workload, reagent consumption, high energy consumption [10]. If the test solution contains chloride ions, nitrite ions, which will react with digestive agent or catalystcause large deviation of measurement[11], For a large number of samples in the area of water quality, water quality monitoring and sewage treatment plants in the water treatment process of the determination, the standard method has great limitations [12],There are some method such as standard improved method, polarography [13] and other methods for the detection of water COD, but still cannot solve the traditional method of secondary pollution, measuring long time, higher testing costs disadvantages.

With advances in optics manufacturing technology and equipment, optical methods and chemometrics method for the analysis of complex system of quantitative and qualitative sample has gradually been recognized by people. That has been successfully applied in many fields.Deepa et al[14] proposed a method to measure dissolved oxygen in water, using an optical measurement range 2-9 mg/L, with high efficiency, low cost, simple operations and other advantages.Kelley et al [15] put forward a method based on the use of optical fiber sensor technology developed economy turbidity, which can be realized without reagents,measuring water turbidity and particle concentration with high sensitivity. Optical metrology method combined chemometrics algorithm can be applied to the detection of chlorophyll.O'Connell et al [16] proposed a novel optical fiber sensors for real-time monitoring of the marine environment, and be able to identify the type of water chlorophyll. Chen et al[17]precented an optical sensor combined ECRSA algorithm to detect the

concentration of chlorophyll in turbid water.Azema et al [18]studied the optical method to detect water suspended solids in water body. Optical methods can no regents, high sensitivity, fast measurement of water quality. although in situ, precise sensing device is still in the research stage [15, 19], but with the development of computer technology and modern scientific instruments, advanced water quality monitoring equipment will gradually be widely used.

Optical methods have also been applied to the measurement of water COD, there are visible spectroscopy [20], visible-near infrared spectroscopy [21], near infrared spectroscopy [22], dual-wavelength spectroscopy [23], UV spectroscopy [24], photochemical luminescence method [25] and other methods, optical detection method is fast, easy operation, ideal for water COD online real-time monitoring. In this paper, different bands spectroscopic methods to detect water COD research status and characteristics were reviewed, and elaborated the chemometrics algorithm which frequently used for optical method measuring water COD. And then introduced some online COD optical sensors, in order to provide a reference for the research on optical method of monitoring water COD.

2Different bands spectroscopy method for measuring water COD

Based on spectral analysis of water quality monitoring technology is an important development direction of modern water environment monitoring, compared with traditional methods, sensitive, rapid, simple and many other advantages, to meet the environmental requirements of the water environment monitoring, showing the broad application prospects. Therefore, launching the research of spectroscopy monitoring water COD is important. Currently, based on UV/UV-visible spectrum and near infrared spectra method research more extensive, other band spectroscopy method for measuring COD in water research literature failed to mention, pursuant to the above article only describes two spectroscopic methods.

2.1 UV spectroscopy

In recent years, International and domestic academics carry out a lot of research about the UV absorption spectroscopy detection of COD technology. Utilizing the relationship between wastewater in UV spectral region absorbance and water COD

calculate the COD value, which directly according to the organic matter has a very sensitive optical absorption principle. UV-visible spectroscopy can be measured the concentration of organic pollutants in water directly or indirectly [26, 27], and the analysis of its components[28]， with advantages of sensitive, fast and simple. For the first time by using ultraviolet absorption spectrometry water COD is Japanese scholars [29]. In 1965, Ogura studied the relationship between water quality of rainwater, rivers and other natural water bodies and UV absorption, published a UV absorption spectrum of substances which found organic matter at 220nm exists a certain correlation between the absorbance and water COD. But in order to masking ultraviolet absorption interference for the water containing a large amount of nitrate, 250nm wavelength was a more suitable point fororganic compounds measured. UV method has been included in the Japanese Industrial Standard K-0807, require determination of sewage absorbance at the wavelength of 253.7nm,estimated COD value by the standard relationship between pre-established absorbance and COD. TheJapanese government had made the official water quality monitoring indicators to evaluate the organic matter content of the water. Europe had been monitoring indicators to monitor water treatment effect of organic matter [30]. Langergraber et al[31] applied UV-visible spectrometer to obtain the absorption spectra of paper mill wastewater, Compared with single wavelength and full band analysis model is established, the experimental results prove that the model based on full-band COD values are better prediction. Kong et al[32]studied UV spectrometer to detect the COD of industrial wastewater and dyeing wastewater, with fast, accurate, and other advantages. Su et al [33] utilized UV photolysis and photochemical method to achieve a rapid, sensitive, on-line detection of COD, reached a very low detection limit.Roig et al [34]measured a variety of water quality monitoring parameters by UV spectrum instrument, analysis showed that UV spectroscopy was a powerful tool for the detection of water COD and other water quality parameters.

