# Analysis on influencing factors of detecting chemical oxygen demand in water by ultraviolet absorption spectroscopy*

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Taking the standard solution and actual water samples as the research object, this paper studies the influence of various environmental factors (temperature, alkalinity (pH), inorganic salt ions and salinity) on the detection of chemical oxygen demand (COD) in water by ultra-violet (UV) spectrometry, analyzes the influence mechanism, and draws relevant conclusions. The results show that the UV absorbance of the COD standard solution and the actual river water samples varies very little with temperature. The value of pH has certain impact on both the standard solution and the actual water samples, but the pH values of the affected experimental samples are in different ranges. The effects of nitrogen salt ions ($NO_2^-$ and $NO_3^-$) on the UV absorption spectra can be eliminated by intercepting the UV spectrum interval less affected for modeling. The influence of salinity values below 35‰ on the UV absorption spectrum of water is mainly concentrated in the spectral band of 200—250 nm, and the influence above 250 nm is very little. This paper provides a preliminary analysis and discussion on the influence mechanism and laws of various environmental factors in the detection of water quality parameters by UV spectrometry, which provides an experimental basis for selecting the optimal test conditions when establishing the COD prediction model.

At present, the application of spectral detection technology is widely used in many fields, such as medicine and health[1,2], environmental monitoring[3], public safety[4,5], food safety[6] and so on. When spectrometry is used to detect chemical oxygen demand (COD)[7-9] in water, the accuracy of spectral information is crucial, which is closely related to the effect and accuracy of prediction model, and different detection environments will also have a great impact on that[10]. The influence on the spectral information is the result of the simultaneous action of many environmental factors, so how to eliminate the interference signal and identify the effective spectral information is a key problem in the detection of water quality parameters by the spectroscopy. Ultraviolet absorption spectrum belongs to the electron energy spectrum, and changes in temperature will change the electron energy emission, and then change the shape of the spectrum. Suspended particles in water will scatter the incident light during transmission, greatly weakening the effective transmitted light signal[11-13]. The acidity and alkalinity (pH) of solution will also influence the position of absorption peak and absorption coefficient of spectrum[14]. In addition, some soluble inorganic salt ions have strong absorption in the ultraviolet band[15], which will cause interference to the spectral analysis process.

The samples used in the experiment include COD standard samples and actual water samples. The standard samples are obtained by diluting 1 000 mg/L mother solution with redistilled water in proportion. The actual water samples are surface water obtained from actual rivers, and the rapid digestion spectrophotometry is used to evaluate its COD. The digestion device is DRB200 (HACH, USA), and the measuring device is a spectrophotometer DR6000 (HACH, USA). Samples are collected using AvaSpec 2048 UV-Vis spectrometer (Avantes, Holland). The light source is deuterium/halogen combined fiber light source

with a wavelength range of 190—1 100 nm. The sample cell is a quartz colorimeter of 10 mm×10 mm.

The temperature of DRB200 digester is set at 150 °C and the digester works for 120 min when measuring COD in actual water samples. In the process of collecting the UV absorption spectrum, the integration time is set to 2 ms, and the sampling frequency is 200. In this paper, the effects of temperature, turbidity, pH, nitrite nitrogen, nitrate nitrogen and salinity on the detection of organic pollution index of water are investigated by UV absorption spectrum.

The UV absorption spectra of 18 experimental water samples measured at room temperature are shown in Fig.1, in which (a) is the UV spectra of 8 COD standard solutions with a concentration range of 1—80 mg/L, and (b) shows the UV spectra of 10 river water samples with concentrations ranging from 0.64 mg/L to 35.4 mg/L in different regions.
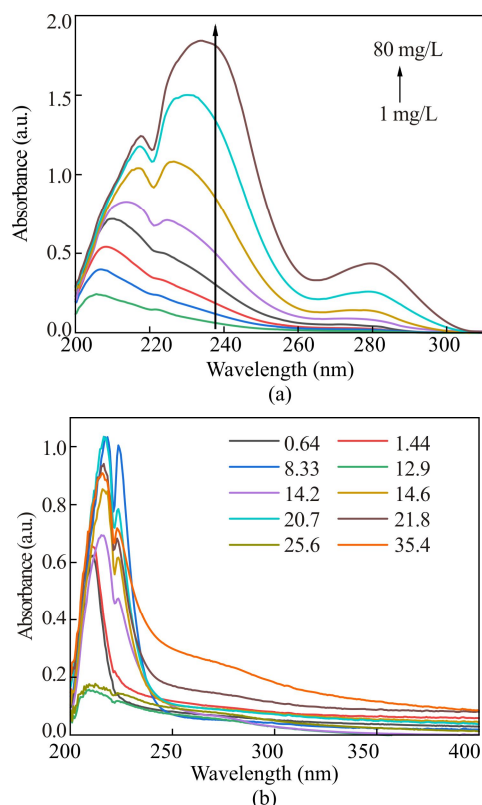


**Fig.1 UV absorption spectra of experimental samples: (a) COD standard solutions; (b) Actual water samples**

According to Fig.1, the UV absorption spectra of the standard solutions and the actual water samples are quite different, and there are also significant differences between different river water samples. This is because the solute composition of the standard solution is single (potassium hydrogen phthalate), while the composition of the river water is very responsible, so the difference is obvious.

When the temperature changes, the number of excited state electrons in the sample will change, and the detector

of the spectrometer is also sensitive to temperature, so it is very important to study the influence of the UV spectrum by the external temperature and the law of the spectrum with the temperature change. As can be seen from Fig.1(a), the standard solution has an obvious absorption peak at 232 nm. Therefore, the absorbance of the standard solution with COD concentration of 60 mg/L at 232 nm is selected as the research object in this paper to study the influence of temperature changes within the range of 18—48 °C on the UV absorbance of the standard solution. The experimental result is shown in Fig.2.
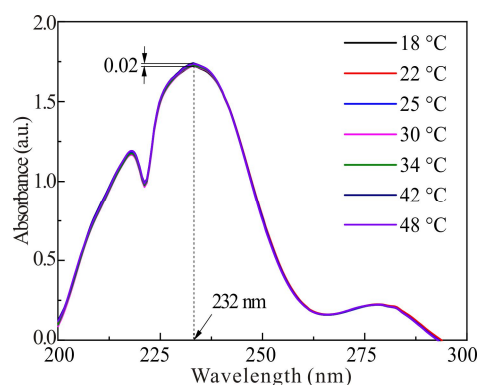


**Fig.2 Influence of temperature for UV spectrum of standard solution**

It can be seen from Fig.2 that at 232 nm, for COD standard solution, the influence of temperature change on the UV absorption spectrum is about $6.666\ 7\times10^{-4}$ a.u./°C. Depending on Fig.1(a), when the concentration changes by 1 mg/L, the change of absorbance is about 0.017 a.u., which is about 25 times of the former. Therefore, compared with the influence caused by the change of concentration, when the temperature changes within the range of 18—48 °C, the influence on the UV spectrum of the standard solution can be ignored. It is also found by repeated experiments that the variation of UV absorbance of other standard samples with temperature is consistent with that of this sample.

The composition of actual water sample is much more complex than that of the standard solution. In this paper, the river water sample with COD concentration of 14.2 mg/L is selected as the research object, and the relationship between UV spectral intensity and absorbance with temperature changes is analyzed at 232 nm and 254.5 nm, respectively, when the temperature changes within the range of 4—50 °C. The relationships between UV spectral intensity/absorbance and temperature are shown in Fig.3 and Fig.4, respectively.

It can be observed in Fig.3 and Fig.4 that at the two wavelength points, the value of UV spectrum changes in opposite directions to the value of UV absorbance. The spectral value decreases gradually, while the absorbance increases gradually in a positive correlation, and the relative change is low. The influence of temperature change on the UV absorption spectrum is 0.003 93 a.u./°C at