Chen et al [35]measured the COD of tap water which have been treatment close to pure water at 220nm, the results showed that such water sample of UV spectroscopy obtained very good correlation between acidic potassium permanganate method, but the UV method is more simple and fast. Song et al [36] found the UV absorbance value and COD existed good linear correlation, which the sample collected from the SBR wastewater treatment plant secondary effluent filtered through a little suspended solids. Hu et al [37] monitored the water COD by UV spectroscopy using a new nozzle, the experimental results showed that the relative error of experiment was less

than ten percent comparing with standard method.Chen et al [38]made liner regression about the detecting data of UV absorbance and COD in industrial wastewater, sewage and surface water. A strong correlation between UV absorbance and COD, in certain conditions UV absorbance under the water body can calculate the results of COD.

Fig. 1.UV spectroscopy development trends

Wu et al[39] found that the integrated area scanned by UV spectroscopy and scanning water samples COD had a good linear relationship. Xing [40] determined by UV spectroscopy and COD compared with potassium dichromate method, it had no secondary pollution and high measuring speed. Wang et al[41]studied the relationship UV absorption in wastewater after biochemical treatment of the WISCO coking plant and COD value, the regression equation is established. The results showed that the relative errors are less than 6.4% when wastewater COD values in the range of 0-100ppm. That leading to a rapid predictive biological treatment plant effluent quality. Zhao et al [30] designed and implemented online testing water COD instrument, but these principle are single-wavelength spectral data reflect organic pollutants in water, which demand high precision of the instrument. There were also using UV spectral measurements combined algorithm to detect water COD. Be of the regression model, neural network method. Feng et al[24] studied the spectral analysis of water quality, used the least squares method combined full-band ultraviolet absorbance establish calibration model to estimate the water COD. When processing the water samples because water turbidity and other related factors[42], general used visible light absorbance to amend UV254. Charef et al [43] established the correction model with a wavelength range of 200-800nm UV-visible absorption combined with neural network algorithm, the estimated value and measured value had a high correlation.Şahin et al [44]get the UV-visible absorption spectrum of the dyeing wastewater, through the whole spectrum method combined with neural network established calibration model had good prediction accuracy. Vaillant et al [45]studied the ultraviolet spectrometry for qualitative and quantitative detection of the urban water quality, and described the development process of UV spectroscopy to detect the quality of water, the tendency isfrom the single-wavelength spectroscopy to the whole spectrum method for measure the absorbance of the water body. Directlydetermination of COD UV spectroscopy development process as figure 1

shown:

Currently no chemical reagents detection technology has begun to apply in foreign countries, Europe and the United States free of chemical reagents Instrument's market share is substantial growth [46]. Simple single/dual wavelength photometer structure only applies to measure a single component of the water COD,but determine the actual water samples COD will be disturbed by many factors, and the different components of organic matter in water, the maximum absorption peak is not all at 254nm,therefore, only at 254nm spectral data to reflect the concentration of organic matter is very difficult. Most organics have ultraviolet absorption at the range of 200-400nm, organic compounds by measuring absorbance in the ultraviolet band can indirectly reflect the content of organic matter in water, and thus optical measurement method is widely used in water and organic matter in the qualitative and quantitative determination.