232 nm and 0.003 57 a.u./°C at 254.5 nm. The influence of temperature at 232 nm is higher than that at 254.5 nm, which may be due to the strong absorption of some inorganic ions in UV band lower than 240 nm. Furthermore, the temperature range selected in this paper is wide, while the temperature range of liquid water in nature is relatively narrow. Therefore, it can be recognized that the influence of temperature change on the UV absorption spectra of water samples is very small. It should be emphasized that when UV spectroscopy is used to detect water COD, in order to ensure the consistency of the measurement data, it is necessary to give the calibration spectrum at the current temperature.
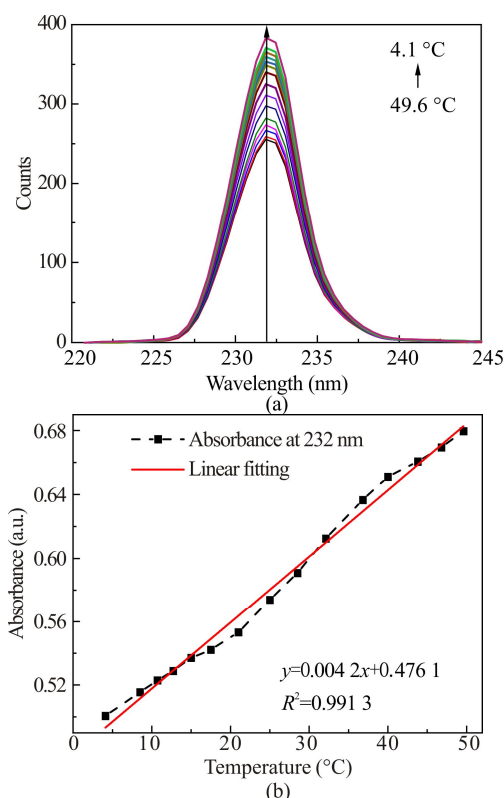


**Fig.3 (a) UV spectra at different temperatures; (b) Absorbance versus temperature at 232 nm**

When the standard method is used to detect COD in water, acid and alkalinity are important factors, and the oxidation capacity of oxidants in different pH reaction environments are very different, which is directly related to the error of the final analysis value. This section mainly analyzes the influence of pH on the change of UV absorbance. SW-730 pH meter is used to detect the pH of the solutions. The acid and base regulator are commonly utilized in $H_2SO_4$ solution and NaOH solution, with the concentration of 0.1 mol/L.

The standard solution sample with a concentration of 10 mg/L is acidic, and the pH of the solution is about 4. The UV absorption spectra of the solution are collected in the pH range of 1.2—12.3, and the UV absorbances at 235 nm, 255 nm and 280 nm are taken in the pH range, as shown in Fig.5.
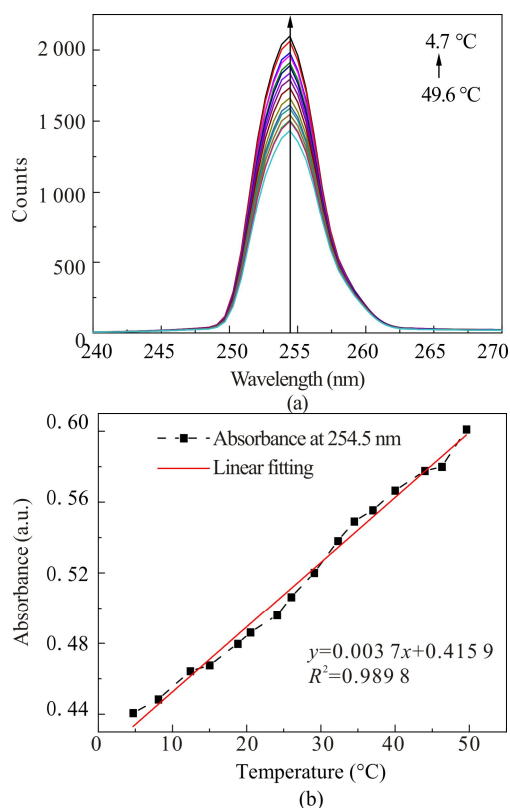


**Fig.4 (a) UV spectra at different temperatures; (b) Absorbance versus temperature at 254.5 nm**
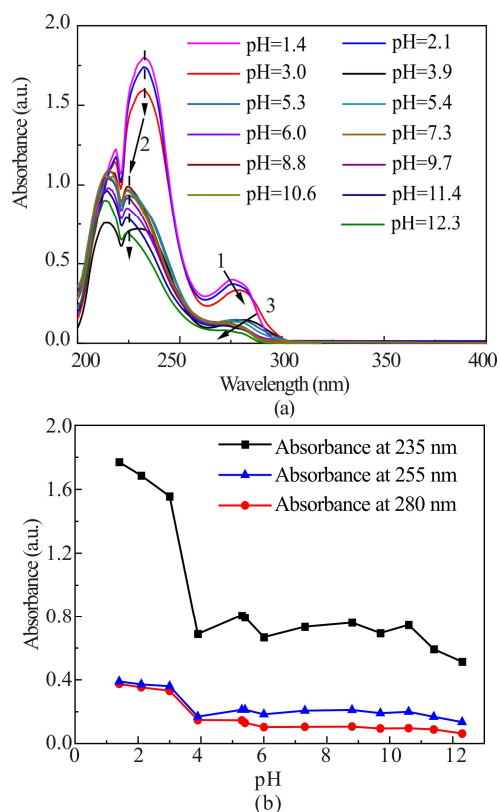


**Fig.5 Influence of pH on UV absorption spectrum of standard solutions: (a) Absorbance spectra at different pH values; (b) Absorbance versus pH at different wavelengths**

As can be seen from Fig.5, for the standard solutions, the absorbance gradually decreases with the increase of pH, and the absorption has a red shift phenomenon. When pH>4, the absorbance basically remains unchanged, however, the absorption band has a blue shift. The reasons for the above phenomenon are as follows. Water is a polar solvent, with the increase of pH in the solution, and $OH^-$ neutralizes part of $H^+$, making it more polar and causing the red shift of $\pi \rightarrow \pi^*$ absorption band, while the molar absorption coefficient $\varepsilon_{max}$ decreases slightly, as shown by arrow 1 in Fig.5(a). Potassium hydrogen phthalate is not difficult to form -COOH ion in acidic medium and -COO- ion in alkaline medium. The characteristic absorption K band will blue shift from 230 nm to 224 nm. $\varepsilon_{max}$ will decrease from 10 000 to 8 700. The characteristic absorption B band will blue shift from 280 nm to 270 nm, and $\varepsilon_{max}$ will decrease from 800 to 560. Arrows 2 and 3 in Fig.5(a) are indicated.

The UV absorption spectra of a river water sample with COD concentration of 14.2 mg/L are collected in the pH range of 1.2—12.3, and the relationship curves of the UV absorbance corresponding to the three single wavelengths of 235 nm, 250 nm and 280 nm in different pH ranges were taken. The results are shown in Fig.6.

According to the analysis in Fig.6, for the river water sample with COD concentration of 14.2 mg/L, when the pH is between 1.5 and 11, the UV absorbance of water remains basically unchanged, but when the pH is higher than 11, the absorbance begins to increase. The reasons are as follows. The actual water sample composition is complex. The ionization of organic molecules in water under acidic conditions is less affected. The structure and state of internal electrons are relatively stable. Alkaline conditions promote the ionization of organic molecules, modify the structure of the internal electrons, and lead to the polarization of the color system, which changes the electronic state of organic molecules and causes changes in of absorption bands. When the pH of the water environment is alkaline and reaches a certain value, the absorption band becomes wider and the linear range becomes smaller, leading to the change in absorbance. In addition, when pH>11, electron transitions within organic molecules in aqueous solution produce abnormally strong absorption, resulting in an increase in absorbance.
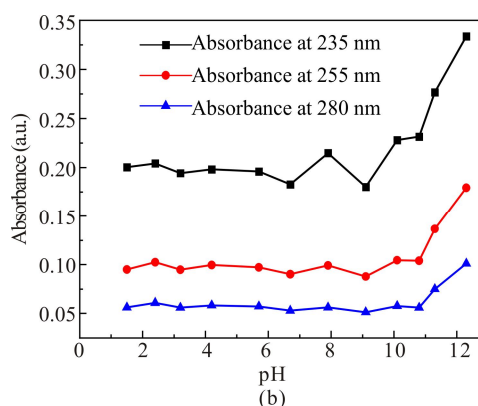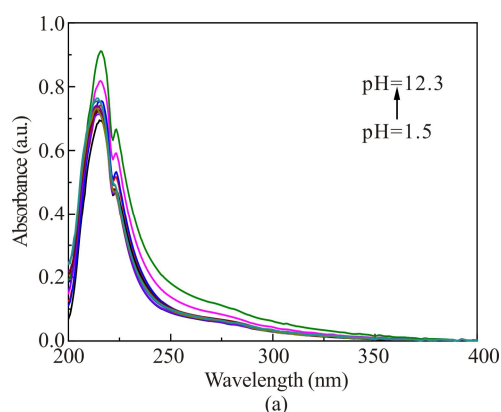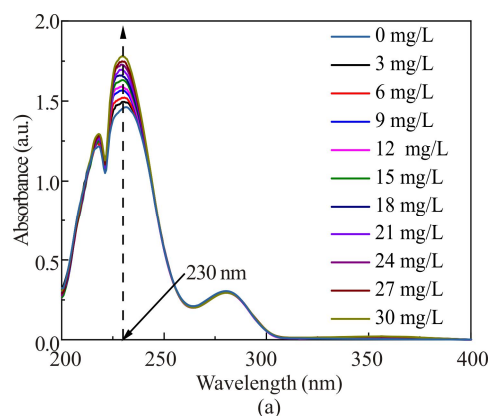