The development of modern spectroscopy allows the full spectrum measurement becomes a reality, once detected in the water samples can be obtained by UV-visible absorbance curve over a wide spectral range,capable of a more comprehensive reflect water pollution, despite the many advantages of direct determination of COD by UV absorption spectroscopy, But at the moment for the combination of different water bodies of the organic components， and ultraviolet absorption spectrum and the COD value relationship exist shortage of research. For the particular wastewater, the regression equation should be determined according to the measured results or calibration curve. Due to the different water samples interfering factors specific makes calibration model no universality. UV absorption spectra measured COD directly, eliminating interfere of suspended solids, non-soluble colloidal substances and certain inorganic ions in water samples still need further study. Although the method is not perfect, but with the development of computer technology and chemo metrics, research and development of new sensing devices, these problems will gradually be resolved. UV absorption spectroscopy monitoring the water quality will be widely available in the future work.

2.2Near Infrared Spectroscopy

NIR spectroscopy is a new technology to quickly detect the chemical composition of the sample content, and the fastest growing spectroscopy since the 1990s, the principle is using of chemical substances in the optical properties of the near-infrared

spectral region. It has been widely used in the agriculture, food, petroleum, chemical industry and other fields.

In recent years, domestic and foreign scholars have carried out the research of detect the water COD,that base on near-infrared spectroscopy and made great progress.Sarraguca et al [47] obtained the activated sludge reaction tank effluent absorbance at the wavelength range of 900-1400nm near-infrared band,utilizing PLS established calibration model based on the absorption spectrum data after SNV and MNCN processed, the model correlation coefficient was 23%.Pan et al[48]utilized S-G smoothing and PLS method through the different NIR spectrum band of sugar refinery wastewater established model, and ultimately selected 808-964nm for the optimal information band, the predictive of validation sample set reached 96%.

He et al [49]studied the feasibility of near infrared spectroscopy to measure the COD, based on the varied divisions for the COD standard solution and wastewater samples, a regression model was established. The correlation coefficient of the standard theory and predicted COD valuesin standard solution was 0.9999.The correlation coefficientof measured and predicted COD values in sewage treatment plant effluent was 0.9453. It showed that the near-infrared spectroscopy applied for the determination of COD in sugar refinery waster was feasible. Furthermore,Xu[50] measured the COD in river water, combined with PLS algorithm based on the first derivative NIR spectrum established COD analysis model, the correlation coefficient of the predicted model reached 0.991, the Root Mean Square Deviation Correction equivalent 4.3% of average COD value in water samples, met the needs of daily monitoring, the RMSEC and RMSEP was closely. The analysis showed that the model had better applicability. NIR spectrometry for the determination of water COD had a stability result, which for the rapid determination of organic pollution in water bodies provided a viable analysis techniques. JI et al[22]measured the COD of sugar refinery wastewater, based on the FTIR/ATR spectroscopy, combined with the PLS method and SG smoothingbuilt regression model, Prediction correlation coefficient reached 96.8%.

These studies demonstrated the feasibility of measuring water indicators by near-infrared spectroscopy, but to establish a functional COD prediction model of near-infrared spectroscopy, that need to collect a sufficient number of representative samples of wastewater, so that the useful information and background information should be contained wide enough in the sample set. Eliminating interfere of temperature, pH, turbidity in still need further study, thereby reduced the SEC and

SEP of regression model. Although near infrared spectroscopy has many advantages, but it also exists weak absorption intensity, low sensitivity and other defects. Material in the near infrared absorption coefficient generally small, which make the measured components should be greater than 0.1% in general. In addition, the spectrum of water samples easily suffered influence by the state of the sample,measurement conditions and other external conditions [51]. But with the development and application of new chemometrics methods and new devices, these problems will gradually be resolved. Near-infrared light have excellent transmission performance in optical fibers, making near-infrared spectroscopy technology can achieve remote applications through fiber optic technology, which brings the industry on-line analysis and in situ measurements a great possibilities.

NIR spectroscopy has many advantages, such asno chemical reagents, simple analytical process, low cost analysis, etc, and NIR spectroscopy can fast, safe and operate easily for the quantitative determination of COD in wastewater. And can be combined with the near-infrared optical fiber technology to build large-scale online monitoring system, which has important practical significance for control the pollution sources of water and monitoring pollution.

2.3Comparison of several spectroscopic methods for COD measurement

Using the NIR spectrometer was possible to measure COD in water on-line and in-situ, without sample pretreatment and consumes no chemicals, almost all of the main structure and organic matter composed of spectral information, which can be found in near infrared spectroscopy signal and spectrum stable. UV spectroscopy is use of the relationship between water sample absorbance and COD concentration obtained the COD values indirectly. From the absorbance intensity can determine the extent of organic pollution in water bodies, based on most of the organic matter in the UV band has the absorption peak. Using UV-visible spectroscopy and near-infrared spectroscopy to monitor reactor wastewater sludge wastewater treatment process

Sarraguca et al[47]utilized UV-visible spectroscopy and near-infrared spectroscopy to monitor wastewater in the treatment process of activated sludge reactor.The results showed the UV-VIS modeling results were more accurate than the results obtained with NIR.Analysis believed the presence of water had a huge impact on the near-infrared spectrum, masking some spectral characteristics that could be important for calculating the COD. Wu et al [52] utilized UV-visible spectroscopy and

near-infrared spectroscopy to monitor the standard solution of potassium hydrogen phthalate. After different pretreatments established UV-VIS modeling and NIR modeling by PLS, found that the UV absorption method had a higher correlation than the infrared transmission method. The prediction accuracy was slightly lower than the latter. However, these results were based on a standard solution for the object, did not have extensive, but also did not take into account the actual measurement of turbidity, pH effects on measurement accuracy.

Table 1.spectroscopic methods based on different bands detected COD in water

Optical method	Range of measurement （mg/L）	LOD (mg/l)	Accuracy R^2	Water sample	IInstrument complexity	Papers
UV spectroscopy	0-500	1.98	0.940	wastewater	Simple ， No Pollution	Surya et al[53]
	0.2-20	0.08	0.989	River lake	Detect fast, no chemicals, high sensitivity, simple structure	Su et al [33]
	115-427	137.37	0.88	municipal wastewater	Simple structure, no pollution	Charef et al[43]
NIR spectroscopy	41-416	-	0.976	Sugar refinery wastewater	Simple structure, no pollution, Fast	Pan et al [48]
	30-500	33.9	0.9436	municipal wastewater	No pollution, Simple structure	He et al [49]

To accommodate the technology development requirements of automated, real-time COD monitoring, although UV spectroscopy can achieve real-time on-line COD measurement. But there are some problems due to water absorption have a larger coefficient in the UV spectral region, make the higher requirements of sample pretreatment, so the tested water samples should be clear and transparent, the suspended solids that contribute to the COD values are removed after pretreated,

which make the estimated COD inaccurately. Furthermore, many organic have no absorption spectrum in the UV spectrum region, it will cause the estimated value lower than actual [49]. Table 1 gave the data for the optical method detection of the COD in water.

Suryani et al [53]combined with UV spectral deconvolution to build regression model, the LOD of COD reached 1.98mg/L, the correlation coefficient of predicted and detection values was 0.94. Su et al [33] utilized UV spectroscopy achieved rapid,highly sensitive on-line monitoring water COD, the LOD reached 0.08mg/L in the range of 0.2-20m/L, the correlation coefficient was 0.989. Charef et al [43]detected the COD of municipal wastewater combined with ANN algorithmand UV modeling,tested COD value in the range of 115-427mg/L, the LOD was 134.25mg/L, the correlation coefficient of model between the estimated and measured COD was 0.88.Pan et al [48]utilized NIR spectroscopy combined with the SG smoothing and MWPLS method built regression model, the determination of COD in the range of 41 to 416mg/L, the correlation coefficient was 0.976.He et al [49]utilized NIR spectroscopy combined with PLS built model, the correlation coefficient of predicted between detection values was 0.94, the LOD of COD in the range of 30 to 500mg/L was 33.9mg/L.