**Fig.6 Influence of pH on UV absorption spectrum of a river water sample: (a) Absorbance spectra at different pH values; (b) Absorbance versus pH at different wavelengths**

As can be seen from the above analysis, for actual water samples, when pH is between 1.5 and 11, the variation of UV absorption spectra of samples is very small, and the influence of pH on UV absorbance within this range is insignificant and can be ignored. When pH>11, there may be a large error in the application of the spectrometry to detect water quality, which should be compensated. However, for common surface water, such as rivers and lakes, the pH value does not exceed the range of 1.5—11 generally, so the influence of pH value on water quality detected by UV absorption spectrometry can be ignored.

Some inorganic ions have strong absorption in the UV band, so this kind of inorganic ions will have a certain influence on the detection of water COD by UV. Some anions, such as $Cl^-$, $SO_4^{2-}$ and $HClO_3^-$, have strong absorption peaks in the EUV band, while nitrite ($NO_2^-$) and nitrate ($NO_3^-$) ions have strong absorption peaks in the near UV region.

Nitrite nitrogen ($NO_2$-N) and nitrate nitrogen ($NO_3$-N) in water are the products of oxidative decomposition of nitrogenous organic matter, which exist in the form of nitrite and nitrate in water. Fig.7(a) and Fig.7(b) respectively show the UV absorption spectra of COD standard solution with concentration of 20 mg/L under different $NO_2^-$ and $NO_3^-$ ion concentrations, where the ionic concentrations of $NO_2^-$ and $NO_3^-$ vary from 0 to 30 mg/L.
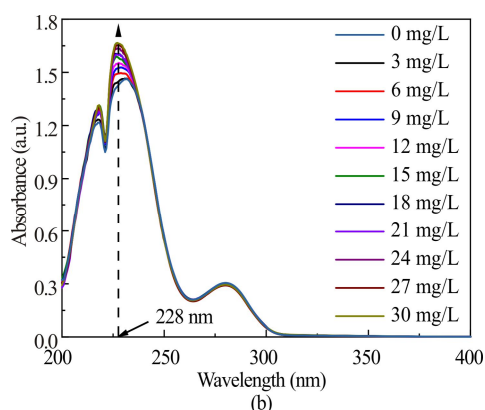

(a)


(a)

**Fig.7 Influence of nitrogen salt on UV spectrum of standard solution: (a) Influence of $NO_2^-$; (b) Influence of $NO_3^-$**

As can be observed in Fig.7, both $NO_2^-$ and $NO_3^-$ ions have obvious absorption peaks near 230 nm, which overlap with one of the absorption peaks of the standard solution. It is not difficult to see that when the concentration of $NO_2^-$ and $NO_3^-$ ions gradually increases from 0 to 30 mg/L, the absorbance increases by 0.331 4 a.u. and 0.239 9 a.u., respectively. Compared with Fig.1(a), this corresponds to an increase in standard solution concentration of at least 20 mg/L. Therefore, the influence of $NO_2^-$ and $NO_3^-$ ions cannot be ignored.

When building a model based on UV absorption spectra, in order to quickly remove the influence, the method of truncating the absorption regions of $NO_2^-$ and $NO_3^-$ ions can be adopted, that is, starting from the data after 240 nm for modeling.

Salinity represents the amount of soluble salts per kilogram of water, which can be interpreted as the concentration of salt in the water[16]. The average salinity of ocean water is 35‰, or 35 g of salt per kilogram of ocean water. The salinity of fresh water is very low, usually not higher than 0.5‰. As NaCl is the main salt substance in seawater, NaCl solutions with mass fractions of 5‰, 15‰, 25‰, 35‰ and 45‰ are prepared by ourselves during the experiment to simulate the change of water salinity. With distilled water as the blank background, the UV absorption spectra of each NaCl solution sample are collected successively. During the collection process, the integral time of the UV spectrometer is set to 2 ms, and the average sampling time is 200. The spectra after collection are presented in Fig.8.

As can be seen from Fig.8, with the increase of NaCl solution concentrations, the UV absorbance also increases, which changes greatly in the range of 200—250 nm, and the main absorption peak is located at about 205 nm. In addition, there is absorption in the range of 250—300 nm, and the absorption peak is at 275 nm, but it is not strong. When the mass fraction of NaCl is lower than 35‰, the absorbance is almost unchanged. Therefore, when the salinity of a water sample is lower than 35‰, the influence of salinity at 275 nm

can be ignored. Combined with the influence of $NO_2^-$ and $NO_3^-$ ions on the UV absorbance, the influence of $NO_2^-$, $NO_3^-$ and salinity on the UV absorbance can be ignored when analyzing the COD of salt water based on the UV spectrometry, if the initial wavelength is greater than 250 nm. If the characteristic band selected during modeling includes the range of 200—250 nm, the impact of $NO_2^-$, $NO_3^-$ and salinity on UV absorbance should be considered.
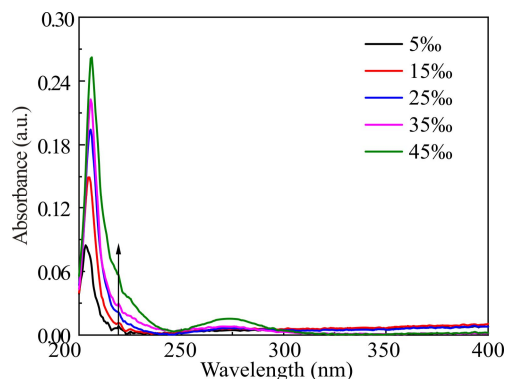


**Fig.8 Influence of NaCl concentration on UV spectrum of standard solutions with different mass fractions**

In this paper, the influence mechanism and rule of environmental conditions on the UV absorption spectra of COD standard solution and actual river water are analyzed respectively. The results are shown as follows.

Temperature change does not have much effect on UV absorbance. When the temperature changes within a reasonable range, the variation of UV absorbance is relatively small in both standard samples and actual water samples. In addition, it is necessary to give the calibration spectrum at the current temperature, when detecting COD in water by UV spectroscopy.

The UV absorbance of both standard sample and actual water sample is affected by pH. When pH<4, the UV absorbance of standard sample changes significantly, and when pH>11, the UV absorption spectrum of actual water sample changes dramatically. However, the UV absorbance of the two types of samples does not vary significantly at other pH values, and the pH of water in nature is generally within the range of 4—11, and the pH range is not large. Therefore, when UV spectroscopy is used to detect the concentration of organic pollutants in water, the influence of pH can also be ignored.

Nitrite nitrogen and nitrate nitrogen ($NO_2^-$ and $NO_3^-$ ions) have obvious light absorption characteristics when they are around 230 nm, and their absorbance changes significantly, so their influence on the UV absorption spectrum cannot be ignored. In order to eliminate the influence of $NO_2^-$ and $NO_3^-$ ions on the UV spectrum, the characteristic spectrum cannot be selected in this band range during modeling, and generally can be carried out from the band after 240 nm.

The salinity of water in nature is generally lower than

35‰. When the salinity changes in the range of 5‰—45‰, it will have a significant influence on the UV absorption spectrum of water in the wavelength range of 200—250 nm, while the spectral data after 250 nm can be modeled. In the modellable band range, the UV spectrum of water is not subject to salinity. It is just not affected by nitrite and nitrate nitrogen.

The experiments in this study are all performed in the laboratory environment, while in practical application, water environmental factors (such as water temperature, turbidity, pH, ion concentration, etc.) are bound to cause interference to the UV spectrum. In the next step, comprehensive interference caused by actual water environmental factors in UV spectroscopy will be studied and suppressed, in order to improve the adaptability and accuracy of the prediction models in different environments.

Based on different feature extraction algorithms and modeling methods, the UV absorption spectrum data of standard solution and actual water sample are modeled, and the prediction effects of various models are compared. The results show that the modeling method used in this paper is feasible, and the prediction effect of the optimal model obtained from the experiment is excellent and it can be used as an effective method for rapid detection of COD in water quality. This study is completed in the laboratory environment, but the substances in the natural water and the environment of the water are more complex, and the interference of the UV spectrum needs to be further studied.

## Statements and Declarations

The authors declare that there are no conflicts of interest related to this article.

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