3Chemometrics methods for optical measurement of water COD

3.1Spectral preprocessing methods

When using an optical method for measuring water COD, the spectra obtained except contains the chemical information of water sample itself, also contains the circuit noise, the sample background, and other stray light noise and other unwanted information. Therefore, in order to improve the accuracy of the regression model built by chemometrics methods, eliminating noise and unwanted spectral data interference information becomes necessary, spectral preprocessing methods can be largely solved these problems. There are many commonly used methods such as Mean Centering, Normalization, Smoothing, Derivative method, SNV and detrendingalgorithm, Multiplicative Scatter Correction and other methods.

SNV pre-processing method for processing a spectrum, using the data points on the spectrum curve subtract the mean of spectral curve, and then divided by the standard

deviation, which is mainly used to remove the interference of solid particle size, surface scattering, and optical path changes. WU et al [27]utilized UV spectroscopy to detect the COD of wastewater combined with different calibration methods and SNV, the model had better prediction accuracy, but less effective compared to other pretreatment methods, the experimental results showed that the spectral preprocessing not necessarily possible to improve the accuracy of the model unless suitable.

Derivative pretreatment is essentially intensity distribution derivation of spectral signal.the principle is to choose a few points of the original spectrum constitutes a window and obtained derivative spectra in the window by derivation. Derivative spectra can effectively eliminate the baseline and other background interference, and improve the resolution and sensitivity. But the derivative spectrum will also introduce noise information and reduce noise ratio. The first derivative and second derivative spectra were more commonly used. Xu et al [50]detected the COD of river water by NIR spectroscopy, and used the original spectrum, utilized the first derivative and second derivative spectra of the water samples established regression model, the first derivative of NIR spectrum modeling predicted the best results after comprehensive comparison.

Smooth pretreatment is to choose an odd number of the wavelength points on original spectrum as the window, and take on average or fitting of wavelength points within the window. Complete smoothing of all the points by moving the window from left to right. Where the width of the window is a key smoothing parameter, if the window width is too small, it will lead to poor smoothing effects, if the spectral width of the window oversize the general will cause signal distortion. Moving average smoothing and SG convolution smoothing is the denoising smoothing algorithm that commonly used. Pan et al[48]detected the COD in wastewater by NIR spectroscopy combined with SG smoothing method, the modeling results were better than the original spectrum modeling. JI et al [22]utilized the PLS algorithm combined with SG smoothed data established prediction model, built relationship between FTIR/ATR spectrum and COD values, prediction correlation coefficient reached 0.968, the SG modeling were better than the PLS modeling without SG smoothing.

Spectral deconvolution means the original spectrum is decomposed from a few number of features of spectra and a commonly tool for water COD determination combined with UV spectroscopy. Nam et al [54] utilized the NV spectral deconvolution detected the nitrite content in frozen spinach, the correlation coefficient reached 0.9843.Martins et al [55]used the spectral deconvolution method to estimate

the COD value of hospital discharge wastewater, the UV absorbance and COD values were well correlated.Thomas et al [56] measured the COD and TOC of wastewater by UV spectral deconvolution, the correlation coefficient of the estimated between measured values were 0.94,0.92, which achieved a very good prediction.

3.2Regression Approach

Research on the use of spectroscopy measurement data for COD value prediction has been further developed, the key technology of optical analysis method is to build a mathematical model of spectral data, which between the concentration of organic pollutants, as well as to improve the extrapolate ability of the model, Namely establisheda stable functional relationship between the spectral information and the nature of components, the stability and prediction accuracy of the calibration mode depend on the regression approach is very important. Established method calibration model is divided into linear and nonlinear correction method, which used multivariate calibration method based on linear regression have MLR, PCR and PLS,based on the non-linear regression methods have Artificial Neural Network, Support Vector Machine, Kernel Partial Least Squares. The following describes the above-described regression method used for the measurement of COD.

In spectral analysis, linear regression was developed earlier, which used to evaluate the correlation of the spectra prediction predicting outcomes between reference method for the determination results in a set of sample. Wu et al [52] utilized the linear regression method established regression model based on the UV absorbance of the potassium hydrogen phthalate standard solution, the correlation coefficient was 0.986, standarddeviation was 15.26344.Wang et al [41] detected the coking wastewater COD value by UV spectro-photometry, the measured absorbance and COD value were better reliability and practicality through the establishment of linear regression line equation. A linear regression can only use one variable,modeling of spectral data using only a single wavelength point absorbance as a reference data, but when using spectroscopy measured water COD actually, the temperature of water sample will affect the measurement accuracy. Mu et al [57] utilized the UV spectroscopy measured the water COD, through the experiment determined the data based on the ultraviolet absorbance of the standard solution changes with the temperature.Andobtained the relationship between the two by multivariate regression method to fit the data, thereby eliminated the influence of the temperature and

improved the model predictive power. Fogelman et al [58] measured the COD values by UV spectroscopy combined with MLR algorithm, the correlation coefficient of the predicted and measured values was 0.85

PCA (Principal Component Regression) for the main purpose is to exclude the overlapping information of the spectral data.The algorithm idea is to transform the original variable of the spectral matrix into a small number of linear combinations of several variables, the new variables should characterized the spectral features of the original variable as much as possible, and then select the main combinations for multiple linear regression. PCR overcomes the problem of multicollinearity between MLR input variables, and can improve the predictive ability of the mathematical model. The method can be used for more complex analysis system.It can be more accurately estimate the content of the component under test without knowing which interfering components.But the operating rate of PCR is lower than MLR.If you ignore the useful component in the selection of principal components retained noise, it will make a large deviation of the regression model prediction.Lourenco et al [59]proved UV spectroscopy combined with PCA can be used to identify contaminants. Şahin et al [44] analyzed the PCR modeling and PLS modeling predicted the COD of dyeing wastewater based on UV spectroscopy, PCR method was faster but slightly lower than the accuracy of PLS algorithm.

PLS can establish the relationship between the spectral data and composition and using the full spectrum and partial spectral data modeling. The decomposition of data matrix and regression interaction combined into one step, and the resulting characteristics vector are directly related to the measured components,therefore, it is a popularly multivariate calibration method at present [21]. The PLS combined the predict method of modeling with data analysis methods, and can simultaneously achieve regression modeling, simplify data structure and correlation analysis between the two groups of variables, which gave the multidimensional analysis of complex systems brought a great convenience. PLS is a multivariate analysis algorithms based on PCA. The principle is that decomposition treatment the spectral matrix X and density matrix Y at the same time, and taking into account the relationship between the two in the decomposition, overcoming the limitations of PCR performed only on the spectral matrix X decomposition. PLS method is a good combination of multiple linear regression and principal component analysis. Its basic step is to eliminate the multicollinearity of spectral data, and then reuse the potential factor for egressions.The number of PLS factors which are the most critical parameters, If the

number of factors introduced too little in modeling, the regression model prediction accuracy will be lower, while if introduced too many modeling factor, it will introduce noise impact of the predictive power of the regression model. Şahin et al [44]used UV spectro-photometry combined with the PLS established the modelbased on the spectrum of textile wastewaterand COD,which improved the prediction accuracy of the model.Platikanov et al [60] achieved multi-parameter water quality monitoring system by UV spectroscopy combined with PLS modeling, for the detection and analysis of sewage treatment plant effluent treatment conditions. and the prediction error is less than 20%.

ANN (Artificial Neural Network) is proposed based on the simulation of the human brain structure, which the information storage and computing simultaneously in nerve cells. So to some extent, the neural network can simulate the brain nervous system active process, ANN possess self-learning, self-organizing, adaptive fault tolerance capabilities,distributed storage, highly nonlinear expression ability and parallel processing of information, which is the other traditional multivariate calibration methods are not available. More and more researchers began using ANN analysis method to solve the issue of Analytical Chemistry. In many neural networks, the most widely used is Back Propagation-artificial Neural Network,which is a typical feedforward artificial neural network model and has excellentnon-linear approximation ability.

The essence of BPalgorithm is transformed a set of input and output problem into a nonlinear mapping problem,and through the gradient descent algorithm iterative to solve the weights. BP algorithm is divided into the net input forward calculation and the error back-propagation of two processes.When Network training, the two processes appear alternately until the total error reaches the preset accuracy of the network, this part of the work called network training process, the weights are no longer change in the process of network training. For each given input, network through the forward calculation shows the output response, the work of this section shall be using the training to derive the network for predict or classify. BP network structure is shown in Figure 2.

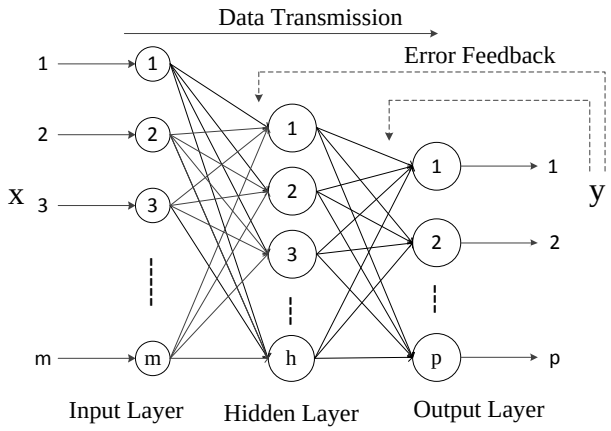

Fig.2. The BP neural network topology

Kato et al [61] detected the COD by UV-VIS spectroscopy combined with neural network algorithm, the regression models obtained a higher prediction accuracy. Fogelman et al [58]utilized UV-VIS spectroscopy combined with different algorithms to measure wastewater COD values, the prediction accuracy of ANN modeling is higher than the MLR modeling. Charef et al [43]used a novel smart sensing equipment to monitor water quality, the use of UV-visible spectroscopy combined with ANN calibration model established regression model, the correlation coefficient of estimated values of the training set and measured values was 0.952, the correlation coefficient of estimated values of the validation set and measured values was 0.88,

In recent stage, optical methods for water quality measurement commonly used partial least squares (PLS), principal component regression (PCR) and artificial neural network (ANN) and so on. PLS and PCR can significantly compress high-dimensional data and effectively remove the multicollinearity, so they widely used in spectral analysis, but the accuracy of the model that established by the PLS and PCR depends on the number of principal components, Principal component number of too little or too much will lead to the model of training sample fitting insufficient or excessive, which will reduce the accuracy of model predictions. And currently the method used to select the number of principal components is cross-validation, which has a larger calculated and prone to over-fitting. Although ANN method has a strong ability of approximation, but it needs a lot of experiments training to determine the appropriate neural network model and its application effect depends on the user's experience. Therefore, it is adverse to real-time spectrum analysis.Du et al [62] established the model of COD and UV absorption spectrum

based on SVM method, the experiments showed that the predictive power of the SVM modeling is better than PLS modeling. Wu et al [63] proposed an iterative regression modeling algorithm based on Boosting theory, compared to the PLS, PCR, ANN algorithm had improved the prediction accuracy of TOC.

At present, using optical method combined with a variety of chemometrics methods to establish a mathematical prediction model for monitoring COD is the development trend. It can solve various problems, such as suspensions, PH, inorganic ions and other influence factor, which make the measurement of COD easier and practical. Chemometrics in dealing with chemical measurements of the experimental design, data processing, signal analysis and distinction, decision of chemical classification and prediction, solved a large number of the complex problem that traditional chemical methods are difficult to solve, and showed a strong vitality.

4COD on-line optical sensors

Optical sensor should meet the on-line analysis requirements of the analytical instrument miniature, high efficiency, rapidly detection and detection of COD in a wider spectral range,so that could improving the accuracy of on-line analyzers. With the development of optical fiber and optical fiber communication technology, Optical fiber sensing technology is a new rapidly developed sensing technology with light as a carrier, optical fiber as medium, perception and transmission of external signals. Compared with traditional sensors, fiber optic sensor has a high sensitivity, the flexural optical path,anti-electromagnetic interference, ease of connection with the computer,etc[64].Gu et al [62, 65]developed an online submersible water quality monitoring system for the measurement of COD based UV spectroscopy, the instrument can be put directly into the water samples, according to the set time intervals and measured parameters at the same water samples at 200~720nm spectral data, Determination the spectral data of water samples at the range of 200 to 700nm under the set time intervals and measured parameters, and then automatically transmitted, storage and analysis the data of COD, achieved a real-time, online, in situ water quality testing.Langergraber et al [31] detected the water quality of paper mill wastewater by UV-visible spectrometer, obtained a more accurate real-time spectral data, achieved the measurement of without reagents, no sample preparation, in-situ. Van den Broeke et al [66]utilized insitu, on-line Invasive water quality monitor based

on the UV-visible spectroscopy measured a variety of water samples,from sewage treatment plant aeration tank effluent and Vienna municipal wastewater to drinking water.The instrument was provided by Scan company. Different standards apply to the spectrometer detector has brought great challenges, but through adjusting the optical path of spectral absorption cell and the optimization of algorithms, and ultimately get a better measurement results, the spectrometer structure and application examples of Austrian Scan company shown in figures 1 and 2 in that paper.

In order to meet water quality monitoring data in real time, reliable higher standards, combined with spectral monitoring technology and wireless network technology to achieve monitoring a large area of water body is the inevitable trend, which will achieve monitoring the water quality changes in the water resources and grasp the overall message, providing an important reference for the comprehensive analysis of the water quality in the water basin.

The development of modern optical sensors for water quality monitoring has opened up a new field, and greatly expanded the application range of water quality monitoring instrument. It can be used in the wastewater treatment monitoring, leak detection in industrial production, monitoring environment summary hydrocarbon compounds and organic matter in drinking water, etc. Although some products have been put into market application in the world, the research and development of optical sensor lags fall behind the computer and communication technology, which greatly limits the water quality monitoring system of precision and test efficiency. In situ and real-time wide spectroscopy measurement is restricted by the optical sensors. It is the development requirement of water quality monitoring equipment. In order to get the breakthrough of key technology, we should strengthen on the technology research and development of the optical sensor, and overcome the technical bottleneck to speed up the development of water environment monitoring technology.

5Conclusion

This article describes an optical method for measuring COD in water research progress and status indomestic and foreign. Briefly explained the chemometricsmethod that commonly used in the analysis of spectral data,the principle of optical method for measuring water COD is built on the regression model between spectral data and COD value, the extrapolation of model determines the measurement

accuracy. So there are important significance for the research of spectral preprocessing and calibration methods for optical methods.

Water quality monitoring method based on optical technology is an important development direction of modern environmental monitoring,Compared with traditional chemical analysis, electrochemical analysis and chromatographic analysis methods, Spectroscopy is more simple operation, a small amount consumption of reagent, good repeatability, high accuracy and rapid detection of obvious advantages, which is very suitable for environmental water samples quick on-line monitoring.

Combination with optical methods for monitoring water COD technology and wireless sensor network technology to achieve a large area of water is the development trend. This will timely grasp the total information of the water quality monitoring in the area of the water resources.Developing based on integrated micro-spectrometer miniaturization water quality monitoring equipment, implementing intelligent, network-based, real-time in-situ monitoring of the water quality monitoring is the requirement ofdevelopment. With the rapid development of sensor technology and computer technology, we believe that the direct determination of optical methodsfor monitoring water COD will get more and more widely application.

Acknowledgments

This work was supported by National High Technology Research and Development Program of China (No. 2013AA10230202).

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